J Therm Anal Calorim
DOI 10.1007/s10973-017-6306-4

Lattice energetics and thermochemistry of acridine derivatives and substituted acridinium trifluoromethanesulphonates

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Received: 11 February 2017 / Accepted: 10 March 2017

Abstract The enthalpies and temperatures of melting of eight 9-substituted acridines (alkyl, aryl or alkoxy) (**I**) and six their 10-methylated-acridinium trifluoromethanesulphonate (**II**) derivatives were measured by DSC. The enthalpies and temperatures of volatilisation of the first group of compounds were also determined by DSC or obtained by fitting TG curves to the Clausius–Clapeyron relationship. By combining the enthalpies of formation of gaseous acridines or 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. 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 between molecules always predominate in the case of acridine derivatives, whilst the crystal lattices of their quaternary salts are stabilised by electrostatic interactions between ions. Only in the case of 9-bromomethylacridine derivative, which crystallises in the monohydrated form, electrostatic contribution to the crystal lattice energy is significantly higher than in the other investigated acridines.

Keywords Crystal lattice enthalpies · DSC and TG investigations · Enthalpies of formation · Melting and volatilisation enthalpies · Acridine derivatives · Substituted acridinium trifluoromethanesulphonates

Introduction

The heightened interest in chemical processes occurring with the participation of light, expressed primarily by the increasing number of publications on this topic, is understandable, given the enormous importance of such processes in nature and their applications in biotechnology, pharmacology, molecular biology, medicine and environmental protection [1–6]. The phenomenon of chemiluminescence has long been known, and chemical processes accompanied by the emission of radiation from various organisms are common, constituting the basis of bioluminescence [7]. Acridine derivatives substituted in the central ring (at position 9 and the endocyclic nitrogen atom)—i.e. 9-substituted acridinium cations, e.g. 10-methyl-9-phenoxycarbonylacridinium derivatives—are able to react with oxidants in alkaline media, which results in the emission of radiation known as chemiluminescence [1, 8]. The latter process is applied in clinical [3, 9], pharmaceutical [4], chemical and biochemical analysis [10–12], and also in environmental [13] and food analysis [14, 15]. It can be utilised in special lighting products [16], for example, the Cyalume torches used by rescue services, the police and the army.

The first chemiluminogen to be widely investigated was lucigenin [17]. About 40 years ago, the attention of researchers was turned to chemiluminogens derived from 10-methyl-9-phenoxycarbonylacridinium cations [18]. Numerous salts containing such cations have been synthesised, and their chemiluminogenic features have been thoroughly investigated [3, 11, 18–25]. The 9-cyano-10-

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methylacridinium cation is also interesting as a chemiluminogen. The properties and mechanism of chemiluminescence of salts containing this cation and the hydrogen dinitrate anion, as well as the possible analytical applications of the compound, have been described in detail [26, 27]. Zomer and Stavenuiter indicated the potential chemiluminogenic ability of acridinium cations substituted with alkyl, aryl or halogen at position 9 [1]. A literature search reveals that knowledge of the chemiluminogenic and physicochemical (especially thermochemical) features of 10-methylacridinium cations variously substituted at position 9 and their precursors—9-alkyl or 9-aryl-acridines—is incomplete.

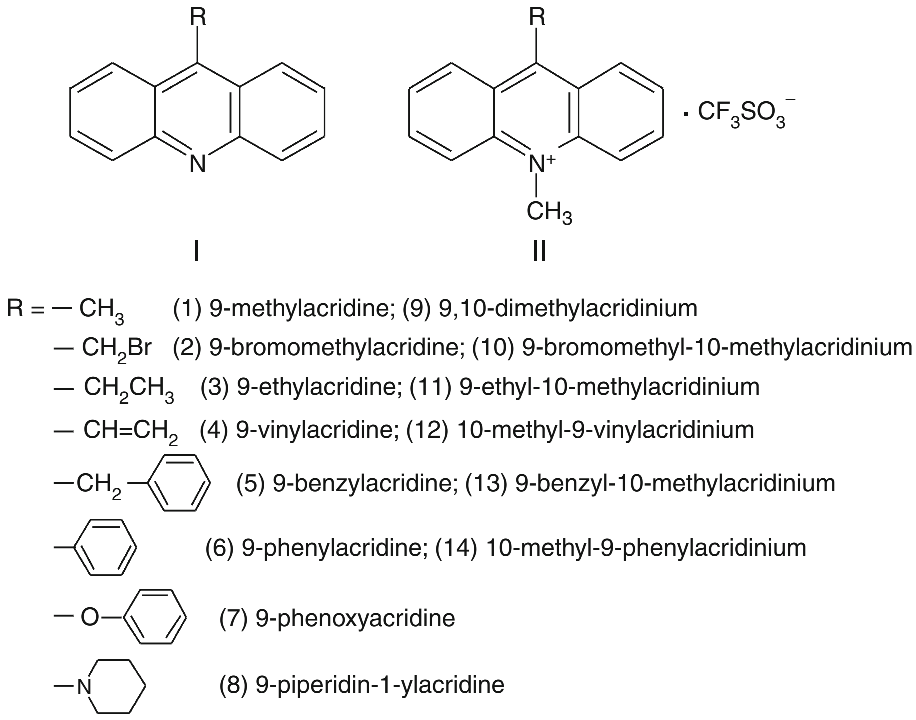
The compounds on which this work focuses are the chemiluminogenic 9-substituted acridinium trifluoromethanesulphonates and their precursors, acridine derivatives variously substituted at position 9 of acridine moiety (Scheme 1). In order to acquire better insight into thermal stability of acridine derivatives, we have presented broader characteristics of their thermal behaviour. To be able to do this, we have examined the thermal properties of these compounds and determined 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 [28–31]. 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.

