# The Potential Energies of Cohesion of a Crystalline Organic Enantiomer and the Racemate; on the Energy for the Liquid Racemate [1]

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**Summary.** The cohesion potential energy of the crystal of one enantiomer of ethyl 3-cyano-3-(3,4-dimethyloxyphenyl)-2,2,4-trimethylpentanoate, $-47.7 \pm 0.1 \, \text{kJ} \, \text{mol}^{-1}$ (0–90°C), was found out from the heat of sublimation ($123.2 \pm 5.1 \, \text{kJ} \, \text{mol}^{-1}$, 78.6°C) and the kinetic energies for the gas phase and the crystal. It was found that the entropy function of *Debye*'s theory of solids mathematically agreed with the vibrational entropy of the gas (variationally obtained), allowing to disclose the vibrational energy using the *Debye* energy function ($E_{\text{vib}}$ 835.0 kJ mol$^{-1}$ (78.6°C), $E^0$ included). $E_{\text{kin}}$ for the crystal (771.1 kJ mol$^{-1}$ (78.6°C)) was obtained by *Debye*'s theory with the experimental heat capacity. The cohesion energy represented a moderate part of the sublimation energy. The cohesion energy of the racemic crystal, $-44.2 \, \text{kJ} \, \text{mol}^{-1}$, was obtained by the heat of formation of the crystal in the solid state (3.0 kJ mol$^{-1}$, 83.3°C) and $E_{\text{kin}}$ for the crystal (by *Debye*'s theory). The decrease in cohesion on formation of the crystal accounted for the energy of formation. The change in potential energy on liquefaction of the racemate from the gas state was disclosed obtaining added-up $E_{\text{vib}+\text{rot}}$ for the liquid in the way as to $E_{\text{vib}}$ for the gas, the *Debye* entropy function being increasingly suited for the liquid ($E_{\text{vib}+\text{rot}}$ 763.4 kJ mol$^{-1}$ (115.4°C)). Positive $\Delta E_{\text{pot}}$, 13.0 kJ mol$^{-1}$, arised from the increase in electronic energy ($\Delta_l \nu_{\text{mean}}$ $-154.3 \, \text{cm}^{-1}$, by the dielectric nature of the liquid), added to the cohesion energy.

**Keywords.** Chirality; Cohesion energy; Phase transformations; Thermodynamics; Vibrational entropy.

## Introduction

In changes of aggregation state of an organic compound the kinetic energy (translational, rotational,

and vibrational) and the potential energy of cohesion are considered as representing the components of the internal energy, that pertinent to such kind of transformations ($U$, Eq. (1)) [2]. The change in internal energy on a change of state ($\Delta U$, the observable quantity) is actually indivisible. Also, it is only a small part of the whole internal energy pertaining to the change of state.

$$\Delta U = \Delta E_{\text{kin}} + \Delta E_{\text{pot}} \qquad (1)$$

The potential energy of cohesion results from dipole and dispersion forces, the forces of cohesion other than strongly directional interactions [3]. A distinct kind of potential energy which may be considered is the very slight modification of the enormous electronic energy of a molecule as a consequence of the dielectric nature of matter. On condensation from the gaseous state such modification manifests as a small decrease in molecular vibrational frequencies and so in the force constants [4a]. Contrary to the potential energy of cohesion, this variation in the electronic potential energy is positive, as if the molecule expanded on the condensation. With respect to the energy of change of aggregation state ($\Delta U$), the effect may become important for the liquid state on account of the higher dielectrical mobility.

It has been shown that one enantiomer of **1** in the crystalline solid state is stable in relation to the crystalline racemate ($G_{\text{en}} < G_{\text{rac}}$) [5]. In the present work the values of the potential energies of cohesion of the two crystals were found out, which was accomplished

