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Odd–even effect in melting properties of 12 alkane-α,ω-diamides

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Abstract

Fusion and solid-to-solid transitions of a homologous series of 12 linear alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$, where $n = (2$ to 12 and $14)$, were investigated by differential scanning calorimetry (d.s.c.). The temperatures of fusion of even terms decreased from $T_{fus} \approx 572$ K to about 460 K, whereas those of odd terms remained substantially constant at about 450 K. Solid-to-solid transitions were also detected for oxamide, malonamide, succinamide, adipamide, suberamide, and dodecanediamide. Regular odd–even alternation was displayed by the temperature, enthalpy, and entropy of fusion values, terms with even number of carbon atoms showing higher values than odd terms.

This behaviour was attributed to different crystal packing allowing consonance between hydrogen bonding and dispersive interaction in even terms, which are characterised by multilayer structure, whereas in odd terms a strained three-dimensional network results in looser packing. Parallel alternation of densities in solid alkane-α,ω-diamides supports this interpretation. Comparison was made with literature values for temperatures, enthalpies, and entropies of fusion of isoelectronic linear alkanes, dicarboxylic acids, and alkyldiamines.

Keywords: Alkane-α,ω-diamides; Differential scanning calorimetry; Fusion; Odd–even effect; Packing pattern

1. Introduction

Interactions between molecules have attracted increasing attention since the emergence and rapid development of supramolecular chemistry and molecular recognition. They are ruled by intermolecular forces whose energetic and geometric properties are less well understood than those of chemical bonds between atoms in individual molecules. Melting temperature is the typical intensive thermodynamic parameter related to the breaking of these forces in solid-state molecular assemblies [1]. In this paper, we have studied solid-to-liquid and solid-to-solid phase transitions of alkane-α,ω-diamides (hereinafter named alkyldiamides), characterised by both hydrogen bonding and dispersive forces that belong to the ubiquitous interactions of biological structures. The thermodynamics of phase transitions of alkyldiamides has only been investigated for propane-1,3-diamide (malonamide) so far [2]. We therefore used d.s.c. to measure the temperatures and enthalpies of fusion and solid-to-solid transitions of the alkyldiamides from C_2 to C_{14}, except C_{13}, as a part of our research programme on the thermodynamic properties of homologous series of model compounds [3–8].

The values of the thermodynamic parameters of fusion displayed the odd–even effect already described for linear alkanes and many terminally substituted linear alkyl derivatives. In particular, we found an odd–even fusion

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behaviour for homologous series of alkyl-α,ω-diamines [8], alkyl-α,ω-dinitriles and alkyl-α,ω-diols [9]. The odd–even effect also concerns other solid-state properties, such as solubility, density, molar volume, and enthalpy of sublimation [10–16]. Recent studies on crystal structures and their packing patterns provided an explanation for the melting temperature alternation in some cases [17–20]. Solid linear alkanes are solely held together by dispersive interactions and their melting temperature alternation has been recently explained in terms of a simple geometrical model [19]. In the case of alkane-α,ω-diols ($n = 2$ to 10) [20] and ($n = 6$ to 16) [9], and alkane-α,ω-diamines ($n = 3$ to 12) [8], characterised by both hydrogen bonds and dispersive forces, the difference in crystal packing is the main reason invoked for such alternation. For the alkane-α,ω-dicarboxylic acids, it was shown that crystal-packing requirements for odd terms impose restrictions on molecular conformations which tend to lower the temperatures of fusion by respect to even terms [16].

2. Experimental

The homologous series of 12 alkane-α,ω-diamides $H_2NOC–(CH_2)_{(n-2)}–CONH_2$ examined in this work are listed in table 1 with their number of C atoms, molar masses, commercial origins and fusion temperatures, crystal structures, relevant spatial groups, and densities. Some were commercial products from Fluka and Aldrich, but most were prepared by hydrolysis of parent alkane-α,ω-dinitriles, except tridecanediamide whose parent dinitrile is commercially unavailable. For 1 g of dinitrile, reaction was made in 3 cm^3 of anhydrous DMSO solution in the presence of an excess of H_2O_2 30% (~0.5 cm^3) and K_2CO_3 (~0.14 g) as catalyst in accordance with Katritzky *et al.* [31]. This method, conceived for the hydrolysis of mononitriles [32], was suitably modified by us to obtain terminal alkyldiamides from the corresponding terminal dinitriles. All alkyldiamides were purified by successive crystallisations from appropriate ethanol, ethylacetate or their mixed solutions and pure bidistilled water [33]. The n.m.r. analysis was performed for all synthesised compounds and their spectra were compared with those in the literature. The final mass-fraction purity of all diamides was always better than 0.99, as determined by the d.s.c. peak-profile method [34].

