

MELTING, VOLATILISATION AND CRYSTAL LATTICE ENTHALPIES OF ACRIDIN-9(10H)-ONES

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Abstract

The enthalpies and temperatures of melting and sublimation of acridin-9(10H)-one, 10-methylacridin-9(10H)-one, 2,10-dimethylacridin-9(10H)-one, 10-methyl-2-nitroacridin-9(10H)-one, 10-ethylacridin-9(10H)-one and 10-phenylacridin-9(10H)-one were measured by DSC. Enthalpies and temperatures of volatilisation were also obtained by fitting TG curves to the Clausius–Clapeyron relationship. Complementary investigations for anthracene showed the extent to which the thermodynamic characteristics thus obtained compare with those determined by means of other techniques. For compounds whose crystal structures are known, experimental enthalpies of sublimation correspond reasonably well to crystal lattice enthalpies predicted theoretically as the sum of electrostatic, dispersive and repulsive interactions. Analysis of crystal lattice enthalpy contributions indicates that dispersive interactions always predominate. Interactions are enhanced in acridin-9(10H)-one where intermolecular hydrogen bonds occur: this is reflected in the relatively high enthalpy of sublimation.

Keywords: acridin-9(10H)-ones, anthracene, crystal lattice enthalpies, enthalpies and temperatures of melting, enthalpies and temperatures of sublimation

Introduction

Acridin-9(10H)-ones are heterocyclic compounds containing amino and keto fragments within the ring system enabling them to interact specifically with other molecules from their immediate surroundings [1, 2]. As a result of these properties, these compounds are convenient models for investigating various features of chemical entities. The spectral [3–5] and physicochemical [6] properties of these compounds were the subject of our recent investigations. As acridin-9(10H)-ones efficiently emit radiation in the short-wavelength visible region, they have been applied as spectral sensors [7, 8] or fragments of fluorescent labels [9,10]. Electronically excited acridin-9(10H)-ones are also formed when strong oxidants, e.g. hydrogen peroxide, react with 9-substituted-10-methylacridinium cations [11–14]. This property forms the basis for the use of the latter entities as chemiluminescent indicators or fragments of chemiluminescent labels, which are of practical importance in assays of macro-

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molecules present in living matter [12, 14–16]. In the design of fluorescent or chemiluminescent indicators, sensors or labels, it is important to know the basic properties of light emitting molecules. This is the reason for our interest in acridin-9(10H)-ones.

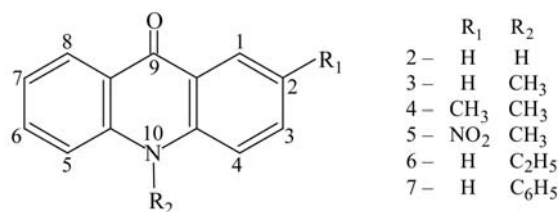
This work presents the results of thermoanalytical investigations and theoretical studies, the central idea of which was to gather information on the thermodynamics of solid acridin-9(10H)-ones, i.e. enthalpies of melting and volatilisation, as well as crystal lattice enthalpies. The latter quantity is a measure of the natural tendency towards the organisation of matter [17]. In the case of molecular crystals, for example, those formed by anthracene and acridin-9(10H)-ones, the lattice enthalpy can be determined experimentally as the sublimation enthalpy [18] by using various techniques [19–22].

Undertaking this subject thus gave us an opportunity to discover what forces retain molecules in condensed phases, and how experiment and theory are applied in the determination of basic thermodynamic characteristics such as sublimation and lattice enthalpies [23–24].

Methods

Determination of volatilisation enthalpy

The compounds investigated (Scheme 1) were obtained or synthesised and purified as described in [3–5].



Scheme 1 The acridin-9(10H)-ones investigated

Thermogravimetric measurements were carried out on a Netzsch TG 209 thermobalance. Samples weighing 1.5–6.5 mg were placed in a platinum crucible and heated at 2.5 and 5.0 K min⁻¹ in a dynamic Ar atmosphere.