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by the heat of sublimation for the enantiomer and the heat of formation in the solid state for the racemate (from the crystalline enantiomers) along with the kinetic energies for the gaseous phase and the two solids (in agreement with Eq. (1)). The heat of sublimation of the enantiomer has been determined by the method of molecular effusion (for low vapour pressures [6a, 7]) and the heat of allotropic formation of the racemate has been derived from heats of melting and heat capacities determined by differential scanning calorimetry (DSC) [8, 9].
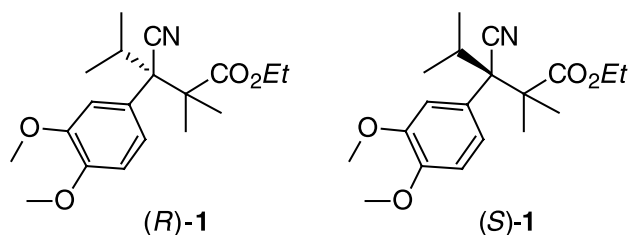


The kinetic energy for the crystalline enantiomer as well as its entropy has been derived from the experimental heat capacity using *Debye*'s theory of heat capacities of solids [10, 11] with its mathematical functions for the vibrational energy and entropy [12]. The suitability of this theory for the crystal was examined and verified. The entropy of the crystal served to know the entropies of the gaseous phase and the racemic crystal. The kinetic energy for the latter was thus obtained by its entropy using the correlated *Debye* functions for entropy and energy.

The vibrational energy of the gas molecule represented a difficult point. It was found in the end that the whole vibrational entropy of the molecule could be accounted for by the *Debye* function for entropy, which permitted to reach the entropy itself by a variation method and then the energy by the *Debye* function for energy. The finding that the *Debye* function for entropy is suitable from a mathematical point of view for the vibrational entropy in a state of matter different from the solid state makes a feature of the work.

The cohesion potential energy of the crystalline enantiomer proved to share only moderately in the internal energy of sublimation on account of the strong vibrational energy of the organic compound. However, the small decrease in cohesion on formation of the racemate in the solid state was similar to the internal energy of the transformation as the vibrational energies of the involved solids are balanced.

We have previously considered energetics for the liquid state in terms of equilibrium constants for liquefaction of the vapour ($\Delta_l G$) [13]. Presently wishing to know the potential energy for the racemate in the liquid state the kinetic energy was found similarly to the gaseous phase: the joint vibrational and rotational entropy of the liquid was reached by the very well fitting *Debye* entropy function, and the energy was obtained by the energy function. On liquefaction there occurs an overall increase in potential energy ($_l E_{pot} > 0$), which stands for the increase in electronic potential energy resulting from the dielectric character of the liquid, as added to the cohesion energy of the liquid.

## Results and Discussion

### The Cohesion Potential Energy of the Crystalline Enantiomer

The heat of sublimation of enantiomer **1** was achieved determining the vapour pressure of the solid by effusion at different temperatures and using *Clausius-Clapeyron* equation [11] for the change in vapour pressure with the temperature (Fig. 1). The corresponding internal energy of sublimation was obtained subtracting quantity $p_v$ for the vapour as an ideal gas (Table 1, $p_v$ for the crystal can be neglected since even at $10^5$ Pa it is $0.03$ kJ mol$^{-1}$ only). The heat capacity of the crystalline enantiomer is shown in Fig. 2. The $C$ values at approximately con-
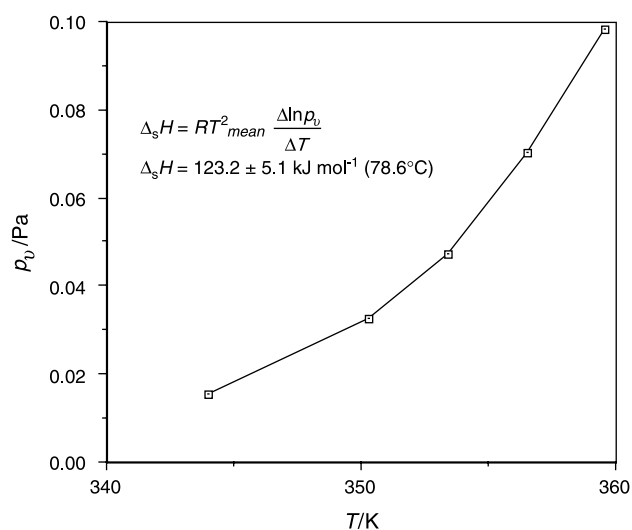


**Fig. 1.** Experimental vapour pressure of enantiomer **1** in the crystalline solid state and the heat of sublimation derived from the data