High-purity indium and tin from NBS-ICTA, naphthalene (CRM No. M16-03, mass fraction 0.9999), and benzoic acid (CRM No. M16-06, mass fraction 0.9999) from NPL were used as reference materials.

The enthalpies of solid-to-solid transition and fusion, and the corresponding onset temperatures of alkyldiamides were measured with a Setaram DSC 111 differential scanning calorimeter at the heating rate $16.7\ mK \cdot s^{-1}$, over the temperature range 300 K to 600 K. Further DSC runs at higher scanning rates were performed to check reversibility of solid-to-solid transitions and possible decomposition during fusion. The calorimetric output was both graphically recorded by a 8210 Sefram recorder and digitally acquired through a home-made software whose data were processed with Microcal Origin 6.1 software. Enthalpies associated with solid-to-solid transitions and fusion were obtained from d.s.c. peak areas measured with a Sal-

TABLE 1
List of the linear alkane-α,ω-diamides with number of carbon atoms n, molar mass M, commercial origin and temperature of fusion T_{fus}, crystal structure, spatial group, and density

Compound	n[a]	M[b]/$(g \cdot mol^{-1})$	Origin[c]	T_{fus}/K	Crystal structure	Spatial group	Density/$(g \cdot cm^{-3})$
Oxamide	2	88.066	Fluka	>573 (dec.)	Triclinic[d]	$P_{\bar{1}}$[d]	1.667[d]
Malonamide	3	102.092	Fluka	441–445	Monoclinic[e]	$P2_1/c$[e]	1.430[e]
Succinamide	4	116.119	Fluka	>535 (dec.)	Monoclinic[f]	$C2/c$[f]	1.442[f]
Glutaramide	5	130.146	Synthesis		Monoclinic[g]	$C2/c$[g]	1.280[g]
Adipamide	6	144.173	Aldrich	499–502	Monoclinic[h]	$P2_1/c$[h]	1.360[h]
Pimelamide	7	158.200	Synthesis		Monoclinic[i]	$C2/c$[i]	
Suberamide	8	172.226	Synthesis		Monoclinic[j]	$C2/c$[j]	1.230[j]
Azelamide	9	186.253	Synthesis		Monoclinic[k]	$C2/c$[k]	1.200[k]
Sebacamide	10	200.280	Synthesis		Monoclinic[l]	$P2_1/c$[l]	
Undecanediamide	11	214.307	Synthesis				
Dodecanediamide	12	228.334	Synthesis				
Tetradecanediamide	14	256.387	Synthesis				

[a] Number of carbon atoms in the molecule.
[b] Based on the 1999 IUPAC table of standard atomic weights of the elements and its 2001 revision [21].
[c] Syntheses made in our laboratory from parent terminal dinitriles.
[d] Reference [22].
[e] Reference [23].
[f] Reference [24].
[g] Reference [25].
[h] Reference [26].
[i] Reference [27].
[j] Reference [28].
[k] Reference [29].
[l] Reference [30].

moiraghi 237 high-precision manual planimeter, the uncertainty being evaluated as less than 0.3% for areas larger than $1 \cdot 10^3\ \mathrm{mm}^2$. The enthalpy values obtained by the treatment of digitally acquired data were in very good agreement.

The actual temperature T of the samples as well as enthalpy changes associated with the phase transition was obtained by using the empirical equations supplied by the manufacturer as described earlier [7,8].

Several melting runs with certified reference materials (naphthalene, benzoic acid, indium, and tin) were performed under the same conditions as the experimental determinations, and showed agreement with recently recommended IUPAC values [35–37] within 0.08% for temperature and 0.25% for enthalpy (table 2).

