

Lattice energetics and thermochemistry of phenyl acridine-9-carboxylates and 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates

Nitro-, methoxy- or halogen-substituted in the phenyl fragment

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Abstract The melting points and melting enthalpies of nine phenyl acridine-9-carboxylates—nitro-, methoxy- or halogen-substituted in the phenyl fragment—and their 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonate derivatives were determined by DSC. The volatilisation temperatures and enthalpies of phenyl acridine-9-carboxylates were either measured by DSC or obtained by fitting TG curves to the Clausius–Clapeyron relationship. For the compounds whose crystal structures are known, crystal lattice energies and enthalpies were determined computationally as the sum of electrostatic, dispersive and repulsive interactions. By combining the enthalpies of formation of gaseous phenyl acridine-9-carboxylates or 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonate ions, obtained by the DFT method, and the corresponding enthalpies of sublimation and/or crystal lattice enthalpies, the enthalpies of formation of the compounds in the solid phase were predicted. In the case of the phenyl acridine-9-carboxylates, the computationally predicted crystal lattice enthalpies correspond reasonably well with the experimentally obtained enthalpies of sublimation. The crystal lattices of phenyl acridine-9-carboxylates are stabilised predominantly by dispersive interactions between molecules, whilst the crystal lattices of their quaternary salts are stabilised by electrostatic interactions between ions.

Keywords Crystal lattice energies and enthalpies · DSC and TG investigations · Enthalpies of formation ·

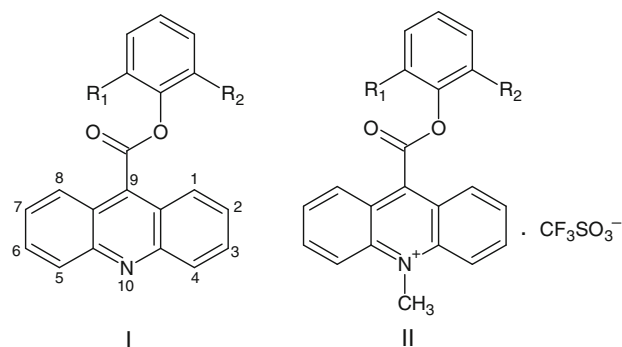
Melting and volatilisation enthalpies · Phenyl acridine-9-carboxylates · 9-Phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates

Introduction

Acridinium cations alkyl-substituted at the endocyclic nitrogen atom and containing electron-attracting substituents at C9 (Scheme 1) display chemiluminogenic features if they are treated with oxidants (H_2O_2 , peroxides) in alkaline media [1–6]. Initiated by the attack of peroxide anions (e.g. HO_2^-) on C9, this process gives rise to electronically excited *N*-alkyl-9-acridinones whose relaxation is accompanied by the emission of light. The efficiency of chemiluminescence, which reaches a few percent [7], is affected by the presence of nucleophilic species competing with oxidants for the substitution at C9 [8, 9]. This effect, exhibited by acridinium chemiluminogenic indicators, is utilised in the assay of oxidants or nucleophiles [1–4, 8, 9]. Acridinium chemiluminogens can also be linked via a spacer (e.g. alkyl chain) to an active group able to react with relevant fragments of macromolecules. The use of such compounds, known as chemiluminescent labels, is standard in environmental, biological and medical analyses [2–4, 7, 10–15].

The main aim of this study was to discover the thermal properties of 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates displaying chemiluminogenic features, and of their precursors, phenyl acridine-9-carboxylates substituted with an electronegative methoxy group, nitro group or halogen in position 1 or positions 1 and 2 of the phenyl fragment (Scheme 1; Table 1). These compounds were selected for investigations since the electron-attracting features of the substituents in the phenyl

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Scheme 1 Canonical structures of phenyl acridine-9-carboxylates (**I**) and 9-phenoxy carbonyl-10-methylacridinium trifluoromethanesulphonates (**II**) (Table 1)

fragment may substantially affect their affinity for nucleophiles and susceptibility to oxidation (chemiluminescence efficiency), and consequently their applicability. A further objective was to determine the thermodynamic characteristics of the compounds, i.e. their melting points, melting and volatilisation enthalpies, crystal lattice enthalpies, enthalpies of formation and Gibbs free energies of formation, by combining the results of experimental investigations and computational predictions. There are numerous examples confirming the utility of such an approach in determining the thermal and thermodynamic characteristics of chemical substances in the gaseous and solid phase

[16–24]. In undertaking the investigations, our intention was to focus on the applicability of the compounds investigated, which substantially depends on their thermal behaviour and stability.