Volatilisation enthalpies ($\Delta_v H^0$) were obtained by fitting TG curves to the Clausius–Clapeyron relationship [20]

$$\ln \alpha = -\frac{\Delta_v H^0}{R} \frac{1}{T} + \frac{\Delta_v H^0}{R} \frac{1}{T_v} \quad (1)$$

in which α represents the extent of volatilisation ($\alpha = p/p^0$, where p is the equilibrium vapour pressure at a given temperature (T) and p^0 the standard atmospheric pressure (0)), R denotes the gas constant and T_v is the temperature at which p attains p^0 . As the volatilisation enthalpies obtained in the above manner suffer from errors that are difficult to assess and also from the lack of reliable means of estimating the thermal energy contributions upon reduction of the data to 298.15 K, we standardised the measurement procedure for anthracene, for which the mean sublimation enthalpy is equal

to 105 kJ mol^{-1} [25–33]. (All literature values of the enthalpy of sublimation were reduced to 298.15 K as described in [33]). Using this approach, we found that $\Delta_v H^0$ for anthracene obtained in this manner is 88 kJ mol^{-1} , i.e. 1.193 times lower than the literature value. We therefore modified all the directly obtained values for anthracene and acridin-9(10H)-ones by multiplying them by this coefficient (the thus corrected values (the mean from at least three replicate measurements) – denoted $\Delta_{v,298} H^0$ – are given in Table 1).

The DSC measurements were carried out on a Netzsch DSC 204 instrument. Samples weighing 1.5–6.0 mg were placed in an aluminium crucible (either tightly wrapped in aluminium foil or covered with an aluminium lid with pinholes) and heated at $1.0\text{--}10.0 \text{ K min}^{-1}$ in a dynamic Ar atmosphere. Enthalpies of melting and sublimation were obtained by selecting the appropriate temperature range and using the ‘horizontal sigmoidal’ option of the baseline in the data processing program. The mean values from at least three replicate measurements of enthalpies and temperatures characterising both processes are listed in Table 1.

Crystal lattice energy calculations

Crystal lattice energies (E_c) were calculated by summing the electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) contributions [18, 20, 23, 24],

$$E_c = E_{el} + E_d + E_r \quad (2)$$

and neglecting the zero point energy and thermal energy terms [23]. E_{el} in Eq. (2) represents Coulombic interactions [20],

$$E_{el} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{Ne^2 Q_i Q_j}{4\pi\epsilon_0 R_{ij}} \quad (3)$$

while the sum of E_d and E_r is expressed by Buckingham’s formula [37]

$$E_d + E_r = \frac{1}{2} \sum_i \sum_{j \neq i} \left[-\frac{D_i D_j}{R_{ij}^6} + A_i A_j \exp(-B_i B_j R_{ij}) \right] \quad (4)$$

In Eqs (3) and (4) N is the Avogadro number, e is the elementary charge, and ϵ_0 is the permittivity of free space, while Q_i (Q_j) denote the relative partial charges at atoms, D_i (D_j), A_i (A_j) and B_i (B_j) are atomic parameters, and R_{ij} is the distance between interacting centres (the summation extends over all pairwise interactions between each atom of a molecule selected as the basic stoichiometric unit (denoted by ‘i’) and all the atoms from its surroundings (denoted by ‘j’)).

The crystal structures for calculating E_c were taken from the following sources: **1** [38], **2** [39], **3** [40], **6** [41] and **7** [42]. The relative atomic partial charges necessary for calculating the energy of electrostatic interactions were fitted in such a way as to reproduce the molecular electrostatic potential around molecules (MEP fitted charges) [43] derived at the density functional theory (DFT) level [44]. These charges were obtained using the B3LYP functional [45, 46] together with the 6–31G** basis set [47] included in the SPARTAN 5.0 program package [48]. Crystal lattice energies

Table 1 Thermodynamic data for melting and sublimation of anthracene and acridin-9(10H)-ones obtained from TG and DSC measurements together with theoretically predicted crystal lattice enthalpies^a

Compound ^b	TG		DSC				Theory			
	T_v	$\Delta_{v,298}H^0$	T_m^c	$\Delta_m H^d$	T_{ev}	$\Delta_v H^e$	$-E_{cl}$	$-E_d$	E_r	$-\Delta_{c,298}H^0$
1	500	105	491 491*	26.9 31.5*	535	106	9.9	127.1	37.5	102.0
2	600	126	640 640*	22.5 32.5*	660	133	39.2	140.6	71.0	111.3
3	565	98	478 479*	29.0 29.7*	615	105	23.9	147.3	44.0	129.7
4	615	111	426 426*	22.4 22.4*	625	119				
5	625	124	560 561*	30.5 37.6*						
6	580	106	434 434*	27.0 27.5*	610	117	17.0	173.0	74.4	118.1
7	600	118	551 550*	36.7 38.9*	630	128	17.0	166.1	42.2	143.4