All measurements were performed in static air conditions. Eight to ten runs with fresh samples were made for each compound to determine solid-to-solid transitions and fusion thermodynamic quantities. Separate runs for solid-to-solid transition and fusion were adopted due to the substantial departure between corresponding onset temperatures (more than 40 K) and the relevant very different endothermic effects requiring different calorimetric sensitivities. However, all values reported are averaged from the results of at least four distinct first runs (on fresh samples). In addition, 2nd and sometimes 3rd runs were performed to check both reversibility of solid-to-solid transitions and possible decomposition during fusion, and gave thus rise to a total number of 8–10 runs. Crimped aluminium crucibles were generally employed, but sealed stainless steel crucibles were needed for oxamide and succinamide that decompose during melting. Sample mass was $(1\ \text{to}\ 10) \cdot 10^{-3}$ g as determined with a Mettler electrobalance AE163 whose sensitivity is $1 \cdot 10^{-5}$ g.

3. Results and discussions

3.1. Temperature of fusion

The experimental temperatures, enthalpies, and the derived entropies of fusion and solid-to-solid transitions for the 12 alkyldiamides are presented in table 3, together with the literature values for malonamide, the only alkyldiamide investigated so far [2].

TABLE 2

Comparison between temperatures of fusion T_{fus} and molar enthalpies of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ measured with our d.s.c. apparatus and literature values for the four selected reference materials

Compound	Origin	N^a	T_{fus}/K		$\Delta_{\mathrm{fus}}H_{\mathrm{m}}/(\mathrm{kJ \cdot mol^{-1}})$	
			This work	Literature	This work	Literature
Naphthalene	NPL	4	353.11 ± 0.09	353.39 ± 0.03^b	19.072 ± 0.045	19.05 ± 0.04^b
Benzoic acid	NPL	4	395.23 ± 0.12	395.55 ± 0.03^c	18.017 ± 0.075	18.06 ± 0.05^c
Indium	NBS-ICTA	4	429.40 ± 0.08	429.748 ± 0.00034^d	3.266 ± 0.05	3.273 ± 0.022^d
Tin	NBS-ICTA	4	504.89 ± 0.02	505.06 ± 0.01^d	7.130 ± 0.01	7.148 ± 0.022^d

Uncertainties are expressed as twice the standard deviation of the mean.

[a] Number of calorimetric runs.

[b] Reference [36].

[c] Reference [37].

[d] Reference [35].

TABLE 3

Temperatures, molar enthalpies and entropies of solid-to-solid transition ($T_{\mathrm{trs}}, \Delta_{\mathrm{trs}}H_{\mathrm{m}}, \Delta_{\mathrm{trs}}S_{\mathrm{m}}$) and fusion ($T_{\mathrm{fus}}, \Delta_{\mathrm{fus}}H_{\mathrm{m}}, \Delta_{\mathrm{fus}}S_{\mathrm{m}}$) of alkane-α,ω-diamides