Methods

Syntheses

The compounds investigated (Scheme 1; Table 1) were synthesised and purified as described earlier [10, 25]. Their identity was confirmed by MS, NMR spectroscopy and, in some cases, X-ray crystallography [25–31]. The purity of the compounds, evaluated from HPLC analyses, was better than 99.5%.

Determination of melting and volatilisation characteristics

Differential scanning calorimetry (DSC) measurements were carried out by a Netzsch DSC 204 instrument. Samples weighing 0.7–3.8 mg were placed in an aluminium crucible (covered with an aluminium lid with pinholes) and heated at 2.5 or 5.0 K min⁻¹ in a dynamic Ar atmosphere. The melting and volatilisation enthalpies were obtained by selecting the appropriate temperature range and using the

Table 1 The compounds investigated (Scheme 1)

| Compound no. | Compound name | R ₁ | R ₂ |
|--|--|------------------|------------------|
| <i>Phenyl acridine-9-carboxylates (I)</i> | | | |
| 1 | 2-nitrophenyl acridine-9-carboxylate | NO ₂ | H |
| 2 | 2-methoxyphenyl acridine-9-carboxylate | OCH ₃ | H |
| 3 | 2-fluorophenyl acridine-9-carboxylate | F | H |
| 4 | 2-iodophenyl acridine-9-carboxylate | I | H |
| 5 | 2,6-dimethoxyphenyl acridine-9-carboxylate | OCH ₃ | OCH ₃ |
| 6 | 2,6-difluorophenyl acridine-9-carboxylate | F | F |
| 7 | 2,6-dichlorophenyl acridine-9-carboxylate | Cl | Cl |
| 8 | 2,6-dibromophenyl acridine-9-carboxylate | Br | Br |
| 9 | 2,6-diiodophenyl acridine-9-carboxylate | I | I |
| <i>9-Phenoxy carbonyl-10-methylacridinium trifluoromethanesulphonates (II)</i> | | | |
| 10 | 9-[(2-nitrophenoxy)carbonyl]-10-methylacridinium | NO ₂ | H |
| 11 | 9-[(2-methoxyphenoxy)carbonyl]-10-methylacridinium | OCH ₃ | H |
| 12 | 9-[(2-fluorophenoxy)carbonyl]-10-methylacridinium | F | H |
| 13 | 9-[(2-iodophenoxy)carbonyl]-10-methylacridinium | I | H |
| 14 | 9-[(2,6-dimethoxyphenoxy)carbonyl]-10-methylacridinium | OCH ₃ | OCH ₃ |
| 15 | 9-[(2,6-difluorophenoxy)carbonyl]-10-methylacridinium | F | F |
| 16 | 9-[(2,6-dichlorophenoxy)carbonyl]-10-methylacridinium | Cl | Cl |
| 17 | 9-[(2,6-dibromophenoxy)carbonyl]-10-methylacridinium | Br | Br |
| 18 | 9-[(2,6-diiodophenoxy)carbonyl]-10-methylacridinium | I | I |

For **I**, the compound is named; for **II**, the cation is named

Table 2 Thermochemical data corresponding to the melting and volatilisation of the compounds investigated (Table 1)

| Compound no. | T_m^a | T_v | | $\Delta_m H^0$ | $\Delta_v H^0$ | |
|--|----------|-------|-------|----------------|----------------|-------|
| | | DSC | Eq. 1 | | DSC | Eq. 1 |
| <i>Phenyl acridine-9-carboxylates (I)</i> | | | | | | |
| 1 | 422 | | | 24.4 | | |
| 2 | 462 | 632 | 635 | 38.8 | 98.7 | 121.6 |
| 3 | 437 | 583 | 578 | 28.1 | 84.1 | 92.0 |
| 4 | 438 | 617 | 601 | 32.4 | 103.8 | 104.8 |
| 5 | 480 | 610 | | 23.2 | 110.0 | |
| 6 | 467 | 594 | 598 | 34.3 | 96.3 | 85.7 |
| 7 | 418 | 620 | 612 | 28.5 | 88.5 | 92.3 |
| 8 | 432 | 625 | 656 | 31.9 | 105.0 | 107.6 |
| 9 | 453 | | | | | |
| <i>9-Phenoxy carbonyl-10-methylacridinium trifluoromethanesulphonates (II)</i> | | | | | | |
| 10 | 506, 509 | | | 34.5 | | |
| 11 | 516 | | | 49.9 | | |
| 12 | 503 | | | 34.3 | | |
| 13 | 489 | | | 33.3 | | |
| 14 | 542 | | | 32.8 | | |
| 15 | 517 | | | 37.7 | | |
| 16 | 527 | | | 41.6 | | |
| 17 | 520 | | | 44.1 | | |
| 18 | 463, 481 | | | 36.6 | | |