Materials and methods

Syntheses

The compounds investigated (Scheme 1) were synthesised by optimising known methodologies [32–37]. All chemicals were purchased from Sigma-Aldrich, unless indicated otherwise. The purity of the compounds was checked by HPLC (Waters 600 E Multisolvent Delivery System, Waters 2487 Dual λ Absorbance Detector; mobile phase: acetonitrile/water = 70%/30% supplemented with 0.1% of TFA; stationary phase: C-8 column, 3 × 150 mm, ‘Symmetry’) (the relative areas under the main signal were >99.5% in all cases) and their identity confirmed by mass spectrometry. The compounds obtained were subjected to elemental analyses (EAGER 200, Carlo Erba Instruments) and TLC tests in the above-mentioned system. ^{1}H spectra were recorded at room temperature on a Bruker AVANCE III 500 MHz.

9-Methylacridine (**1**) A mixture of 10 g of diphenylamine (59.1 mmol), acetic acid (10.0 mL) and anhydrous zinc chloride (40.0 g, 293.5 mmol) was heated at 220 °C for 17 h. The reaction mixture was digested with hot 10% aqueous sulphuric acid and then strongly alkalified with concentrated aqueous ammonia to dissolve the zinc



Scheme 1 Canonical structures and names of investigated 9-substituted acridines (**I**) and 10-methyl-9-substituted acridinium trifluoromethanesulphonates (**II**); for **I**, the compound is named; for **II**, the cation is named

chloride. The insoluble residue was extracted with toluene. The organic phase was washed with water (100 mL) and dried over sodium sulphate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent *n*-hexane/ethyl acetate = 5/1 v/v). Yield 81%; the % of elements found/calculated, C 86.93/87.01, H 5.74/5.74, N 7.09/7.25; ^{1}H NMR (CD$_3$CN), δ, ppm (J, Hz): 3.06 (3H, s); 7.52 (2H, t, J = 7.5); 7.71 (2H, t, J = 7.4); 8.04 (2H, d, J = 8.6); 8.28 (2H, d, J = 8.8).

9-Bromomethylacridine (**2**) To a solution of 9-methylacridine (0.193 g, 1 mmol) in dichloromethane (10 mL) was added *N*-bromosuccinimide (0.178 g, 1 mmol) portionwise in an ice-water bath. After complete addition, the solution mixture was warmed to room temperature and stirred overnight. The resulting solution was washed with water and brine. The organic phase was dried over anhydrous sodium sulphate, and the solvent was removed. The residue was purified by column chromatography (eluent ethyl acetate/petroleum ether = 1/5 v/v). Yield 77%; the % of elements found/calculated, C 61.26/61.79, H 3.64/3.70, N 5.03/5.15; ^{1}H NMR (CDCl$_3$), δ, ppm (J, Hz): 5.38 (2H, s); 7.62 (2H, t, J = 7.7); 7.78 (2H, t, J = 7.7); 8.31 (4H, d, J = 8.8).

9-Ethylacridine (**3**) A mixture of 0.17 g of diphenylamine (1 mmol), 1.1 mL propionic acid (15 mmol) and 0.46 g zinc chloride (3 mmol) was stirred and microwave irradiated at 110 °C and 120 W for 2 h. The mixture was diluted with dichloromethane, washed with water, diluted with sodium hydroxide, washed again with water and dried over magnesium sulphate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent 1–3% 2-propanol in chloroform). Yield 87%; the % of elements found/calculated, C 86.69/86.92, H 6.34/6.32, N 6.71/6.76; ^{1}H NMR (CDCl$_3$), δ, ppm (J, Hz): 1.47 (3H, t, J = 7.7); 3.65 (2H, q, J = 7.7); 7.56 (2H, t, J = 7.7); 7.77 (2H, t, J = 8.0); 8.26 (4H, d, J = 8.8).

9-Vinylacridine (**4**) To a suspension of 0.535 g (1.5 mmol) triphenylmethylphosphonium bromide in 10 mL dry diethyl ether was added 0.168 g (1.5 mmol) of potassium tert-butylate and stirred for 30 min. Then 0.207 g (1.0 mmol) acridine-9-carboxaldehyde was added, and the mixture stirred at ambient temperature overnight. After dilution with 50 mL dichloromethane, the solution was washed with water three times, after which the organic layer was separated, dried over magnesium sulphate and evaporated to dryness. The target compound was purified by column chromatography (eluent 1% 2-propanol in chloroform). Yield 73%; the % of elements found/calculated, C 87.27/87.77, H 5.66/5.40, N 6.48/6.82; ^{1}H NMR (CDCl$_3$), δ, ppm (J, Hz): 5.60 (1H, d, J = 11.8); 5.98 (1H, d, J = 11.8); 7.32 (1H, dd, J = 11.8); 7.39 (2H, t, J = 7.5); 7.65 (2H, t, J = 7.5); 8.13 (4H, d, J = 8.9).