Compound	N^a	T_{trs}/K	$\Delta_{\mathrm{trs}}H_{\mathrm{m}}/(\mathrm{kJ \cdot mol^{-1}})$	$\Delta_{\mathrm{trs}}S_{\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	T_{fus}/K	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}/(\mathrm{kJ \cdot mol^{-1}})$	$\Delta_{\mathrm{fus}}S_{\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$
Oxamide	10	356.15 ± 0.90	1.88 ± 0.13	5.28 ± 0.37	~572 (dec.)	~50	
		455.45 ± 1.24	3.56 ± 0.31	7.82 ± 0.68			
		494.25 ± 0.87	62.40 ± 3.32	12.63 ± 6.72			
Malonamide	8	418.89 ± 1.67	1.89 ± 0.01	4.51 ± 0.02	444.19 ± 0.34	29.85 ± 0.43	67.19 ± 0.97
		393.0^b	1.90^b	4.83^b	443.0^b	35.8^b	80.81^b
Succinamide	8	$485.92 \pm .077$	6.08 ± 0.86	12.51 ± 1.77	~536 (dec.)	~46	
Glutaramide	8				453.95 ± 0.07	38.36 ± 0.04	84.50 ± 0.09
Adipamide	10	458.39 ± 1.27	1.59 ± 0.34	3.46 ± 0.74	499.09 ± 0.07	52.72 ± 0.90	105.63 ± 1.80
Pimelamide	8				446.82 ± 0.02	44.56 ± 0.21	99.73 ± 0.47
Suberamide	10	431.28 ± 0.36	5.45 ± 0.35	12.64 ± 0.81	493.23 ± 0.38	58.37 ± 1.60	118.34 ± 3.24
Azelamide	8				450.41 ± 0.22	55.02 ± 0.71	122.16 ± 1.58
Sebacamide	10				484.31 ± 0.17	68.75 ± 0.76	141.93 ± 1.57
Undecandiamide	8				451.20 ± 0.04	64.38 ± 1.48	142.69 ± 3.28
Dodecandiamide	10	422.79 ± 0.77	5.09 ± 0.28	12.03 ± 0.66	466.07 ± 0.56	73.73 ± 1.29	158.20 ± 2.77
Tetradecandiamide	10				469.26 ± 0.56	77.45 ± 1.83	165.05 ± 3.90

Uncertainties are expressed as twice the standard deviation of the mean.

[a] Total number of calorimetric runs.

[b] Reference [2].

In figure 1, the fusion temperatures of the 12 alkyldiamides are shown as a function of the number of carbon atoms *n* in their alkyl chains. Comparison is made with the (approximately) isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$ [16]. The T_{fus} values of the isoelectronic dicarboxylic acids $HOOC–(CH_2)_{(n-2)}–COOH$ [38] are included as they show a remarkable similarity with the behaviour of alkyldiamides.

The T_{fus} values of the alkyldiamides are higher than those of the corresponding nearly isoelectronic linear alkanes due to the presence of H-bond interactions whereas only dispersion forces are present in alkanes. The T_{fus} values of dicarboxylic acids are lower than those of alkyldiamides due to the difference in shared H-bonds: four for dicarboxylic acids [17] against eight for alkyldiamides [22–30].

For both alkyldiamides and dicarboxylic acids, temperatures of fusion of even terms are higher than those of odd terms. This odd–even effect is more pronounced than for linear alkanes. Moreover, a common tendency to level out on increasing *n* was clearly observed. The T_{fus} values of even terms decreased on increasing *n*, whereas odd terms displayed only very slight increase or even rather constant values. This gave rise to a T_{fus} trend in contrast with that of alkanes [19], alkyldiamines [8,20], dithiols [39] and diols [9,20], where T_{fus} values of both even and odd terms clearly increase on increasing *n*. This trend correlates well with the density values of alkyldiamides (table 1), namely even terms possess slightly higher T_{fus} and densities than the corresponding odd terms and both properties show a clear descending tendency on increasing *n*. Nevertheless, the crystal structure of even and odd alkyldiamides is similar, as shown by X-ray studies of terms with $n = (2 \text{ to } 10)$ [22–30]. All alkyldiamides from C_3 to C_{10}, in fact, display a common monoclinic structure, except oxamide (triclinic structure) and randomly belong to two spatial groups, $P2_1/c$ and $C2/c$. There is no parallel alternation of spatial group with fusion properties as we found for alkyldiamines [8]. Difference in crystal structure cannot thus be invoked as the reason for alternating T_{fus} in alkyldiamides. However, parallel alternation of densities and decreasing trend of temperatures of fusion suggest that the odd–even effect may be related to different packing patterns in odd and even terms, if any. Refinement of the crystal structures of the even terms, oxamide, succinamide, adipamide, suberamide, and sebacamide, showed that molecules are tied into layers by a net of hydrogen bonds. There are two sets of non-equivalent hydrogen bonds, whose length, however, is almost the same. In oxamide [22] and succinamide [24], the adjacent molecules form an eight-numbered ring around a centre of symmetry, whereas in adipamide [26], suberamide [28] and sebacamide [30], a chain structure is formed. Moreover, adjacent rings or chains aggregate into layers through both hydrogen bonds and dispersive interactions. The spacing between molecular layers, connected by dispersive forces only, slightly increases from oxamide (0.3007 nm) to suberamide (0.37 nm), a distance typical for van der Waals forces. All these structural features can reasonably explain the higher values of T_{fus} for C_2 and C_4 as well as their decreasing trend for the even alkyldiamides.

