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Thermochemistry and crystal lattice energetics of phenyl acridine-9-carboxylates and 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates

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Abstract The melting enthalpies and melting points of phenyl acridine-9-carboxylate, its eleven alkyl-substituted derivatives in the phenyl fragment and eight 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates derived from them, were determined by DSC. The volatilisation enthalpies and temperatures of twelve 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 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-phenoxycarbonyl-10-methylacridinium and trifluoromethanesulphonate ions, obtained by quantum chemistry methods, and the corresponding enthalpies of sublimation 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 to the experimentally obtained enthalpies of sublimation. Analysis of crystal lattice enthalpy contributions indicates that the crystal lattices of phenyl acridine-9-carboxylates are stabilised predominantly by dispersive interactions between molecules, whereas the crystal lattices of their quaternary salts are stabilised by electrostatic interactions between ions.

Keywords Crystal lattice enthalpies · DSC and TG investigations · Enthalpies of formation · Melting and volatilisation enthalpies · Phenyl acridine-9-carboxylates · 9-Phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates

Introduction

An interesting group of acridine derivatives are those capable of chemiluminescence. This ability is displayed by acridinium cations alkyl-substituted at the endocyclic nitrogen atom and containing electron-attracting substituents at C9; this latter atom is thus susceptible to the attack of anionic oxidants [1–5]. Oxidation gives rise to electronically excited *N*-alkyl-9-acridinones. Their relaxation is accompanied by the emission of light, i.e. chemiluminescence [1–6]. The efficiency of chemiluminescence, no greater than a few per cent [7], is affected by the presence of nucleophilic species competing with oxidants for the substitution at C9 [8, 9]. This effect is utilised in the assay of oxidants or nucleophiles, and in such cases acridinium cations serve as chemiluminogenic indicators [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; such chemiluminescent labels are widely used in medical, biological and environmental analyses [2–4, 7, 10–14].

This paper is dedicated to Professor Eugen Segal on his 75th birthday. With his published work and his many innovative ideas, he has been an inspiration for scientists working in the field of solid-state chemistry for many decades. In congratulating him on his achievements, we wish him continued good health, personal and professional successes, and further interesting research tasks.

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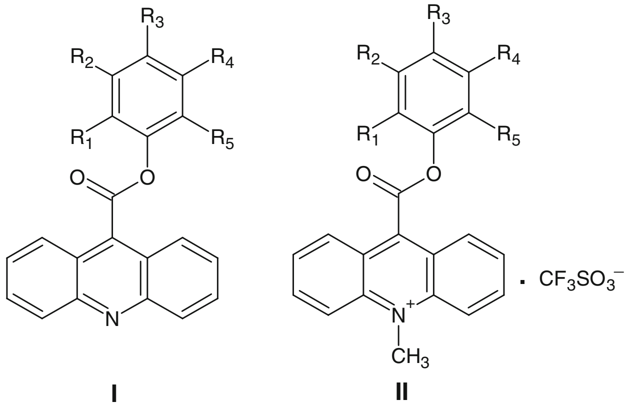

Scheme 1 Canonical structures of phenyl acridine-9-carboxylates (**I**) and 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (**II**) (Table 1)

The compounds on which this work focuses are the chemiluminogenic 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates and their precursors, phenyl acridine-9-carboxylates (Scheme 1 and Table 1) [15, 16]. The aim of these investigations was to discover the thermal properties of these compounds and to determine their thermodynamic characteristics—melting points, melting and volatilisation enthalpies, crystal lattice enthalpies and enthalpies of formation. We undertook these investigations in view of the fact that thermoanalytical and computational methods are good tools for determining the thermodynamic characteristics of compounds in the gaseous and solid phase [17–24]. A further aim was to discover whether and to what extent the thermal stability and behaviour of the compounds investigated affect their utilitarian potency.