9-Benzylacridine (**5**) A mixture of 10 g of diphenylamine (59.1 mmol), an equimolar amount of phenylacetic acid (7.70 g, 59.0 mmol) and anhydrous zinc chloride (30.8 g, 226.0 mmol) was heated at 210 °C for 24 h. The reaction mixture was digested with hot 10% aqueous sulphuric acid and then strongly alkalified with concentrated aqueous ammonia to dissolve the zinc chloride. The insoluble residue was extracted with toluene. The organic phase was washed with water (100 mL) and dried over sodium sulphate. After evaporation of the solvent, the crude product was purified by gravitational column chromatography (eluent cyclohexane/ethyl acetate = 5/2 v/v). Yield 84%; the % of elements found/calculated, C 89.27/89.19, H 5.58/5.61, N 5.15/5.20; ^{1}H NMR (CDCl$_3$), δ, ppm (J, Hz): 4.21 (2H, s); 7.09 (2H, t, J = 7.5); 7.18 (2H, d, J = 8.9); 7.23 (2H, t, J = 7.5); 7.31 (5H, m); 7.92 (2H, d, J = 8.9).

9-Phenylacridine (**6**) A mixture of dimethyl phthalate (20 mmol), diphenylamine (10 mmol), benzoic acid (10 mmol) and zinc chloride (20 mmol) was stirred and microwave irradiated at 100 °C and 120 W for 2 h. The mixture was diluted with dichloromethane, washed with water, diluted with sodium hydroxide, washed again with water and dried over magnesium sulphate. After evaporation of the solvent, the crude product was recrystallised from toluene/ethanol. Yield 65%; the % of elements found/calculated, C 89.42/89.38, H 5.10/5.13, N 5.48/5.49; ^{1}H NMR (CDCl$_3$), δ, ppm (J, Hz): 7.21 (1H, m); 7.39 (2H, m); 7.42 (2H, m); 7.57 (2H, m); 7.69 (2H, dd, J = 11.8); 7.74 (2H, m), 8.28 (2H, dd, J = 11.8).

9-Phenoxyacridine (**7**) In phenol (1.27 mol), 7.2 g (180 mmol) of sodium hydroxide was dissolved at 100 °C, and 9-chloroacridine (28 g, 131 mmol) added with stirring. The solution was kept at 100 °C for 1.5 h, then poured into 2 M sodium hydroxide (500 mL), stirred and set aside overnight. The precipitated material was filtered off, washed with water, powdered and dried. The crude product was purified by gravitational column chromatography (eluent toluene/methanol = 10/1 v/v). Yield 78%; the % of elements found/calculated, C 84.19/84.11, H 4.81/4.83, N 5.20/5.16; ^{1}H NMR (DMSO-d6), δ, ppm (J, Hz): 6.88 (2H, d, J = 8.6); 7.08 (1H, t, J = 7.5); 7.32 (2H, t, J = 7.5); 7.59 (2H, t, J = 7.5); 7.88 (2H, t, J = 7.5); 8.04 (2H, d, J = 8.9); 8.23 (2H, d, J = 8.6).

9-Piperidylacridine (**8**) In 2 mL piperidine, 0.213 g (1.0 mmol) of 9-chloroacridine hydrochloride was dissolved and heated to 90 °C with constant stirring for 6 h. The solvent was evaporated under vacuum at 50 °C. The residue was washed with aqueous methanol and dried in a vacuum. Yield 91%; the % of elements found/calculated, C 81.96/82.41, H 7.01/6.92, N 10.93/10.68; ^{1}H NMR (CDCl3), δ, ppm (J, Hz): 1.80 (2H, m); 1.84 (4H, m); 3.59

(4H, m); 7.38 (2H, t, J = 7.6); 7.64 (2H, t, J = 7.6); 8.15 (2H, d, J = 8.6); 8.28 (2H, d, J = 8.9).

General procedure for the synthesis of 10-methylacridinium trifluoromethanesulphonate derivatives (**9–14**) To a solution of 1 mmol of an acridine derivative in 10 mL dry dichloromethane were added 4 mmol 2,6-ditert-butylpyridine and 5 mmol methyl trifluoromethanesulphonate. The solution was stirred at room temperature for 3 h. The precipitate was filtered off and washed with dichloromethane. The filtrate was evaporated under vacuum at room temperature to 5 mL and diluted with diethyl ether. The precipitate was filtered and vacuum dried.

9,10-Dimethylacridinium trifluoromethanesulphonate (**9**) Yield 89%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 3.48 (3H, s); 4.73 (3H, s); 7.98 (2H, t, J = 7.3); 8.38 (2H, t, J = 7.3); 8.54 (2H, d, J = 8.4); 8.81 (2H, d, J = 8.4).

9-Bromomethyl-10-methylacridinium trifluoromethanesulphonate (**10**) Yield 87%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 4.79 (3H, s); 5.73 (2H, s); 8.10 (2H, t, J = 7.3); 8.43 (2H, t, J = 7.3); 8.63 (2H, d, J = 9.2); 8.81 (2H, d, J = 8.7).

9-Ethyl-10-methylacridine trifluoromethanesulphonate (**11**) Yield 82%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 1.59 (3H, t, J = 7.3); 4.00 (2H, t, J = 7.3); 4.75 (3H, s); 8.01 (2H, t, J = 7.1); 8.40 (2H, t, J = 7.1); 8.57 (2H, d, J = 9.0); 8.82 (2H, d, J = 8.5).

10-Methyl-9-vinyl-acridinium trifluoromethanesulphonate (**12**) Yield 83%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 4.78 (3H, s); 5.94 (1H, d, 17.5); 6.46 (1H, d, 11.8); 7.80 (1H, m); 7.97 (2H, m); 8.42 (2H, m); 8.58 (2H, d, J = 8.4); 8.74 (2H, d, J = 7.7).

9-Benzyl-10-methylacridinium trifluoromethanesulphonate (**13**) Yield 88%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 4.81 (3H, s); 5.52 (2H, s); 7.18 (5H, m); 7.97 (2H, d, J = 8.4); 8.03 (2H, t, J = 7.1); 8.43 (2H, t, J = 7.1); 8.91 (2H, d, J = 8.4).