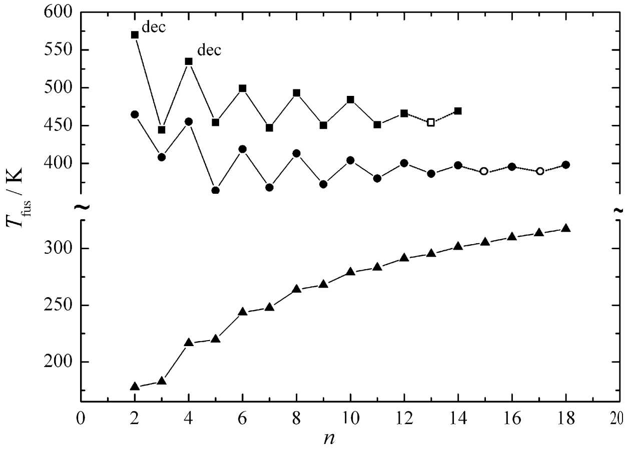

FIGURE 1. Plot of temperatures of fusion T_{fus} as a function of the number of carbon atoms *n* in the alkyl chain: ■, alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$; ●, isoelectronic alkane-α,ω-dioic acids $HOOC–(CH_2)_{(n-2)}–COOH$ [37]; ▲, isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$ [15]. Void symbols: estimated values.

The X-ray studies of the odd terms, namely malonamide, glutaramide, pimelamide and azelamide, revealed a three-dimensional network characterised by a specific position of the mean plane of methylene chain and those of amide groups and hydrogen bonds linking parallel molecules [23,25,27,29]. The molecules are no longer coplanar as found for even terms and spacing between mean planes is ruled by twisting amide groups. This network results in looser packing attributable to the torsional conformations of the molecules, which also hinder cooperation between hydrogen bonding and dispersive interaction. Strained molecular conformations, in fact, can be assumed to be responsible for the lowering of both temperatures of fusion and crystal densities of odd as opposed to even terms. X-ray diffraction analyses of dicarboxylic acids showed that hydrogen bonding and dispersive interaction operate in consonance in even terms, and therefore culminate in dense packing, but run into geometrical conflicts and lead to looser packing in odd terms [17]. These structural features also appear to be responsible for the rather constant T_{fus} values within odd series of both alkyldiamides and dicarboxylic acids.

Besides, it is worth noting that T_{fus} of even diamides can be modelled quite well by a hyperbolic function depending on the number of methylene groups in the molecule, as in the case of other homologous series, such as hydrocarbons, cycloalkanes, functionalised alkanes, and symmetrically substituted derivatives [40]. As expected, both even and odd terms appear to converge in the limit to the melting temperature of polyethylene [8,40]. Moreover, the hyperbolic behaviour exhibited by the melting temperature in most series seems to be characteristic of molecules that pack similarly in the solid state [40].

3.2. Fusion enthalpy and entropy (molar and massic)

In figures 2 and 3, the molar enthalpies $\Delta_{fus}H_m$ and entropies $\Delta_{fus}S_m$ of fusion of alkyldiamides are reported as a function of n and compared with those of the isoelectronic linear alkanes [11,16]. The common odd–even effect is an evident aspect of these plots as expected. Even so, the trend of both $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ values showed an average linear increase, in contrast with T_{fus} values (figure 1). The enthalpies of fusion of oxamide and succinamide are roughly evaluated because of extensive decomposition during melting, but are in agreement with the zig-zag pattern of the series. Adipamide and tetradecanamide showed slight decomposition only at the end of melting and computation of their $\Delta_{fus}H$ was not affected. Suberamide, sebacamide, and undecanamide were totally free from decomposition.