Methods

Syntheses

The compounds investigated (Scheme 1 and Table 1) were synthesised and purified as described elsewhere [15, 16]. They were identified by MS [15], NMR spectroscopy [25] and, in some cases, X-ray crystallography [16, 26–29]. The purity of the compounds, evaluated from HPLC data, was better than 99.5%.

Table 1 The compounds investigated (Scheme 1)

Compound no.	Compound name	R_1	R_2	R_3	R_4	R_5
Phenyl acridine-9-carboxylates (**I**)						
1	Phenyl acridine-9-carboxylate	H	H	H	H	H
2	2-Methylphenyl acridine-9-carboxylate	CH_3	H	H	H	H
3	3-Methylphenyl acridine-9-carboxylate	H	CH_3	H	H	H
4	4-Methylphenyl acridine-9-carboxylate	H	H	CH_3	H	H
5	2-Ethylphenyl acridine-9-carboxylate	CH_2CH_3	H	H	H	H
6	2,5-Dimethylphenyl acridine-9-carboxylate	CH_3	H	H	CH_3	H
7	2,6-dimethylphenyl acridine-9-carboxylate	CH_3	H	H	H	CH_3
8	3,4-Dimethylphenyl acridine-9-carboxylate	H	CH_3	CH_3	H	H
9	3,5-Dimethylphenyl acridine-9-carboxylate	H	CH_3	H	CH_3	H
10	2-Isopropylphenyl acridine-9-carboxylate	$CH(CH_3)_2$	H	H	H	H
11	2,4,6-Trimethylphenyl acridine-9-carboxylate	CH_3	H	CH_3	H	CH_3
12	2-*Tert*-butylphenyl acridine-9-carboxylate	$C(CH_3)_3$	H	H	H	H
9-Phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (**II**)						
13	9-[(Phenoxy)carbonyl]-10-methylacridinium	H	H	H	H	H
14	9-[(2-Methylphenoxy)carbonyl]-10-methylacridinium	CH_3	H	H	H	H
15	9-[(4-Methylphenoxy)carbonyl]-10-methylacridinium	H	H	CH_3	H	H
16	9-[(2-Ethylphenoxy)carbonyl]-10-methylacridinium	CH_2CH_3	H	H	H	H
17	9-[(2,6-Dimethylphenoxy)carbonyl]-10-methylacridinium	CH_3	H	H	H	CH_3
18	9-[(2-Isopropylphenoxy)carbonyl]-10-methylacridinium	$CH(CH_3)_2$	H	H	H	H
19	9-[(2,4,6-Trimethylphenoxy)carbonyl]-10-methylacridinium	CH_3	H	CH_3	H	CH_3
20	9-[(2-*Tert*-butylphenoxy)carbonyl]-10-methylacridinium	$C(CH_3)_3$	H	H	H	H

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

Determination of melting and volatilisation characteristics

DSC measurements were carried out on a Netzsch DSC 204 instrument. Samples weighing 0.8–5.0 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 '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 on a Netzsch 209 thermobalance. Samples weighing 1.5–5.0 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 ($\Delta_v H^o$) were obtained by fitting TG curves to the Clausius–Clapeyron relationship [21]

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

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

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 energy contributions on reducing the data to 298.15 K, we standardised the measurement procedures for anthracene, for which the mean sublimation enthalpy is 105 kJ mol^{-1} [21]. Using this approach, we found that $\Delta_v H^o$ for anthracene, obtained as described above, is 88 kJ mol^{-1}, i.e. 1.193 times lower than the literature value [21]. We therefore multiplied all the values obtained for phenyl acridine-9-carboxylates (Table 2) by this coefficient; the corrected values (the mean from DSC and TG,

