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ENTHALPIES OF SUBLIMATION AND CRYSTAL LATTICE ENERGIES OF 9-ACRIDINAMINE AND ITS DERIVATIVES

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Abstract

Enthalpies of sublimation of acridine, 9-acridinamine, N-methyl-9-acridinamine, 10-methyl-9-acridinimine, N,N-dimethyl-9-acridinamine and N-methyl-10-methyl-9-acridinimine were determined by fitting to thermogravimetric curves with the Clausius-Clapeyron relationship. These values compare well with crystal lattice energies predicted theoretically as the sum of electrostatic, dispersive and repulsive interactions. Partial charges for these calculations were obtained on an ab initio level, while atomic parameters were taken from literature.

Keywords: acridine, 9-acridinamine and its derivatives, crystal lattice energy, heat of volatilization

Introduction

Crystal lattice energy reflects the natural tendency towards the organization of matter. In the case of molecular crystals, the lattice energy can be determined experimentally as sublimation enthalpy [1]. Crystal lattice energy may also be predicted by using various theoretical approaches [2–4]. All of these assume that three contributions are important, namely, electrostatic, dispersive and repulsive, which together give an energy corresponding to the minimum on the potential energy surface. To bring the system to ambient temperature or any temperature above 0 K, the zero point energy and thermal energy must be added [2].

In this communication we describe the application of thermogravimetric technique and theoretical methods to determine the lattice energy of molecular crystals of acridine, as well as 9-acridinamine and its derivatives, compounds important for cognitive and applicative reasons [5].

Methods

Volatilization enthalpy determination

Thermogravimetric measurements were carried out on a Netzsch TG 209 Thermobalance.

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Volatilization enthalpies ($\Delta_V H^0$) were obtained from the Clausius-Clapeyron relationship [6]

$$\ln\alpha = -\left(\frac{\Delta_V H^0}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta_V H^0}{R}\right)\left(\frac{1}{T_V}\right) \tag{1}$$

in which α represents the extent of volatilization (α equals to p/p^0, where p is the equilibrium vapour pressure at a given temperature (T) and p^0 the standard atmospheric pressure (^{0})), R denotes the gas constant and T_V is the temperature at which p attains p^0.

As obtained in the above described manner, values of the volatilization enthalpy can suffer as the outcome of errors difficult to assess, we standardized the procedure by performing measurements for anthracene whose $\Delta_{V,298}H^0$ equals 100.2 kJ mol^{-1} [7–9].

Calculations

Crystal lattice energies (E_c) were calculated by summing up three contributions: electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) [1–4]

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

E_{el} in Eq. (2) represents Coulombic interactions [10],

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

while the sum of E_d and E_r can be expressed by the formulae of Lennard-Jones [11]

$$E_d + E_r = \frac{1}{2}\sum_{i}\sum_{j\neq i}\left[-\frac{D_iD_j}{R_{ij}^6} + \frac{A_iA_j}{R_{ij}^{12}}\right] \tag{4}$$

or Buckingham [12]

$$E_d + E_r = \frac{1}{2}\sum_{i}\sum_{j\neq i}\left[-\frac{D_iD_j}{R_{ij}^6} + B_iB_j\exp(-C_iC_jR_{ij})\right] \tag{5}$$

In Eqs (3)–(5) N is the Avogadro number, e – the elementary charge, ε_o – the permittivity of free space, while $Q_i(Q_j)$ denote the relative partial charges at atoms, $D_i(D_j)$, $B_i(B_j)$ and $C_i(C_j)$ atomic parameters, and R_{ij} the distance between interacting centres (summation extends over all pairwise interactions between each atom of a molecule chosen as a basic stoichiometric unit (denoted as i) and all atoms from its surroundings (denoted as j).

Table 1 Atomic parameters for calculating energies of dispersive and repulsive interactions [3, 4]

Atom	Parameter^a			
	D	A	*B*	*C*
H	20.3	198.4	36.1	1.64
C	50.0	1389.6	520.3	1.94
N	39.2	825.8	213.0	1.86

$^a D$ in $kJ^{1/2}/mol^{-1/2}$ Å^3; A in $kJ^{1/2}mol^{-1}$Å^6; B in $kJ^{1/2}mol^{-1/2}$; and C in Å$^{-1/2}$.