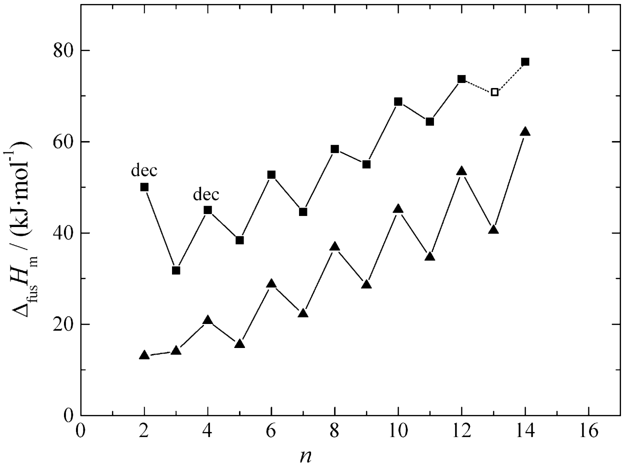

FIGURE 2. Plot of molar enthalpies of fusion $\Delta_{fus}H_m$ as a function of the number of carbon atoms n in the alkyl chain: ■, alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$; ▲, isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$ [15]. Void symbols: estimated values.

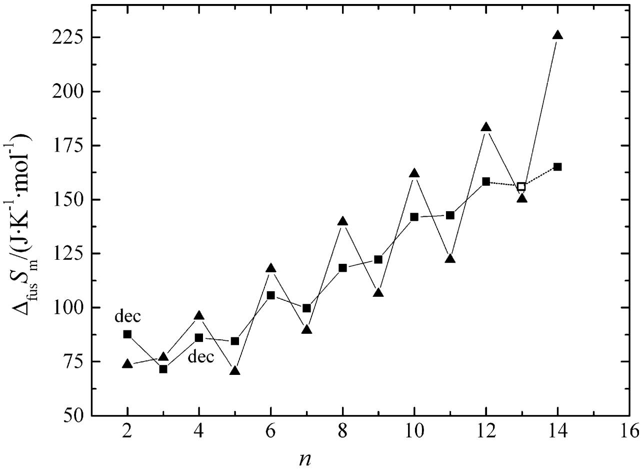

FIGURE 3. Plot of molar entropies of fusion $\Delta_{fus}S_m$ as a function of the number of carbon atoms n in the alkyl chain: ■, alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$; ▲, isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$ [15]. Void symbols: estimated values.

Molar enthalpies of fusion are higher for alkyldiamides than for alkanes: in both series higher values are associated with even terms, in agreement with observed T_{fus} values. The intensity of the zig-zag effect within alkyldiamides tends to decrease, whereas it increases within alkanes. The average increase of molar enthalpies of alkyldiamides is due to the progressively increased dimension of the molecules and corresponding increase of dispersive interaction per mol. The almost constant difference between $\Delta_{fus}H_m$ values of nearly isoelectronic alkyldiamides and alkanes is in connection with the presence of a constant number of H-bonds in alkyldiamides. The comparison of $\Delta_{fus}H_m$ of isoelectronic alkyldiamines [8] (values not represented in figure 2) showed their unexpected superposition to the corresponding values of alkyldiamides, despite their four H-bonds per molecule as opposed to eight. In this regard, it must be stressed that comparison between net values of enthalpies of fusion of different homologous series of alkyl compounds cannot be fully connected to their crystal structures (and relevant energies) since fusion is a transition between two condensed phases. The variety of the interactions in the liquid phase prevents the assignation of a specific physical meaning to the $\Delta_{fus}H_m$ values, as can be done for a solid–gas transition, if sublimation is congruent. Very recent data, in fact, have shown lower $\Delta_{fus}H_m$ values for dicarboxylic acids [38] compared with alkyldiamines and alkyldiamides, *i.e.* practically superposed to those of alkanes. This apparently anomalous behaviour has been interpreted as resulting from the cyclisation of dicarboxylic acids in the liquid phase and formation of intramolecular hydrogen bonded species. The superposition of $\Delta_{fus}H_m$ of the homologous series of alkyldiamides and alkyldiamines can be thus interpreted to be due to the presence of some residual solid-state interactions in liquid alkyldiamides. The $\Delta_{fus}S_m$ values of the alkyldiamides (figure 3), also lower than expected, are equally ascribable to the presence of residual H-bonding structures in the liquid phase.