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

Compound no.	T_m[a]	T_v		$\Delta_m H^o$	$\Delta_v H^o$	
		DSC	Eq. 1		DSC	Eq. 1
Phenyl acridine-9-carboxylates (**I**)						
1	464	601	597	39.2	82.5	94.7
2	415	599	603	30.5	92.4	99.0
3	429	594	586	32.0	78.8	98.3
4	446	592	585	30.7	84.4	112
5	393	589	576	30.4	84.7	101
6	457	596		37.9	97.7	
7	435	598	598	29.1	99.8	95.4
8	442	598		29.2	87.6	
9	469	564		38.4	83.4	
10	396	591	611	29.0	89.9	112
11	405	606	608	24.4	81.8	109
12	462	623	597	39.8	87.1	102
9-Phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (**II**)						
13	502			36.0		
14	500			40.8		
15	504			30.1		
16	471			45.8		
17	555			47.6		
18	466			34.3		
19	535			33.1		
20	504			36.0		

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

[a] Literature values, in K: 411–412 (**2**) [27], 387–389 (**5**) [26], 452–454 (**6**) [26], 489–491 (**14**) [28] and 502–504 (**20**) [29]

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

Compound no.	$\Delta_{s,298}H^{o}$	$-E_{el}$	$-E_{d}$	E_{r}	$-\Delta_{c,298}H^{o}$	$\Delta_{f,298}H^{o}(g)^{a}$	$\Delta_{f,298}G^{o}(g)^{a}$	$\Delta_{f,298}H^{o}(c)$
Phenyl acridine-9-carboxylates (**I**)								
1	145					163.5	369.7	18
2	145	17.2	192.3	53.5	158.5	137.6	376.9	–7
3	138					135.8	369.2	–2
4	148					136.4	370.6	–12
5	141	16.4	178.5	43.0	154.4	127.1	399.4	–14
6	154	15.1	189.5	44.4	162.7	110.1	376.9	–44
7	146					109.7	378.7	–36
8	134					110.4	379.1	–24
9	138					108.2	364.6	–30
10	149					111.3	413.3	–38
11	138					82.7	379.8	–55
12	153					131.7	472.4	–21
9-Phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (**II**)								
13						706.8	962.5	
14		409.1	277.7	91.3	600.5	681.2	969.2	–1055
15						676.7	960.9	
16						671.4	993.5	
17						653.9	973.2	
18						654.5	1006.1	
19		393.1	295.8	91.5	602.4	624.4	972.3	–1114
20		382.0	264.9	87.4	564.5	653.4	1042.7	–1047

$\Delta_{s,298}H^{o}$, E_{el}, E_{d}, E_{r}, $\Delta_{c,298}H^{o}$, $\Delta_{f,298}H^{o}$, $\Delta_{f,298}G^{o}$, all in kJ mol^{-1}, respectively, 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 enthalpy of the crystal lattice, the enthalpy of formation and the Gibbs free energy of formation at standard pressure (°) and temperature 298 K [(g)—gaseous state, (c)—solid state]

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

wherever possible), enlarged by $\Delta_{m}H^{o}$ (Table 2)—denoted as $\Delta_{s,298}H^{o}$, are given 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 [19–21]

$$E_c = E_{el} + E_d + E_r \tag{2}$$

E_{el} in Eq. 2 represents Coulombic interactions [19–21],

$$E_{el} = \frac{1}{2}\sum_{i}\sum_{j\neq i}\frac{Ne^2}{4\pi\varepsilon_0}\frac{Q_iQ_j}{R_{ij}} \tag{3}$$

while the sum of E_d and E_r is expressed by Buckingham's formula [30]

$$E_d + E_r = \frac{1}{2}\sum_{i}\sum_{j\neq i}\left[-\frac{D_iD_j}{R_{ij}^{6}} + A_iA_j\exp(-B_iB_jR_{ij})\right] \tag{4}$$

In Eqs. 3 and 4 N is the Avogadro number, e is the elementary charge, ε_0 is the permittivity of free space, $Q_i(Q_j)$ denotes 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 following sources: **2** [27], **5** [26], **6** [26], **14** [28], **19** [16] and **20** [29]. 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) [31] derived at the density functional theory (DFT) level [32]. These charges were obtained using the B3LYP functional [33, 34] together with the 6-31G** basis set [35] included in the Gaussian 03 program package [36]. The parameters of pairwise interactions (Table 4) were taken from the literature [37, 38]. Crystal lattice energies were calculated using the General Utility Lattice Program (GULP) [39].