10-Methyl-9-phenyl-acridinium trifluoromethanesulphonate (**14**) Yield 79%; ^{1}H NMR (CD_3CN), δ, ppm (J, Hz): 4.87 (3H, s); 7.62 (1H, d, 8.8); 7.78 (2H, m); 7.89 (4H, m); 8.07 (2H, d, 8.8); 8.40 (2H, t, 7.6); 8.65 (2H, d, J = 8.8).

Determination of melting and volatilisation characteristics

Differential scanning calorimetry (DSC) measurements were carried out by a Netzsch DSC Phoenix 204 instrument. Samples weighing 1.70–4.90 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 argon 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 1. Thermogravimetric measurements were carried out by a Netzsch TG 209 thermobalance. Samples weighing 1.88–7.00 mg were placed in an aluminium crucible and heated at 2.5 or 5.0 K min^{-1} in a dynamic argon atmosphere. Volatilisation enthalpies ($\Delta_v H^0$) were obtained by fitting TG curves to the Clausius–Clapeyron relationship [29]

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

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 (°)], R is the 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} [29]. 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 9-substituted acridines (Table 1) by the relevant coefficient. The final values (the mean from corrected TG and DSC wherever possible), enlarged by $\Delta_m H^0$ (Table 1), are denoted by $\Delta_{s,298} H^0$ and were used to obtain the standard enthalpies of formation of solid 9-substituted acridines (**I**), described in *Quantum chemistry and thermodynamic computations* section.

Crystal lattice energy calculations

The lattice energies (E_L) reflecting the global energetics of interactions within the crystals were obtained by employing two approaches. The first approach is based on force field methods as implemented in the General Utility Lattice Program Version 4.0 (GULP) [38, 39]. Here, the lattice energy was evaluated by supplementing the energy of the long-range Coulomb interactions (E_{el}) with energies of the short-range dispersive (E_d) and repulsive (E_r) interactions:

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

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

Compound no.	T_m/K[a]	T_v/K		$\Delta_m H^o$/ kJ mol^{-1}	$\Delta_v H^o$/kJ mol^{-1}	
		DSC	Equation 1		DSC	Equation 1
9-Substituted acridines (**I**)						
1	392	588	549	16.5	43.7	78.0
2	444	579		−35.6	32.4	
3	387	561	486	16.4	48.6	87.8
4	349	527		9.4	24.0	
5	430	659	564	15.3	32.9	78.1
6	460	628	515	24.0	72.2	100.5
7	402	603	623	22.0	48.2	77.7
8	371	555		6.7	30.4	
9-Substituted-10-methylacridinium trifluoromethanesulphonates (**II**)						
9	549			26.6		
10	485			22.4		
11	431			23.2		
12	442			24.7		
13	480			28.7		
14	479			29.0		

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

[a] Literature values, in K: (**1**) 390.5–391.5 [60] and 387 [61]; (**2**) 439–441 [62]; (**3**) 388.5–389.5 [60]; (**4**) 358–360 [63]; (**5**) 446–447 [60] and 430–431 [34]; (**6**) 459–460 [64] and 454–454.5 [65]; (**7**) 396–397 [66] and 398–399 [33]; (**13**) 478–480 [36]

The relative atomic partial charges necessary for prediction of the electrostatic energy interactions, E_{el}, were obtained at the density functional theory (DFT) level [40] by reproducing the electrostatic potential around molecules (ESP fit charges) [41, 42]. In these calculations the M06-2X [43] functional was employed together with the 6-31 ++G** basis set [44, 45]. Calculations were carried out using the Gaussian 09 program [46]. Two-body short-range interactions contributing as E_d and E_r terms to the lattice energy were described by Buckingham potential available within GULP. The atomic parameters for Buckingham potential were those reported in the literature [47, 48]. Such approach was shown in the past to be successful in predicting the experimental sublimation energies for acridine derivatives [30, 31]. Results of GULP calculations are compared with the thermodynamic characteristics originating from the ab initio level calculations.

In the second approach, calculations were carried out with the periodic ab initio CRYSTAL09 program [49] at the B3LYP/6-31G** level of theory. For a given experimental crystal structure, single-point calculations of periodic wave function and energy were performed. Using calculated total energies, being the sum of the electronic energy and nuclear repulsion energy, the cohesive energy of the crystal can be obtained according to the equation: [50]

$$E_c = \frac{E_{bulk}}{Z} - E_{mol} \qquad (3)$$

where E_{bulk} is the total energy of the unit cell, Z is the number of molecules in the unit cell, and E_{mol} is the total energy of the molecule extracted from the bulk. The ab initio DFT total energy obtained was subsequently corrected to take into account dispersive interactions. Here, we employed empirically modified Grimme dispersion correction proposed by Civalleri et al. [50] for molecular crystals (model in original work referred to as B3LYP-D*). In order to avoid overestimation of the strength of interactions within crystals, cohesive energies E_c were additionally corrected for basis set superposition error by the counterpoise method [51] implemented in the CRYSTAL09 code. Final theoretical lattice energy, E_L, from CRYSTAL09 calculation is comprised of three terms:

$$E_L = E_c + E(D*) + E_{BSSE} \qquad (4)$$

Theoretical cohesive energies E_L may be compared with lattice energies obtained from experimental sublimation enthalpies.