^a T_v and $\Delta_{v,298}H^0$ denote the temperature and enthalpy of volatilisation, respectively, resulting from the fit of Eq. (1) to TG curves; T_m and $\Delta_m H$ represent the temperature and enthalpy of melting, respectively, obtained from DSC measurements (values marked with an asterisk indicate those when the sample crucible was tightly covered); T_{ev} and $\Delta_v H^0$ are the temperature of evaporation and the enthalpy of sublimation (the sum of the enthalpy of melting and evaporation) obtained from DSC experiments; $\Delta_{c,298}H^0$ is the crystal lattice enthalpy. All temperatures are in K, the enthalpies are in kJ mol⁻¹.

^b**1** – anthracene; **2** – 9(10H)-acridinone; **3** – 10-methylacridin-9(10H)-one; **4** – 2,10-dimethylacridin-9(10H)-one;

^c**5** – 10-methyl-2-nitroacridin-9(10H)-one; **6** – 10-ethylacridin-9(10H)-one and **7** – 10-phenylacridin-9(10H)-one.

^dLiterature values: 627 (**2**), 476 (**3**), 432 (**6**) and 549 (**7**) [34].

^eLiterature values: 29.4 (**1**) [35].

^fLiterature values corresponding to 298.15 K: 105 (**1**) [25–33] and 136 (**2**) [36].

were calculated using the General Utility Lattice Program (GULP) – a computer program for the symmetry-adapted simulation of solids [49]. The parameters of pairwise interactions proposed by Mirsky were taken from the literature [50].

Crystal lattice enthalpies ($\Delta_{c,298}H^0$) were obtained by including the $pV=RT$ contribution

$$\Delta_{c,298}H^0 = E_c - 298.15R \quad (5)$$

$\Delta_{c,298}H^0$ together with the values of E_{el} , E_d and E_r are listed in Table 1.

Results and discussion

The extent of volatilisation (α) vs. temperature (T) dependencies seen in Fig. 1 is reflected by the thermogravimetric curves. Their smooth shape is evidence for the simple release of molecules held in the condensed phase to the gaseous phase. The energy barrier for such a process is the same as the thermodynamic one, i.e. the enthalpy of volatilisation. It may thus be expected that the system attains equilibrium just as soon as the temperature increases. If this is the case, α represents the ratio p/p^0 and α vs. T dependencies can be fitted to the Clausius–Clapeyron relationship (1) in order to obtain the enthalpies of volatilisation (given in Table 1).

Linear heating following DSC analyses of samples open to the atmosphere brings about two processes: melting and subsequent volatilisation. These processes can be completely separate, as in 2,10-dimethylacridin-9(10H)-one, or more or less overlapping – more in the case of acridin-9(10H)-one and less in e.g. 10-ethylacridin-9(10H)-one (Table 1). When melting occurs separately from volatilisation, the enthalpies and temperatures of the former process are the same, no matter whether they are measured in tightly covered crucibles or crucibles open to the atmosphere. If melting and volatilisation do not occur separately, the enthalpies measured in a tightly covered crucible are always higher than those obtained in open crucibles. This is because in open crucibles part of the sample sublimates before or during melting, and the enthalpy of melting therefore corresponds to a lower sample mass than the origi-

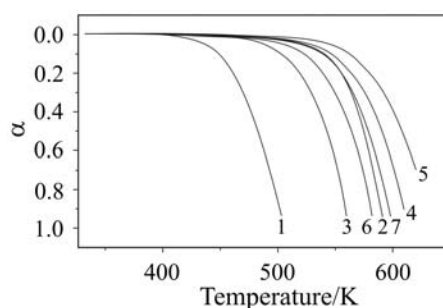


Fig. 1 Extent of volatilisation vs. T dependencies for the compounds investigated (for names, Table 1). Conditions (mass of sample in mg/heating rate in $K \text{ min}^{-1}$):
1 (6.170/5.0), **2** (2.000/5.0), **3** (3.950/5.0), **4** (4.000/5.0), **5** (2.910/5.0),
6 (4.620/2.5), **7** (4.150/2.5)

nal one. In a tightly covered crucible the only effect that occurs is melting, and the enthalpy of the process corresponds to the mass of the whole sample.