Our results can be usefully presented as plots of the massic enthalpies and entropies of fusion as a function of n (figures 4 and 5) as for alkyldiamines in a previous paper [8]. The odd–even effect is still present for massic enthalpy values and its trend is similar to that of T_{fus}, which is an intensive quantity, too. This behaviour can be ascribed to the decrease of the specific relative contribution of the H-bonds to crystal stability. By contrast, the slight increase of the massic enthalpies of fusion of alkanes can be attributed to the long-range cumulative effect of the CH_2 dispersive interactions. In alkyldiamides, any possible effect of this kind is clearly overwhelmed by the presence of a strong hydrogen bonded network. The massic entropy trend (figure 5) is in agreement with the interpretation given for the massic enthalpies. Moreover, the superposition of massic entropy values to those of alkanes indicates that the loss of order accompanying fusion in alkyldiamides is lower than for alkyldiamines [8]. This provides further evidence of the presence of residual H-bonding structures in their liquid phase.

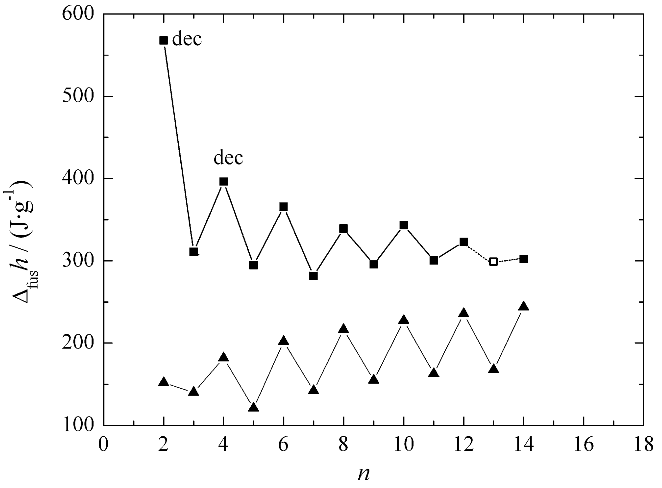

FIGURE 4. Plot of massic enthalpies of fusion $\Delta_{fus}h$ as a function of the number of carbon atoms n in the alkyl chain: ■, alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$; ▲, isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$. Void symbols: estimated values.

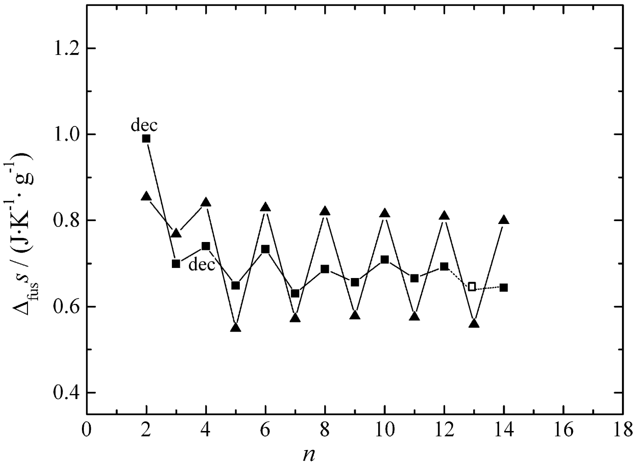

FIGURE 5. Plot of massic entropies of fusion $\Delta_{fus}s$ as a function of the number of carbon atoms n in the alkyl chain: ■, alkane-α,ω-diamides $H_2NCO–(CH_2)_{(n-2)}–CONH_2$; ▲, isoelectronic linear alkanes $H_3C–(CH_2)_{(n+2)}–CH_3$. Void symbols: estimated values.