The crystal structures for calculating E_c were taken from following sources: **1** [37], **2** [37], **3** [37], **5** [34], **6** [32], **7** [33], **8** [37], **10** [37], **11** [35], **12** [37], **13** [36] and **14** [37]. Crystal lattice enthalpies ($\Delta_{c,298}H^0$) were obtained by including the $pV = RT$ contribution

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

where $n = 1$ for 9-substituted acridines (**I**) and $n = 2$ for 10-methyl-9-substituted acridinium trifluoromethanesulphonates (**II**). E_{el}, E_d, E_r, E_L, E_c and $E(D^*)$ are listed in Table 2 and $\Delta_{c,298}H^0$ in Table 3.

Quantum chemistry and thermodynamic computations

Unconstrained geometry optimisations of isolated molecules of 9-substituted acridines, 10-methyl-9-substituted acridinium cations and $CF_3SO_3^-$ were carried out at the DFT level of theory [40] with two functionals and two different basis sets—the B3LYP [52–54] and M06-2X [43] functional and the 6-31G** [55] and 6-31 ++G** [56] basis set, respectively. 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 [57]. 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 (°)) to energies corresponding to optimised structures with the aid of a built-in computational program of statistical thermodynamics routines [58]. The enthalpies of formation of gaseous entities were obtained by following the basic rules of thermodynamics [59]. In the calculations, the thermodynamic 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. In order to obtain the enthalpies of C(c), S(c) and Br_2(l), the predicted enthalpies of the gaseous entities were lowered by 716.67, 277.17 and 30.91 kJ mol^{-1}, respectively, i.e. by the enthalpies of their volatilisation at 298 K, and then raised by 8.53×0.298, 22.7×0.298 and 75.7×0.298 kJ mol^{-1},

Table 2 Theoretical lattice energies (E_L) calculated using GULP and CRYSTAL09 and contributions to the lattice energies: E_{el} (Coulomb energy), E_d and E_r (dispersion and repulsion energy, respectively, calculated according to Buckingham's potential), E_c (cohesive energy calculated from the difference in electronic and nuclear repulsion energy of bulk crystal and molecules in the bulk), $E(D^*)$ (dispersive contribution derived from modified Grimme model), E_{BSSE} (basis set superposition error energy correction) of the compounds investigated

Compound no.	GULP				CRYSTAL09		
	E_{el}/kJ mol^{-1}	E_d/kJ mol^{-1}	E_r/kJ mol^{-1}	$E_L = E_{el} + E_d + E_r$/kJ mol^{-1}	E_c/kJ mol^{-1}	$E(D^*)$/kJ mol^{-1}	$E_L = E_c + E(D^*) + E_{BSSE}$/kJ mol^{-1}
9-Substituted acridine (**I**)							
1	−13.4[a]	−119.4	26.5	−106.3	−18.6[c]	−116.9[c]	−131.6[c]
2	−38.8[a]	−174.5	85.7	−127.6	−139.4 [c]	−151.1[c]	−227.6[c]
	−55.7[b]			−144.4			
3	−10.8[a]	−124.8	27.7	−107.9	−12.3[c]	−122.5[c]	133.1[c]
5	−28.3[a]	−163.4	47.0	−144.7	−22.3[c]	−156.5[c]	−168.6[c]
6	−11.9[a]	−152.2	37.4	−126.7	−9.4	−147.4	−148.6
7	−16.6[a]	−165.6	50.8	−131.4	−13.0	−154.5	−159.1
8	−6.1[a]	−149.7	32.2	−123.6	−6.9[c]	−148.1[c]	−151.4[c]
9-Substituted-10-methylacridinium trifluoromethanesulphonates (**II**)							
10	−359.7[a]	−211.9	58.2	−513.5	−446.1[c]	−192.6[c]	−541.9[c]
	−386.4[b]			−540.1			
11	−357.9[a]	−215.7	61.2	−512.4	−444.0	−189.8	−531.5
	−382.7[b]			−537.2			
12	−361.0[a]	−200.6	52.1	−509.5	−448.8[c]	−176.6[c]	−530.6[c]
	−391.6[b]			−540.2			
13	−387.9[a]	−233.4	65.6	−555.6	−445.5	−206.7	−553.0
	−382.8[b]			−550.6			
14	−358.5[a]	−228.1	61.9	−524.6	−431.9[c]	−202.0[c]	−535.8[c]
	−378.3[b]			−544.3			

[a] Point charges calculated at the M06-2X/6-31 ++G** level for all atoms of the electroneutral asymmetric unit

[b] Point charges calculated at the M06-2X/6-31 ++G** level separately for molecules in the unit cell (assuming charge 0 for acridine molecule or water, +1 for acridinium molecule and −1 for trifluoromethanesulphonate counterpart)

[c] Ref. [37]