T_m and $\Delta_m H^0$ represent the melting point and melting enthalpy obtained from DSC measurements, respectively; T_v and $\Delta_v H^0$ denote the temperature and enthalpy of volatilisation, respectively. All temperatures are in K, and enthalpies are in kJ mol^{-1}

^a Literature values, in K: 454–455 (6) [25], 404–405 (7) [26], 428–429 (8) [28], 448–449 (9) [29], 516–518 (14) [31], 504–506 (15) [25], 515–517 (16) [26], 481–483 (17) [27]

‘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 2.

Thermogravimetric measurements were carried out by a Netzsch 209 thermobalance. Samples weighing 1.0–6.8 mg were placed in a platinum crucible and heated at 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 [19]

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

where α represents the equilibrium extent of volatilisation (fraction of mass loss) [$\alpha = p/p^0$, where p is equilibrium vapour pressure at a given temperature (T), p^0 is standard (atmospheric) pressure (0)], R is gas constant and T_v is the temperature at which p reaches p^0 (volatilisation temperature).

As the volatilisation enthalpies obtained in the above manner suffer from errors that are difficult to assess, and because there are no reliable means of estimating the thermal enthalpy contributions on reducing the data to 298 K, we standardised the measurement procedures for

anthracene, for which the mean sublimation enthalpy is 105 kJ mol^{-1} [19]. Using this approach, we found that $\Delta_v H^0$ for anthracene, obtained by DSC and Eq. 1, are, respectively, 1.06 and 1.087 times lower than the literature value. We, therefore, multiplied all the values obtained for phenyl acridine-9-carboxylates (Table 2) by the relevant coefficient. The final values (the mean from corrected TG and DSC wherever possible), enlarged by $\Delta_m H^0$ (Table 2), denoted by $\Delta_{s,298} H^0$, are listed in Table 3.

Crystal lattice energy calculations

The crystal lattice energy (E_c) was calculated by summing the electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) contributions [18, 19]

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

E_{el} in Eq. 2 represents Coulombic interactions [18, 19],

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

whilst the sum of E_d and E_r is given by Buckingham’s formula [32]

Table 3 Thermodynamic characteristics of the compounds investigated (Table 1)

| Compound no. | $\Delta_{s,298}H^0$ | $-E_{el}$ | $-E_d$ | E_r | $-\Delta_{c,298}H^0$ | $\Delta_{f,298}H^0(g)^a$ | $\Delta_{f,298}G^0(g)^a$ | $\Delta_{f,298}H^0(c)$ |
|--|---------------------|-----------|--------|-------|----------------------|--------------------------|--------------------------|------------------------|
| <i>Phenyl acridine-9-carboxylates (I)</i> | | | | | | | | |
| 1 | | | | | | 169.0 | 432.6 | |
| 2 | 157 | | | | | 28.9 | 292.4 | -128 |
| 3 | 123 | | | | | -29.0 | 184.8 | -152 |
| 4 | 144 | | | | | (196.4) | (388.2) | (52) |
| 5 | 140 | | | | | -99.5 | 218.4 | -240 |
| 6 | 132 | 14.8 | 179.5 | 46.6 | 150.2 | -213.1 | 5.4 | -354 |
| 7 | 126 | 13.0 | 210.9 | 70.2 | 156.2 | 121.5 | 340.3 | -20 |
| 8 | 146 | 10.6 | 199.0 | 53.8 | 158.3 | 197.9 | 390.9 | 46 |
| 9 | | 3.9 | 208.5 | 62.9 | 152.0 | (277.0) | (453.2) | (125) |
| <i>9-Phenoxy carbonyl-10-methylacridinium trifluoromethanesulphonates (II)</i> | | | | | | | | |
| 10 | | 403.8 | 294.3 | 98.3 | 604.8 | 714.4 | 1028.9 | -1026 |
| 11 | | | | | | 561.4 | 875.6 | |
| 12 | | | | | | 512.7 | 777.2 | |
| 13 | | | | | | (742.6) | (985.3) | |
| 14 | | 381.6 | 269.7 | 74.9 | 581.4 | 424.7 | 792.0 | -1293 |
| 15 | | 381.6 | 254.6 | 74.9 | 566.3 | 329.5 | 596.8 | -1373 |
| 16 | | 389.6 | 277.7 | 92.1 | 580.2 | 666.1 | 933.8 | -1050 |
| 17 | | 385.5 | 277.3 | 84.7 | 583.1 | 739.7 | 982.9 | -979 |
| 18 | | | | | | (822.9) | (1,048.6) | |