The relative atomic partial charges necessary when calculating the energy of electrostatic interactions were fitted so, as to reproduce the molecular electrostatic potential around molecules (MEP fitted charges) [13] derived on the ab initio density functional theory (DFT) level [14]. These charges were obtained using the Becke 3 LYP functional [15, 16] together with the 6-31G** basis set [17, 18] included in the SPARTAN 5.0 program package [19]. Atomic parameters (Table 1) were taken from literature [3, 4]. Crystal lattice energy was calculated using PCK 83 program [20].

Results and discussion

Extent of volatilization (α) *vs.* temperature (*T*) dependencies seen in Fig. 1 represent thermogravimetric curves. The smooth shape of these is evidence of the simple release of molecules held in the crystalline to gaseous phase. The energy barrier for such a process equals the thermodynamic one, i.e. enthalpy of

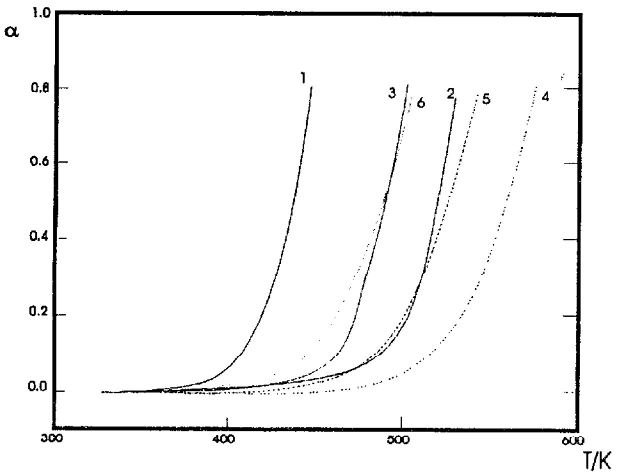

Fig. 1 α *vs.* *T* dependencies for the compounds investigated. Conditions (mass of the sample in mg/heating rate in K min^{-1}): **1** (3.170/1.0), **2** (3.500/1.0), **3** (3.600/2.5), **4** (3.600/10.0), **5** (6.889/10.0), **6** (3.800/2.5)

volatilization. It may thus be expected that the system attains rapidly equilibrium on temperature increase. If so, α represents the ratio p/p^0 and α *vs.* T dependencies can be fitted with the Clausius-Clapeyron relationship (1) in order to obtain the enthalpies of volatilization (listed in Table 2).

Table 2 Volatilization enthalpies and crystal lattice energies theoretically predicted (in kJ mol^{-1})

Compound[a]	$\Delta_V H^0$	$-E_{el}$[b]	$-E_c$[b]	
			Eqs (3) and (4)	Eqs (3) and (5)
1	86	8.4	88.9	85.1
2	115	18.9	161.8	132.2
3	107			
4	94			
5	86	6.4	77.8	71.2
6	72	9.9	97.0	73.3

[a] **1** – acridine; **2** – 9-acridinamine; **3** – N-methyl-9-acridinamine; **4** – 10-methyl-9-acridinimine; **5** – N,N-dimethyl-9-acridinamine; **6** – N-methyl-10-methyl-9-acridinimine.

[b] crystal phase structures required for the lattice energy calculations were taken from: **1** [21], **2** [22], **5** [23] and **6** [23].

1, **5** and **6** form typical molecular crystals in which molecules are bonded as a result of van der Waals interactions. On the other hand, in **2**, **3** and **4** hydrogen bonding occurring additionally is reflected in higher enthalpies of their volatilization.

Electrostatic energies are relatively small (Table 2) which arises from the fact that the compounds are only slightly polar and do not exhibit any ionic character (in the case of ionic crystals the electrostatic term dominates in the lattice energy [10]).

Crystal lattice energies compare quite well with the enthalpies of volatilization in the case of **1**, **5** and **6**. This fact confirms reliability of both experimental and theoretical data, as well as methods of their determination. On the other hand, a relatively large discrepancy between both characteristics in the case of **2** most probably results from uncertainties of theoretical predictions. The improvement of theory could be directed towards the search for more adequate atomic parameters. This is an issue which we are currently tackling.

The results of this work provide further evidence of successful application of the thermogravimetric technique for determination of the enthalpies of volatilization. Theoretical methods used in the lattice energy evaluations are still far from perfection but afford unique insight into the nature of interactions retaining molecules in condensed phases.

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