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

Compound no.	$\Delta_{s,298}H^{o}$/kJ mol^{-1}	$\Delta_{c,298}H^{o}$/kJ mol^{-1} [a]		$\Delta_{f,298}H^{o}$(g)/kJ mol^{-1} [a]		$\Delta_{f,298}H^{o}$(c)/kJ mol^{-1} [a]			
		GULP	CRYSTAL	B3LYP	M062X	B3LYP		M062X	
						GULP	CRYSTAL	GULP	CRYSTAL
9-Substituted acridines (**I**)									
1	82.1	−108.8	−134.1	286.5	260.5	191.1	178.4	165.0	152.4
2	20.6	−130.1[b]	−230.1	304.3	232.0	229.0	179.0	156.7	106.7
		−146.9[c]				220.6		148.3	
3	89.9	−110.4	−135.6	274.6	238.3	174.4	161.8	138.2	125.6
4	43.0			399.3	371.9	356.2	356.2	328.9	328.9
5	75.1	−147.2	−171.1	437.8	383.9	326.6	314.7	272.8	260.8
6	116.9	−129.2	−151.1	442.4	399.9	319.3	308.4	276.9	265.9
7	89.8	−133.9	−161.6	311.2	254.0	199.4	185.6	142.1	128.3
8	38.9	−126.1	−153.9	340.5	261.8	266.1	252.2	187.4	173.5
9-Substituted-10-methylacridinium trifluoromethanosulfonates (**II**)									
9				814.4	799.7				
10		−518.4[b]	−546.8	848.8	785.7	−805.6	−834.0	−880.7	−909.1
		−545.0[c]				−832.2		−907.3	
11		−517.3[b]	−536.4	801.5	776.6	−851.8	−870.9	−888.7	−907.8
		−542.1[c]				−876.6		−913.5	
12		−514.4[b]	−535.5	926.1	911.3	−724.3	−745.4	−751.2	−772.3
		−545.1[c]				−755.0		−781.9	
13		−560.5[b]	−557.9	962.2	919.0	−734.3	−731.7	−789.5	−786.9
		−555.5[c]				−729.3		−784.5	
14		−529.5[b]	−540.7	963.8	933.8	−701.8	−713.0	−743.7	−754.9
		−549.2[c]				−721.5		−763.4	

$\Delta_{s,298}H^{o}$, $\Delta_{c,298}H^{o}$, $\Delta_{f,298}H^{o}$, 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] GULP—carried out using the General Utility Lattice Program Version 4.0; CRYSTAL—carried out using the CRYSTAL09 program; B3LYP—the DFT(B3LYP)/6-31G** level of theory; M06-2X—the DFT(M06-2X)/6-31 ++G** level of theory

[b] Point charges calculated at the M06-2X/6-31 ++G** level for all atoms of the electroneutral asymmetric unit

[c] Point charges calculated at the M06-2X/6-31 ++G** level separately for molecules in the unit cell (assuming charge 0 for acridine molecule or water, +1 for acridinium molecule and −1 for trifluoromethanesulphonate counterpart)

respectively [30, 31], 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 and S are 8.53, 22.7 and 54.4 J mol^{-1} K^{-1}, and that of liquid Br_2 at the same temperature is 75.7 J mol^{-1} K^{-1}; NIST, http://webbook.nist.gov). Quantum chemistry calculations were carried out using the Gaussian 09 program package [46].

The standard enthalpies of formation of solid 9-substituted acridines (**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) [30, 31]. Standard enthalpies of formation of solid 10-methyl-9-substituted acridinium trifluoromethanesulphonates (**II**) were determined by the equation

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

or

$$\Delta_{f,298}H^{0}(\mathrm{c}) = \Delta_{c,298}H^{0} + \Delta_{f,298}H^{0}(\mathrm{g}) - 1269\,\mathrm{kJ\,mol^{-1}} \tag{7}$$

in which −1136 (Eq. 6) and −1269 (Eq. 7) kJ mol^{-1} are the standard enthalpy of formation of gaseous $CF_3SO_3^{-}$ predicted at the DFT(B3LYP)/6-31G** and DFT(M06-2X)/6-31 ++G** level of theory, respectively [30, 31]. The values of the other quantities are given in Table 3.

Results and discussion

The examples of DSC and TG curves of the compounds investigated (Scheme 1) are shown in Figs. 1–3. The decomposition temperature and enthalpies of the studied compounds determined by selecting the appropriate temperature range and using the 'horizontal sigmoidal' option of the baseline in the data processing program are collected in Table 1. As the DSC analyses demonstrate (Fig. 1, lower graph), heating 9-substituted acridine derivatives at a constant rate of temperature increase always leads to two processes: melting and subsequent volatilisation. Melting points varied between 349 and 460 K and were lower than the corresponding volatilisation temperatures, which are between 527 and 659 K (Table 1). Taking into account that 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 1). Melting enthalpies varied between 6.7 and 24.0 kJ mol^{-1}, the lowest value being obtained for compound **8** and the highest for **6**. Only in one case can be observed that the first process of decomposition of compound **2** is exothermic (Table 1). As may be seen from Fig. 2, this compound in a crystalline solid state melts at 444 K and the melting enthalpy is −35.6 kJ mol^{-1}. Our previous and current investigations of thermodynamic characteristics of acridin-9(10*H*)-ones [29], phenyl acridine-9-carboxylates and 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulphonates [30, 31] in the solid phase indicate that exothermic melting occurs for the first time in the group of acridine derivatives. Volatilisation enthalpies varied between 24.0 and 72.2 kJ mol^{-1}: compound **4** had the lowest value and compound **6** the highest. DSC analyses of 9-substituted-10-methylacridinium trifluoromethanesulphonates were carried out in the temperature range in which melting occurs. Melting points varied between 431 and 549 K: the lowest value was recorded for compound **11**, the highest for compound **9**. In the literature, the melting point of only one investigated 10-methylacridinium derivative—compound **13**—was found and the determined by DSC analysis melting point compared well with literature value (Table 1). Melting enthalpies varied between 22.4 and 29.0 kJ mol^{-1}; the lowest value was found for compound **10**, the highest for compound **14**. 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 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.