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

Atom	Parameter		
	D	*A*	*B*
C	42.0	547.3	1.92
H	11.0	143.2	2.07
O	32.9	570.2	2.04
N	32.9	419.2	1.94
S	99.1	991.6	1.87
F	30.1	635.7	2.04

D in $kJ^{1/2}$ $mol^{-1/2}$ $Å^3$; *A* in $kJ^{1/2}$ $mol^{-1/2}$; *B* in $Å^{-1/2}$. The parameters for C, H, O, N and S (parameters by Mirsky) were taken from [37], for F—from [38]

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

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

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

$\Delta_{c,298}H^o$, 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-phenoxycarbonyl-10-methylacridinium cations and $CF_3SO_3^-$ were carried out at the DFT level of theory [32] using Baker's optimisation procedure [40] together with the B3LYP functional [33, 34] and 6-31G** basis set [35]. The validity of the geometry optimisations was proven in the subsequent Hessian (second derivatives of the energy versus nuclear coordinates) calculations followed by normal mode analyses [41]. The bond lengths and vibrational harmonic frequencies so determined were then used to obtain the zero-point energy, thermal enthalpy and the Gibbs free energy contributions, at 298.15 K and standard pressure (°), to energies corresponding to optimised structures, with the aid of a built-in computational program of statistical thermodynamics routines [42]. The enthalpies and Gibbs free energies of formation of gaseous entities were obtained by following the basic rules of thermodynamics [43]. In these calculations, the thermochemical quantities of these gaseous entities, as well as those of H_2, N_2, O_2 and F_2, were taken directly from data files after the computations. To obtain the enthalpies of C(c) and S(c), the predicted enthalpies of the gaseous entities were respectively lowered by 716.67 and 277.17 kJ mol^{-1}, i.e. by the enthalpies of their volatilisation at 298 K, and then raised by 8.5 × 0.298 kJ mol^{-1} and 22.7 × 0.298 kJ mol^{-1}, i.e. by the thermal enthalpies of the solid entities at 298 K (8.5 and 22.7 are the heat capacities of the solid entities, in J mol^{-1} K^{-1}, at 298 K [44]). To obtain the Gibbs free energies of C(c) and S(c), the enthalpies of these entities obtained in the above manner were modified by substracting, respectively, 5.6 × 0.298 kJ mol^{-1} and 32.0 × 0.298 kJ mol^{-1}, i.e. the entropies of the solid entities [44] multiplied by 298 K. Quantum chemistry calculations were carried out with the Gaussian 03 code [36].

Standard enthalpies of formation of solid phenyl acridine-9-carboxylates (**I**) ($\Delta_{f,298}H^o(c)$) were obtained by substracting the enthalpy of sublimation ($\Delta_{s,298}H^o$) from the relevant enthalpy of formation in the gaseous phase ($\Delta_{f,298}H^o(g)$) (Table 3). Standard enthalpies of formation of solid 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (**II**) were determined by the equation

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

where −1136 kJ mol^{-1} is the standard enthalpy of formation of gaseous $CF_3SO_3^-$; the values of the other quantities are given in Table 3.

Results and discussion

Thermoanalytical investigations

DSC analyses of phenyl acridine-9-carboxylates always take account of two processes: melting and the subsequent volatilisation (Fig. 1). Melting points varied between 393 and 469 K and were lower than the corresponding volatilisation temperatures by 95–201 K (Table 2); hence, melting always occurred separately from volatilisation, which made it easy to determine the enthalpies of the two processes. Melting points, when available, compared well with the literature values of this quantity (Table 2). Melting enthalpies varied between 24.4 and 39.8 kJ mol^{-1}, the lowest value being obtained for compound **11** and the highest for **12**. Volatilisation enthalpies varied between 78.8 and 99.8 kJ mol^{-1}: compound **3** had the lowest value and compound **7** the highest. DSC analyses of 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates were carried out in the temperature range in which melting occurs. Melting points varied between 466 and 555 K: the lowest value was recorded for compound **18**, the highest for compound **17**. When available, melting points compared well with literature values (Table 2). Melting enthalpies varied between 30.1 and 47.6 kJ mol^{-1}; the lowest value was found for compound **15**, the highest for compound **18**. Heating the compounds to temperatures substantially exceeding their melting points caused their decomposition, an undefined and cognitively uninteresting process. Our attempts to find relations between the melting