**Table 1.** Thermodynamic quantities for the crystal of enantiomer **1** at 78.6°C

| $\Delta_S U$ | $\Delta_S S$ | $E_{kin}$ |
|---|---|---|
| 120.3 ± | 350.2 ± | 771.1 kJ mol$^{-1}$ [b] |
| 5.0 kJ mol$^{-1}$ [a] | 14.5 J K$^{-1}$ mol$^{-1}$ [a] | |
| $\nu_{mean}^c$ | $S$ | $E_{pot}$ |
| 759.2 cm$^{-1}$ | 310.4 J K$^{-1}$ mol$^{-1}$ [d] | −47.7 ± 0.1 kJ mol$^{-1}$ [e] |

[a] Observed value; [b] *Debye* predicted value, 774.0 (83.3°C), $E^0 = 694.6$ kJ mol$^{-1}$; [c] for all vibrational motions; [d] *Debye* predicted value, 318.7 (83.3°C), 331.6 (90.7°C); [e] average for the interval of 0–90°C
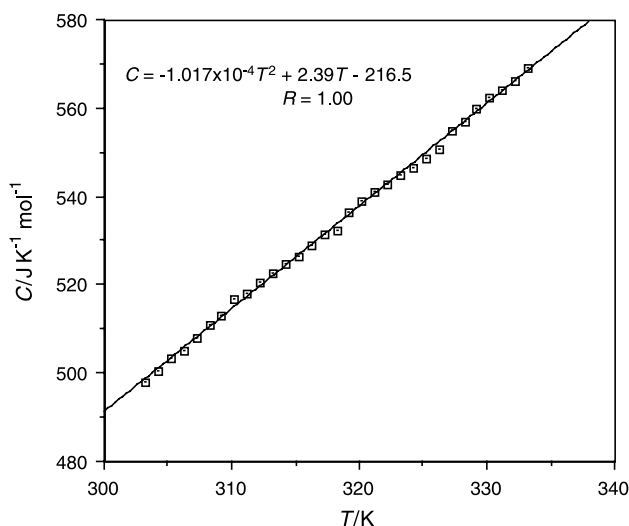


**Fig. 2.** Experimental heat capacity of enantiomer **1** in the crystalline solid state

stant pressure were taken for values at constant volume (required by *Debye*'s theory) as an estimate indicated that they are but *ca.* 0.1 J K$^{-1}$ mol$^{-1}$ larger than the latter ($C_p - C_v \approx p\Delta V/\Delta T$).

In order to determine the suitability of *Debye*'s theory for the crystal, *i.e.* the existence of constant *Debye* temperature (proportional to *Debye* border vibrational frequency, $T_D \equiv h\nu_D/k$), a number of values for $T_D$ were worked out from experimental $C$-$T$ points, obtaining the values for $T_D$ by solving the *Debye* function for heat capacity: $C \approx C_v = N f_{C_v}(T_D/T)$ ($N$ atoms of the molecule, 51), a function which is tabulated [12]. For an interval of 90 degrees (273.0–363.0 K, making use of the extrapolated heat capacity) the $T_D$ values agreed within ±0.41% ($T_D = 1456 \pm 6$ K), which was considered sufficient. *Einstein*'s simpler theory of heat capacities of solids [11] was tried and did not fit so well; it turn out to

give a lower kinetic energy and finally an incorrectly low cohesion for the crystal.

With the characteristic *Debye* temperature for the crystal the kinetic energy was obtained by the *Debye* energy function ($E = N f_E(T_D/T) + E^0$, $E^0 = 9NRT_D/8$ [12]). The $E_{kin}$ value for the temperature of the experimental energy of sublimation is given in Table 1. The zero-point energy represents a 95 to 89% of the energy of the crystal at 0 to 90°C. A mean frequency for the vibrational motions ($\nu_{mean} = 3\nu_D/4$), connected to the average zero-point energy ($E^0/3N$), is given in the Table. The entropy of the crystal was obtained in the same way that the energy, using the *Debye* function for entropy [12] (see Table 1).