$\Delta_{s,298}H^0$, E_{el} , E_d , E_r , $\Delta_{c,298}H^0$, $\Delta_{f,298}H^0$, $\Delta_{f,298}G^0$, all in kJ mol^{-1} represent the enthalpy of sublimation, the electrostatic contribution to the crystal lattice energy, the dispersive contribution to the crystal lattice energy, the repulsive contribution to the crystal lattice energy, the crystal lattice enthalpy, the enthalpy of formation and the Gibbs free energy of formation (estimated values are given in parentheses) at standard pressure (0) and temperature 298 K corresponding to the DFT/6-31G** level of theory [(g)—gaseous state, (c)—solid state], respectively

^a For **I**, values are given for the molecules; for **II**, values are given for the cations

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

In Eqs. 3 and 4 N is Avogadro number, e is elementary charge, ϵ_0 is permittivity of free space, Q_i (Q_j) is relative partial charges on the atoms, D_i (D_j), A_i (A_j) and B_i (B_j) are atomic parameters, and R_{ij} is 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 following sources: **6** [25], **7** [26], **8** [28], **9** [29], **10** [30], **14** [31], **15** [25], **16** [26] and **17** [27]. The relative atomic partial charges necessary for calculating the energy of electrostatic interactions were those reproducing the molecular electrostatic potential around molecules (MEP fitted charges) [33] derived at the density functional theory (DFT) level [34]. In the latter calculations, the B3LYP functional [35–37] together with the 6-31G** basis set [38] and LanL2DZ basis set [39] for the compounds containing iodine were used. Calculations were carried out using the

Table 4 Atomic parameters for calculating the energies of dispersive and repulsive interactions

| Atom | Parameter | | |
|------|-----------|-------|------|
| | D | A | B |
| H | 11.0 | 143.2 | 2.07 |
| C | 42.0 | 547.3 | 1.92 |
| N | 32.9 | 419.2 | 1.94 |
| O | 32.9 | 570.2 | 2.04 |
| F | 30.1 | 635.7 | 2.04 |
| S | 99.1 | 991.6 | 1.87 |
| Cl | 111.7 | 138.4 | 1.50 |
| Br | 108.4 | 502.0 | 1.74 |
| I | 147.7 | 589.3 | 1.70 |

D in $\text{kJ}^{1/2} \text{mol}^{-1/2} \text{\AA}^3$; A in $\text{kJ}^{1/2} \text{mol}^{-1/2}$; B in $\text{\AA}^{-1/2}$. The parameters for H, C, N, O, S and Cl (parameters by Mirsky) were taken from [41], those for F, Br and I from [42]

Gaussian 03 program package [40]. The atomic parameters for calculating the energy of attractive and repulsive pairwise interactions were taken from the literature (Table 4) [41, 42]. Crystal lattice energies were calculated using the General Utility Lattice Program (GULP) [43].

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

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

where $n = 1$ for phenyl acridine-9-carboxylates and $n = 2$ for 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates.

$\Delta_{c,298}H^0$, E_{el} , E_d and E_r are listed in Table 3.