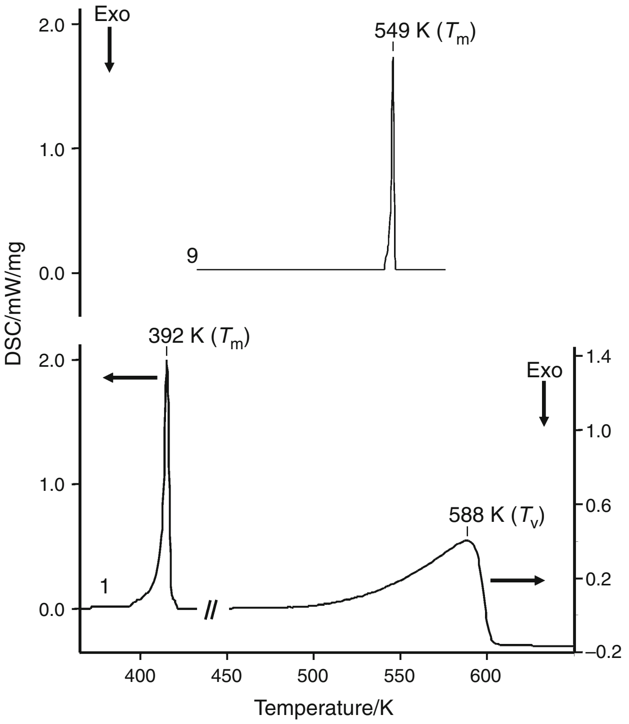


Fig. 1 Examples of DSC analyses of the compounds investigated (mass of the sample in mg/heating rate in K min^{-1}): **1** (3.350/5.0) and **9** (2.110/5.0). T_m—melting point, T_v—volatilisation temperature (assumed to be the temperature of the peak of the first DSC derivative). Lowering the base line during volatilisation is associated with a decrease in the system's heat capacity: sample holder + sample

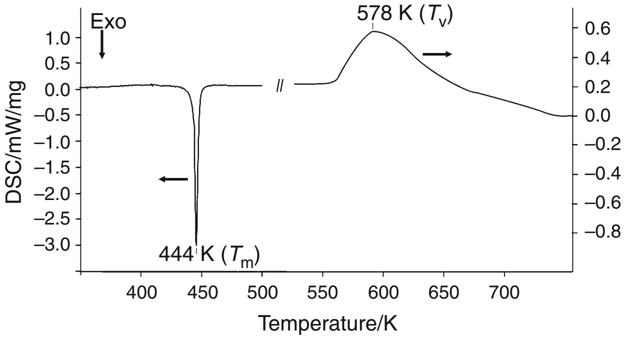


Fig. 2 DSC curve of thermal decomposition of **2** (mass of the sample in mg/heating rate in K min^{-1}: 2.520/5.0). T_m—melting point, T_v—volatilisation temperature (assumed to be the temperature of the peak of the first DSC derivative). Lowering the base line during volatilisation is associated with a decrease in the system's heat capacity: sample holder + sample

The shape of the TG curves of most of the investigated compounds (**1**, **3** and **5**–**14**) suggests that a single-step process occurs (examples of TG curves are shown in Fig. 3 and are similar to the presented TG curve of compound **1**). The type and geometry of substituent in 9 position of the acridine moiety have a fundamental effect on the course of its decomposition. The acridine derivatives with bromomethyl (**2**) or vinyl (**4**) groups are markedly less thermally stable than any other derivatives. During the first step, the formers lose their substituent (bromomethyl and vinyl group, respectively) to form acridine. This is demonstrated by 28.5 and 15.2% mass loss (in TG curve) close to 29.4 and 13.7% as calculated for the loss of mentioned substituent. In the subsequent steps decomposition of the acridine moiety is observed.

The plot showing the extent of volatilisation (α) versus temperature (*T*) (Fig. 4) reflects the thermogravimetric curves. Their smooth shape is evidence for the simple release to the gaseous phase of 9-substituted acridine 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, a represents the ratio p/p^0, 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 1) 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 (ca. 2 times; only in the case of **7** we observed the lower (ca. 1.4) values of the above-mentioned ratio) 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.

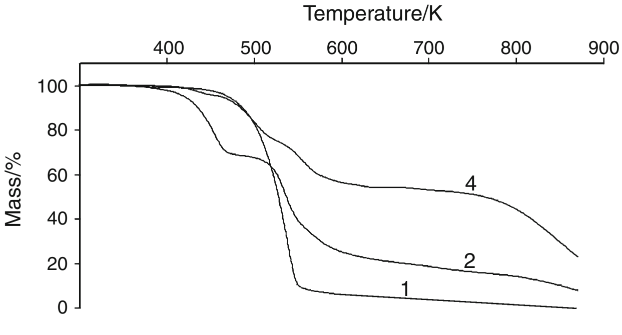


Fig. 3 Examples of experimental TG curves reflecting the decomposition of the compounds investigated (mass of the sample in mg/heating rate in K min^{-1}): **1** (3.200/5.0), **2** (3.390/5.0) and **4** (3.090/5.0)

The crystal lattice energy (E_L) is important thermodynamic characteristics of crystalline substances and reflects the strength of cohesion forces occurring within this kind of solid phase. Theoretical cohesive energies may be compared with the lattice energies, assessed on the basis of experimental data (enthalpies of sublimation). This magnitude can be predicted for compounds whose crystal structures are known. In our [35–37] and others [32–34] authors' previous investigations have been determined the crystal structures of seven 9-substituted acridines (**1–3**, **5–8**) and five 9-substituted 10-methylacridinium trifluoromethanesulphonates (**10–14**). The crystal lattice energies calculated for these compounds together with the electrostatic, dispersive and repulsive contributions to crystal lattice energy, which were determined using two programs: GULP and CRYSTAL09, are shown in Table 2. Despite methodological differences, lattice energies for studied compound calculated by GULP correlate well with those originating from CRYSTAL09. Only in the case of compound **2** calculated by CRYSTAL09, the crystal lattice energy and the electrostatic contribution in the crystal lattice energy are significantly higher than in the other investigated 9-substituted acridines. Additionally, the basis set superposition error energy correction values for this derivative are higher than in the other derivatives (62.9 and 6.0 (average for **1**, **3**, **5–8**) kJ mol^{-1}, respectively). For the mentioned results it may be stated that 9-bromomethylacridine crystallises in monohydrated form. Taking into account general chemical knowledge, as well as the information mentioned above, we consider that monohydrated acridine derivatives behave as acridinium derivatives or acid–base pair. Considering the results obtained