3.3. Enthalpy–entropy of fusion interplay

The interplay plot $\Delta_{fus}H_m = f(\Delta_{fus}S_m)$ gave straight lines for both even and odd alkyldiamides (figure 6). In our earlier work on alkyldiamines, the slope of the molar enthalpy–entropy interplay was assumed to correspond to the temperature of fusion ($\Delta_{fus}H_m/\Delta_{fus}S_m = T_{fus}$) of the solid CH_2 group [8]. For linear even and odd alkanes in close ranges of n, $T_{fus}[CH_2] = 380$ K was compared with the temperature of fusion of polyethylene (415 K) considered as the limiting value of the interplay slope for linear alkanes with the longest chains [41–44]. Our present measurements for alkyldiamides indicate that slope for even terms (400 K) is close to that of alkanes, whereas the slope (450 K) of the odd terms is higher. A similar behaviour can be observed for the interplay plots of even and odd dicarboxylic acids [38], which were drawn by us and gave slopes of about 401 K and 355 K, respectively. The departure of the odd alkyldiamide term slope values from those of the even terms could be referred to the presence of residual associations in the liquid phase as was found for dicarboxylic acids [38].

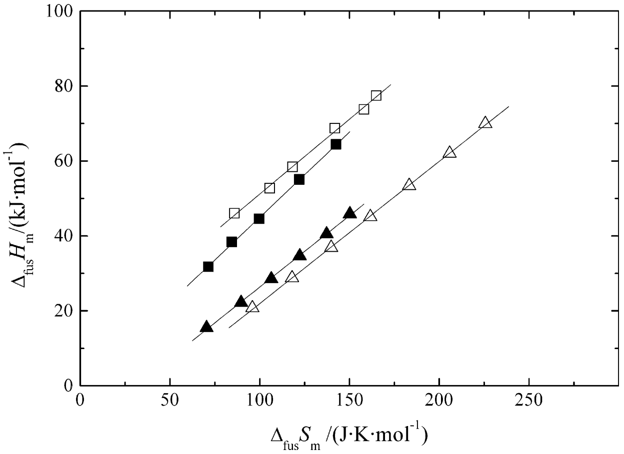

FIGURE 6. Plot of molar enthalpies of fusion $\Delta_{fus}H_m$ against molar entropies of fusion $\Delta_{fus}S_m$ to illustrate the interplay. For the alkyldiamides: □, n is even; ■, n is odd. For linear alkanes: △, n is even; ▲, n is odd.

3.4. Solid-to-solid transitions

Solid-to-solid transitions were observed for almost all even alkyldiamides C_2, C_4, C_6, C_8, and C_{12} plus C_3 (table 3). Oxamide showed three transitions in the solid phase, but only one, that at the lowest temperature, was irreversible. For malonamide, C_3, the only alkyldiamide of this series so far investigated, an irreversible transition at higher temperature than that reported in the literature was found, but the associated enthalpy value was identical [2]. One irreversible transition was found for adipamide and suberamide, and one reversible transition for succinamide and

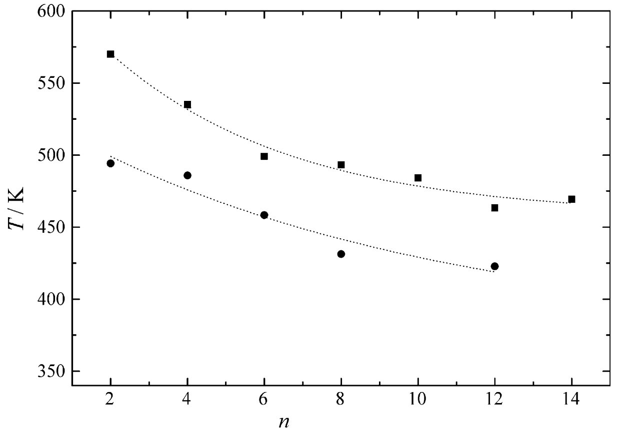

FIGURE 7. Plot of temperatures of fusion T_{fus}, ■, and temperatures of solid-to-solid transitions, T_{trs}, ●, of even alkane-α,ω-diamides as a function of the number of carbon atoms n in the alkyl chain.

dodecanediamide. All these transitions occur well before the temperature of fusion (40 K to 60 K), except for malonamide. As a consequence, the fusion enthalpy value of malonamide reported in figure 2 is the sum of enthalpies of both solid-to-solid and solid-to-liquid phase transitions.

If we compare T_{fus} and T_{trs} as a function of carbon atoms in the molecules, a rather similar descending trend was observed for both temperatures (figure 7).

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