Quantum chemistry and thermodynamic computations

Unconstrained geometry optimisations of isolated molecules of phenyl acridine-9-carboxylates, 9-phenoxy-carbonyl-10-methylacridinium cations and $CF_3SO_3^-$ were carried out at the DFT level of theory [34] using Baker's optimisation procedure [44] together with the B3LYP functional [35–37] and 6-31G** [38] or LanL2DZ [39] basis sets. The validity of the geometry optimisations was confirmed in the subsequent Hessian (second derivatives of the energy vs. atomic coordinates) calculations followed by normal mode analyses [45]. The bond lengths and vibrational harmonic frequencies, therefore, determined were used to obtain the zero-point energy, thermal enthalpy and the Gibbs free energy contributions [at 298 K and standard pressure (0)] to energies corresponding to optimised structures with the aid of a built-in computational program of statistical thermodynamics routines [46]. The enthalpies and Gibbs free energies of formation of gaseous entities were obtained by following the basic rules of thermodynamics [47]. In the calculations, the thermodynamic quantities of these gaseous entities, as well as those of H_2 , N_2 , O_2 , F_2 and Cl_2 , were taken directly from data files after the computations. In order to obtain the enthalpies of $C(c)$, $S(c)$, $Br_2(l)$ and $I_2(c)$, the predicted enthalpies of the gaseous entities were lowered by 716.67, 277.17, 30.91 and 62.42 kJ mol^{-1} , respectively, i.e. by the enthalpies of their volatilisation at 298 K, and then raised by 8.5×0.298 , 22.7×0.298 , 75.7×0.298 and 54.4×0.298 kJ mol^{-1} , respectively [48], i.e. by the thermal enthalpies of the entities in the condensed phase at 298 K (the respective heat capacities at 298 K of solid C, S and I_2 are 8.5, 22.7 and 54.4 $\text{J mol}^{-1} \text{K}^{-1}$, and that of liquid Br_2 at the same temperature is 75.7 $\text{J mol}^{-1} \text{K}^{-1}$; NIST, <http://webbook.nist.gov>). In order to obtain the Gibbs free energies of $C(c)$, $S(c)$, $Br_2(l)$ and $I_2(c)$, the enthalpies of these entities obtained in the above manner were modified by subtracting 5.6×0.298 , 32.0×0.298 , 152.2×0.298 and 116.1×0.298 kJ mol^{-1} , respectively, i.e. the entropies of the entities in the condensed phase (NIST, <http://webbook.nist.gov>) multiplied by 298 K. Quantum chemistry calculations were carried out using the Gaussian 03 program package [40].

As found earlier, thermochemical quantities can be predicted reasonably well at the DFT/6-31G** level of

theory [49, 50]. Unfortunately, the 6-31G** basis set [38] for iodine is not included in the Gaussian 03 program [40], which makes it impossible to determine the standard enthalpies ($\Delta_{f,298}H^0$) and Gibbs free energies ($\Delta_{f,298}G^0$) of formation of the compounds containing this element. In order to tackle this problem, we used for comparison the LanL2DZ basis set [39], which does not have this inconvenience. When we compared $\Delta_{f,298}H^0$ and $\Delta_{f,298}G^0$ for all the compounds except those containing iodine, we found that the values obtained at the DFT/LanL2DZ level were 768.2 and 798.8 kJ mol^{-1} higher for phenyl acridine-9-carboxylates and 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates than the respective values corresponding to the DFT/6-31G** level of theory. We thus lowered $\Delta_{f,298}H^0$ and $\Delta_{f,298}G^0$ obtained at the DFT/LanL2DZ level by the above-mentioned values. Such estimated values of the standard enthalpies and Gibbs free energies of formation corresponding to the DFT/6-31G** level are given in parentheses in Table 3.

The standard enthalpies of formation of solid phenyl acridine-9-carboxylates (**I**) [$\Delta_{f,298}H^0(c)$] were obtained by subtracting the enthalpy of sublimation ($\Delta_{s,298}H^0$), the enthalpy of the crystal lattice ($-\Delta_{c,298}H^0$) or the mean from $\Delta_{s,298}H^0$ and $-\Delta_{c,298}H^0$ from the relevant enthalpy of formation in the gaseous phase [$\Delta_{f,298}H^0(g)$] (Table 3) [48]. Standard enthalpies of formation of solid 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates (**II**) were determined by the equation

$$\Delta_{f,298}H^0(c) = \Delta_{c,298}H^0 + \Delta_{f,298}H^0(g) - 1136 \text{ kJ mol}^{-1} \quad (6)$$

in which $-1136 \text{ kJ mol}^{-1}$ is the standard enthalpy of formation of gaseous $CF_3SO_3^-$ [48]. The values of the other quantities are given in Table 3.