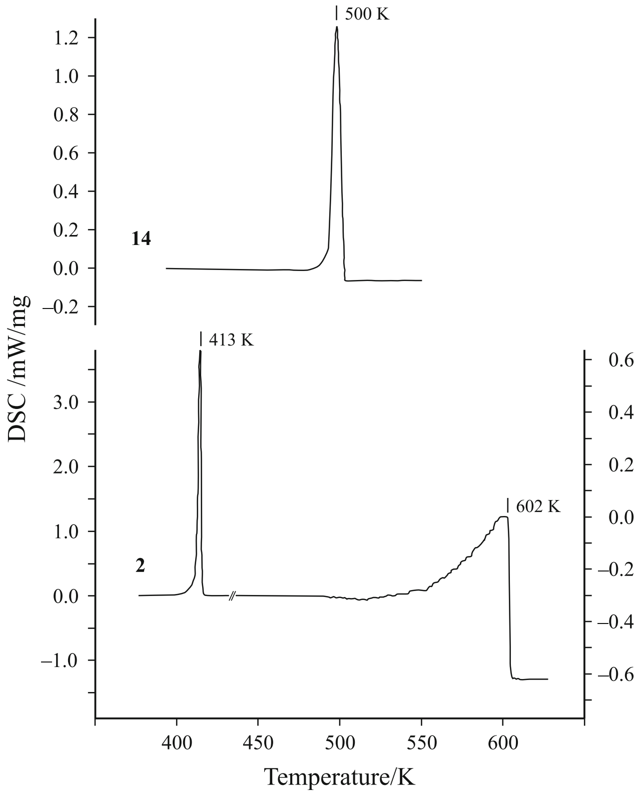

Fig. 1 Examples of DSC analyses of the compounds investigated (mass of the sample in mg/heating rate in K min^{-1}): **2** (2.250/5.0) and **14** (1.900/5.0)

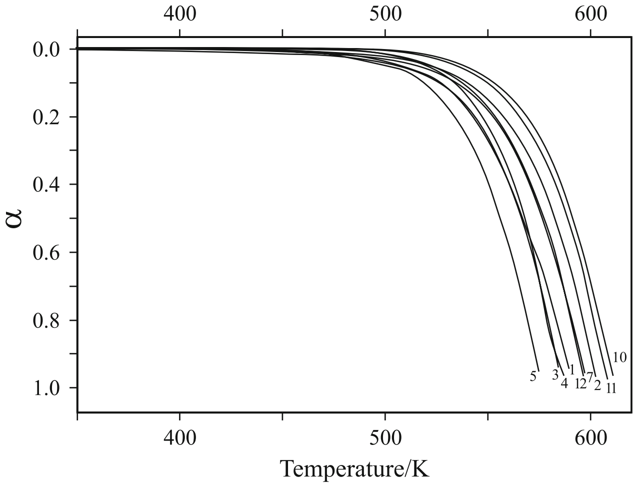

Fig. 2 Extent of volatilisation (α) versus temperature (T) relationships for the phenyl acridine-9-carboxylates investigated (for names, see Table 1). Conditions (mass of the sample in mg/heating rate in K min^{-1}): **1** (2.100/5.0), **2** (2.350/2.5), **3** (3.450/5.0), **4** (2.000/5.0), **5** (2.140/5.0), **7** (1.970/5.0), **10** (4.450/5.0), **11** (2.400/5.0), **12** (2.900/5.0)

points and melting enthalpies on the one hand, and the structural features of the molecules (cations in the case of **II**) on the other, failed to yield any correlations. Presumably, then, the above-mentioned thermochemical characteristics represent individual features of the compounds investigated.