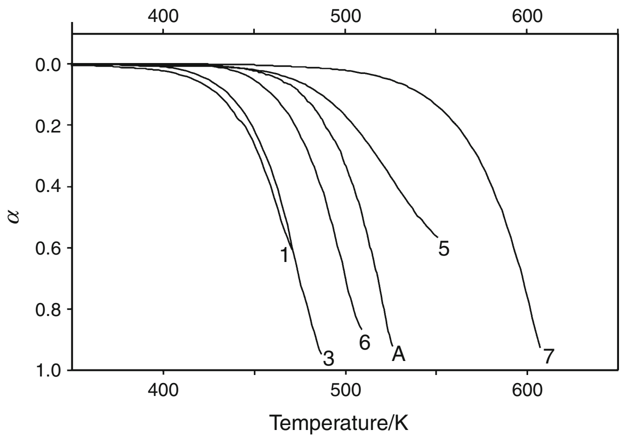


Fig. 4 Extent of volatilisation (α) versus temperature (*T*) relationships for the 9-substituted acridines investigated (for names, see Scheme 1) and anthracene (A). Conditions (mass of the sample in mg/heating rate in K min^{-1}): **1** (3.200/5.0), **3** (2.700/5.0), **5** (2.520/5.0), **6** (2.750/5.0), **7** (7.000/5.0) and **A** (4.693/5.0)

with GULP, for compound **2** and all acridinium derivatives (**10–14**), two E_L values are shown in Table 2, which differ by method determined ESP fitted atomic partial charges on N10 atom of the acridine/acridinium derivatives. In the first approach, the atomic partial charges were calculated for all atoms of the electroneutral asymmetric unit, and in the second, the atomic partial charges were calculated separately for molecules in the unit cell (assuming charge 0 for acridine molecule or water, +1 for acridinium molecule and −1 for trifluoromethanesulphonate counterpart). The lattice energies for studied acridinium derivatives calculated by GULP using the latter approach correlate better with those originating from CRYSTAL09, but for 9-bromomethylacridine despite the improved result, differences are still significant.

The crystal lattice enthalpies and the enthalpies of sublimation calculated, where the crystal structures are known, are presented in Table 3. The calculated crystal lattice enthalpies correlate reasonably well with the enthalpies of sublimation of the corresponding 9-substituted acridines, which is an endorsement of the method applied for predicting the values of this quantity. Only in the case of compounds **2** and **8**, the crystal lattice enthalpies are significantly higher than the corresponding enthalpies of sublimation. The crystal lattice enthalpies of 9-substituted 10-methylacridinium trifluoromethanesulphonates (Table 3) are typical for salts containing complex monovalent ions [30, 31]. 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 2 demonstrate, the main contribution to the crystal lattice energy of acridine derivatives (**1–3**, **5–8**) is due to dispersive interactions, whereas that of 10-methylacridinium salts (**10–14**) results primarily from electrostatic interactions. Theoretical analysis therefore indicates that the nature of the cohesive forces differs in neutral molecules (**I**) and the salts derived from them (**II**).

Further insight into the thermochemistry of the compounds investigated was gained by the application of quantum chemistry methods, which enabled the enthalpies of formation of gaseous 9-substituted acridines, gaseous 9-substituted 10-methylacridinium cations and the trifluoromethanesulphonate anion to be predicted. The data relating to neutral molecules and cations calculated using two different methods and basis sets (first B3LYP functional and 6-31G** basis set and second M06-2X functional and 6-31 ++G** basis set) are shown in Table 3; the corresponding values of enthalpy of formation for the anion are in kJ mol^{-1}: −1136 and −1269, respectively. Knowledge of these characteristics enables one to calculate the enthalpies of formation of acridines (**I**) and of their derivative salts (**II**) in the solid phase—relevant values are given in the last four columns of Table 3 (considering different methods of calculating the crystal lattice energy and enthalpy of formation of gaseous compounds). As presented, the choice of the M06-2X or B3LYP functional in combination with 6-31 ++G** and 6-31G** basis sets has a significant impact (difference between 26.0 and 78.7 kJ mol^{-1}) on the value of $\Delta_{f,298}H^0(g)$. The reason for this may be that the M06-2X functional takes into account the dispersion corrections for density functional theory which are not included in the B3LYP functional. Besides, using the diffuse functions in the 6-31 ++G** basis set has also an effect on the values of enthalpies of formation. However, knowledge of 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

In the present paper, the thermal properties of 9-substituted acridines and their *N*-methylated-acridinium trifluoromethanesulphonates and the thermodynamic characteristics—melting points, melting and volatilisation enthalpies, crystal lattice enthalpies and enthalpies of formation, are reported. The results 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.

Acknowledgements The authors are grateful to Dr. Julian D. Gale for supplying the GULP program and permission to use it. They would also like to thank Mrs Gabriela Nowak-Wiczk for her contribution to the DSC and TG measurements. This study was financed from the State Funds for Scientific Research through National Science Centre grant 2011/03/D/ST4/02419 (contract No. UMO-2011/03/D/ST4/02419). Calculations were carried out on the computers of the Wroclaw Centre for Networking and Supercomputing (WCSS) (Grants No. 196 and 215).

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