Results and discussion

Thermoanalytical investigations

Heating phenyl acridine-9-carboxylates at a constant rate of temperature increase leads to melting and subsequent volatilisation, as the DSC analyses demonstrate (Fig. 1). The melting points, which vary between 418 and 480 K, are lower than the corresponding volatilisation temperatures (from 583 to 632 K) by 127–202 K (Table 2). Melting is always separate from volatilisation, therefore the enthalpies of both processes can be determined. Melting enthalpies vary between 23.2 and 38.8 kJ mol^{-1} , the lowest value being obtained for compound **5** and the highest for **2**. Volatilisation enthalpies lay between 84.1 and 110.0 kJ mol^{-1} : compound **3** has the lowest value and compound **5** the highest. DSC analyses of 9-phenoxy-carbonyl-10-methylacridinium

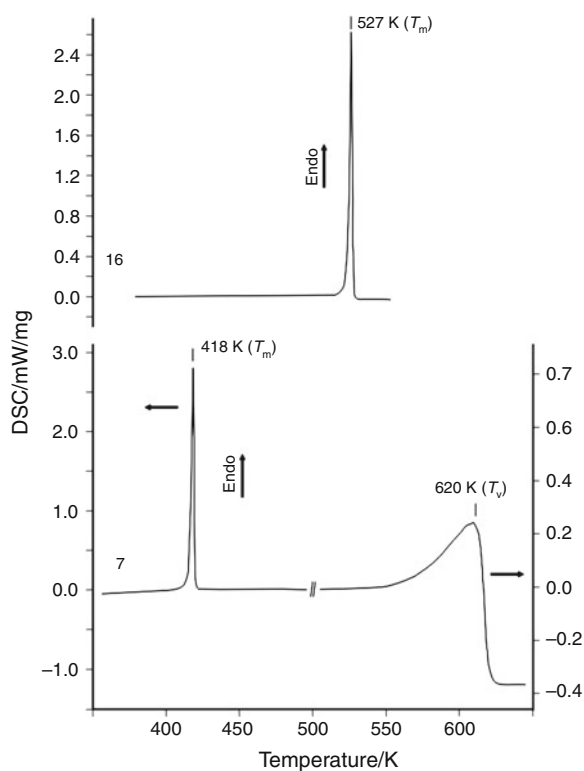


Fig. 1 Examples of DSC analyses of the compounds investigated (mass of the sample in mg/heating rate in K min^{-1}): **7** (1.850/5.0) and **16** (2.850/5.0). T_m —melting point, T_v —volatilisation temperature (assumed to be the temperature of the peak of the first DSC derivative). Lowering the base line during volatilisation is associated with a decrease in the system's heat capacity: sample holder + sample

trifluoromethanesulphonates covered the whole range of melting temperatures, i.e. from 481 to 542 K. Compound **18** has the lowest melting point, compound **14** the highest. Compounds **10** and **18** probably undergo phase transition before melting since two poorly separated signals occur in the expected melting temperature range. Melting enthalpies vary between 32.8 and 49.9 kJ mol^{-1} ; the lowest value is for compound **14**, the highest for **11**. 9-Phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates decompose at temperatures above their melting points. Decomposition of the latter compounds was not investigated due to its complex nature and because cognitively it is not so important. The above-mentioned thermochemical characteristics represent individual features of the compounds investigated. It is thus hard to find any correlation between these characteristics and the structural or physicochemical features of the compounds.

The thermogravimetric curves of phenyl acridine-9-carboxylates are reflected by the plot of the extent of volatilisation (α) versus temperature (T ; Fig. 2). The smooth shape of this relationship is evidence for the simple release of molecules held in the condensed phase to the gaseous phase.