The plot showing the extent of volatilisation (α) versus temperature (T) (Fig. 2) reflects the thermogravimetric curves. Their smooth shape is evidence for the simple release to the gaseous phase of phenyl acridine-9-carboxylate molecules held in the condensed phase. It can be assumed that the energy barrier to such a process is the same as the thermodynamic one, i.e. the volatilisation enthalpy. In such conditions the system attains equilibrium just as soon as the temperature increases. In this case, α represents the ratio p/p^{o}, and α versus T relationships can be fitted to the Clausius–Clapeyron relationship (1) in order to determine the temperatures and enthalpies of volatilisation. The volatilisation temperatures obtained in this manner (Table 2) are roughly comparable with the values of this quantity determined by DSC. On the other hand, volatilisation enthalpies extracted from TG data are usually higher than the corresponding values of this quantity obtained with DSC. There is no simple explanation for these discrepancies. However, since the volatilisation enthalpies were determined by two independent thermoanalytical techniques, we think that it would be optimal to use mean values whenever possible in further discussions.

Crystal lattice energy

An important thermodynamic characteristic of crystalline substances is their crystal lattice energy (enthalpy). This magnitude can be predicted for compounds whose crystal structures are known. So far, we have determined the crystal structures of three phenyl acridine-9-carboxylates and three 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates. The crystal lattice enthalpies calculated for these compounds together with the electrostatic, dispersive and repulsive contributions to crystal lattice energy are given in Table 3. The calculated crystal lattice enthalpies correlate reasonably well with the enthalpies of sublimation of the corresponding phenyl acridine-9-carboxylates, which is an endorsement of the method applied for predicting the values of this quantity. The crystal lattice enthalpies of 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates (Table 3) are typical of salts containing complex monovalent ions [45–47].

A point of interest arising from the calculations relates to the electrostatic, dispersive and repulsive contributions to the lattice enthalpy. As the data in Table 3 demonstrate, the main contribution to the crystal lattice energy of phenyl acridine-9-carboxylates is due to dispersive interactions, whereas that of 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates results primarily from electrostatic interactions. Theoretical analysis therefore indicates that the nature of the cohesive forces differs in esters (**I**) and the salts derived from them (**II**).

Thermochemical characteristics

Further insight into the thermochemistry of the compounds investigated was gained by the application of quantum chemistry methods, which enabled the enthalpies of formation and the Gibbs free energies of formation of gaseous phenyl acridine-9-carboxylates, gaseous 9-phenoxycarbonyl-10-methylacridinium cations and the trifluoromethanesulphonate anion to be predicted. The data relating to neutral molecules and cations are shown in Table 3; the corresponding values for the anion are, in kJ mol^{-1}: -1136 ($\Delta_{f,298}H^o$) and -1142 ($\Delta_{f,298}G^o$). Knowledge of these characteristics enables the enthalpies of formation of esters (**I**) and of their derivative salts (**II**) in the solid phase to be calculated—the relevant values are given in the last column of Table 3. These characteristics can be used to model the thermodynamic properties of the compounds investigated. They should also be useful for evaluating their thermal behaviour, the problems involved with their storage, and their possible applications.

Concluding remarks

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

The computational method used for calculating crystal lattice energy provided important thermodynamic characteristics of crystalline substances and afforded a unique insight into the nature of the cohesive forces that retain molecules in the solid phase.

Quantum chemistry methods enabled the determination of important thermodynamic quantities of the compounds investigated or their constituents, which in turn allowed their thermal behaviour and useful practical features to be evaluated.

Despite the relatively large number of compounds investigated, it was hard to find any relations between their thermal and thermodynamic properties, and their structural features. These properties thus appear to be individual to each compound.

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