The DSC analyses of acridin-9(10H)-one are representative of the whole group of compounds investigated (Fig. 2). In this particular compound, melting and volatilisation substantially overlap. Analyses carried out at heating rates of 1.0 and 2.5 K min⁻¹ show that sublimation is complete before the melting temperature is reached. At higher heating rates – 5.0 and 10.0 K min⁻¹ – melting occurs concurrently with sublimation. The interesting thing, however, is that the enthalpies of sublimation corresponding to various heating rates are almost identical. This means that a slower temperature increase prevents melting and causes direct transfer of molecules from the crystalline to the gaseous phase. Melting is, of course, the only process to occur when acridin-9(10H)-one is heated in a tightly covered crucible.

The temperatures and enthalpies of melting determined on the basis of DSC measurements compare well with literature values for anthracene (Table 1). Moreover, the enthalpies of sublimation of anthracene and acridin-9(10H)-one compare very well with literature values of this quantity [25–33, 36] related to 298.15 K (Table 1). Because of this good agreement, one can assume that the $\Delta_s H$ values in Table 1 correspond to the ambient temperature.

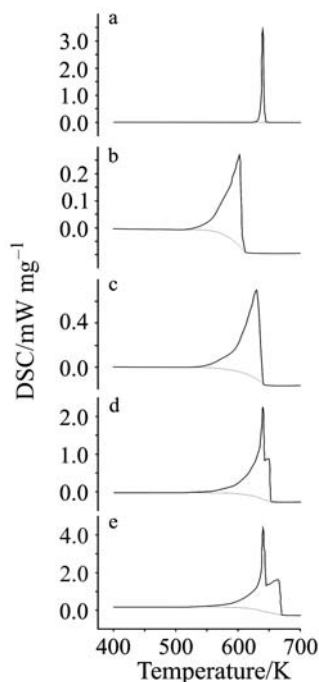


Fig. 2 DSC analyses of acridin-9(10H)-one under various conditions (mass of sample in mg/heating rate in K min⁻¹): a – in an aluminium crucible tightly wrapped in aluminium foil (4.950/5.0); b, c, d, e – in an aluminium crucible covered with an aluminium lid with pinholes (3.950/1.0, 4.050/2.5, 4.250/5.0 and 4.340/10.0, respectively)

An important piece of information emerging from the calculations relates to the electrostatic, dispersive and repulsive contributions to the lattice enthalpy. As can be seen in Table 1, the main contribution to $\Delta_{c,298}H^0$ values is due to dispersive interactions; that from electrostatic interactions is much lower. Oppositely directed repulsive interactions make up 65% of the total lattice enthalpy. Theoretical analysis therefore indicates that the major contribution to the cohesive energy of the compounds investigated comes from dispersive interactions.

In acridin-9(10H)-one, however, there is an additional N–H...O type hydrogen bond [38]. This H-bond enhances the cohesive forces; as it is not taken into account in lattice energy calculations, the resulting enthalpies and temperatures of sublimation and melting are relatively high. Relatively high values of these properties are also noted in the case of 10-phenylacridin-9(10H)-one, a compound in which increased dispersive interactions can be expected.

The crystal lattice energies generally correspond quite well to the enthalpies of sublimation, bearing in mind the fact that both properties were characterised in completely independent ways. A relatively large discrepancy is noted in the case of **2**, since the calculations do not take specific hydrogen bonding interactions into account. Other discrepancies may result from uncertainties of theoretical predictions. The theory could be improved if more suitable parameters of pairwise interactions could be found: this is an issue on which our attention is constantly focused.

The results of this work provide further evidence of the successful application of TG and DSC techniques for determining the sublimation enthalpies of molecular crystals. The theoretical methods used for calculating lattice energies are still far from perfect; nevertheless, they afford a unique insight into the nature of interactions that retain molecules in crystalline phases.

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