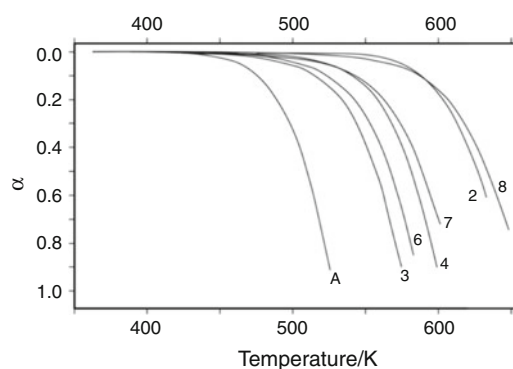


Fig. 2 Extent of volatilisation (α) versus temperature (T) relationships for the phenyl acridine-9-carboxylates investigated (for names, see Table 1) and anthracene (**A**). Conditions (mass of the sample in mg/heating rate in K min^{-1}): **2** (3.825/5.0), **3** (0.800/5.0), **4** (3.610/5.0), **6** (3.120/5.0), **7** (2.350/5.0), **8** (3.150/5.0) and **A** (4.693/5.0)

Such a process does not require an energy activation barrier over and above its endothermicity to be overcome. It can thus be assumed that the only energy barrier to volatilisation is the thermodynamic one, i.e. the volatilisation enthalpy. In these conditions, the system attains equilibrium instantaneously as the temperature increases. Then, α represents the ratio p/p^0 , and α versus T relationships can be fitted to the Clausius–Clapeyron equation (Eq. 1) to determine the temperatures and enthalpies of volatilisation. The volatilisation temperatures (boiling points, sublimation temperatures) and enthalpies obtained in this manner (Table 2) are roughly comparable with the values of these quantities determined by DSC. The volatilisation enthalpies were determined by two independent thermoanalytical techniques; in the following considerations, we therefore assume that the mean values are optimal.

Crystal lattice energies

Crystal lattice energies (enthalpies), which are important thermodynamic characteristics of crystalline substances, can be computed for compounds of known crystal structure. We refined the crystal structures of four phenyl acridine-9-carboxylates and five 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates. The crystal lattice enthalpies calculated for these compounds, together with the electrostatic, dispersive and repulsive contributions to the crystal lattice energy, are shown in Table 3. The predicted crystal lattice enthalpies correlate reasonably well with the enthalpies of sublimation of the corresponding phenyl acridine-9-carboxylates. This confirms the correctness of the methods applied and their utility in determining the values of these quantities. The crystal lattice enthalpies of 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulphonates (Table 3) are typical of salts containing complex monovalent ions [51–53].

Knowing the crystal lattice enthalpy, the electrostatic, dispersive and repulsive contributions to the values of this quantity can be found. As the data in Table 3 demonstrate, the main contribution to the crystal lattice energy of phenyl acridine-9-carboxylates is from dispersive interactions, and that of 9-phenoxyacetyl-10-methylacridinium trifluoromethanesulphonates from electrostatic interactions. Therefore, theoretical analysis shows that the cohesive forces in esters (**I**) and in their derivative salts (**II**) are of differing origin.

Thermochemical characteristics

Quantum chemistry methods were used to calculate the enthalpies and the Gibbs free energies of formation of gaseous phenyl acridine-9-carboxylates, 9-phenoxyacetyl-10-methylacridinium cations and the trifluoromethanesulphonate anion; further insight into the thermochemistry of the compounds investigated was thus gained. The data relevant to neutral molecules and cations are given in Table 3; the corresponding values for the anion are -1136 ($\Delta_{f,298}H^0$) and -1142 ($\Delta_{f,298}G^0$) kJ mol^{-1} [48]. Knowledge of these characteristics enables one to calculate the enthalpies of formation of esters (**I**) and their derivative salts (**II**) in the solid phase (the relevant values are given in the last column of Table 3). These characteristics can be used in modelling the thermodynamic features of the compounds investigated. They also form a convenient framework within which to consider their reactivity and thermal behaviour, as well as problems of their storage and possible applications.

Concluding remarks

The results of this study provide further evidence of the successful application of TG and DSC for determining the melting, volatilisation and sublimation temperatures and enthalpies of molecular crystals.

Computational methods are useful for calculating crystal lattice energies, important thermodynamic characteristics of crystalline substances that afford a unique insight into the origin of the cohesive forces that retain molecules in the solid phase.

Quantum chemistry methods are useful for determining the basic thermodynamic quantities of the compounds investigated or their constituents, which in turn allows their behaviour, thermal features and utilitarian features to be evaluated.

Despite the relatively large number of compounds investigated in this and our previous study [48], it is hard to find any relations between their thermal and thermodynamic properties, and their structural features. The calculated crystal lattice enthalpies do not correlate, e.g. with the

volume of the molecule in the case of esters (**I**), or with the volume of the ion pair in the case of salts (**II**), in the crystal structure, although such a relationship has been recorded in other compounds [54–57].

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