Concerning the kinetic energy for the gaseous phase, the heat capacity of the vapour of the crystal was estimated using *Rihani* and *Doraiswamy*'s group-contribution method for the heat capacity of gases [14], a method which is considered distinctly accurate [15] (Fig. 3). The vibrational heat capacity of the vapour ($C_{vib}$, obtained withdrawing the minor translational and rotational contributions of the molecule to heat capacity) was poorly accounted for by the function for the heat capacity of the harmonic oscillator ($C_{vib} = (3N-6)f_{C_{vib}}T_{vib}/T$, $T_{vib} \equiv h\nu/k$) [11, 12], a model otherwise suitable. The resulting $T_{vib}$ value for the harmonic oscillator representative of the vibrations in the molecule had an error so large as ±4.8% for a temperature interval of 90 degrees, completely thwarting an accurate knowledge of the vibrational energy. Furthermore, summation of the energies of
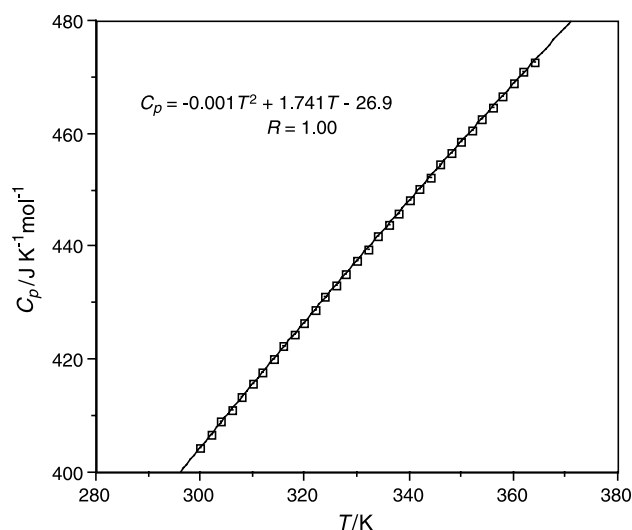


**Fig. 3.** Heat capacity of ester **1** as a gas according to *Rihani* and *Doraiswamy*'s estimation method

the individual vibrations using adequate harmonic-oscillator frequencies suitable for the heat capacity [15] in conjuction with the harmonic-oscillator energy function [12], gave a manifestedly wrong total vibrational energy for the gas molecule.

Having met this problem, it was thought of using the vibrational entropy of the gas molecule rather than the vibrational heat capacity. Moreover, the entropy would be used in combination with the *Debye* vibrational function for entropy in the solid state (above mentioned) as a mathematical alternative to the more logical and simpler harmonic-oscillator function for entropy. The choice turned out successful, and it will be described in the following.

*The Vibrational Entropy and Energy for the Gas*

The vibrational entropy of the gas can be expressed as a function of temperature by Eq. (2), in reference to the unknown value for the vibrational entropy of the gas at the temperature of the experimental entropy of sublimation. The equation is easily deduced by integration using the heat capacity of the gas in Fig. 3 $(\mathrm{d}S_{\mathrm{vib}} = C_{\mathrm{vib}}\mathrm{d}T/T, \; C_{\mathrm{vib}} = C_p - 4R)$. Setting a tentative approximate $S_{\mathrm{vib}}^{351.8}$ value it was found that the *Debye* vibrational function for entropy accounted well for the equation, making use of the *Debye* function for only the vibrational degrees of freedom of the gas molecule (*i.e.* with N-2 (49), $S = (N-2)f_{\mathbf{S}}(T_D/T)$) [12].

$$S_{\mathrm{vib}}^{T} = -5 \times 10^{-4}T^2 + 1.741T - 60.17\ln T \\ - 197.82 + S_{\mathrm{vib}}^{351.8} \quad (2)$$

From this point the $S_{\mathrm{vib}}^{351.8}$ value was methodically varied to optimize the agreement between Eq. (2) and the *Debye* entropy function. A maximal agreement was reached with a value of $213.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$: the *Debye* temperature was constant within $\pm 0.35\%$ for an interval of 90 degrees (273–363 K, $T_D = 1706 \pm 6\,\mathrm{K}$), and such entropy value was taken as the correct value. The harmonic-oscillator function for entropy was not mathematically fit despite being in principle more logical than the *Debye* function for entropy.

From the $S_{\mathrm{vib}}^{351.8}$ value the rotational entropy of the gas at the same temperature can be calculated by Eq. (3). The total entropy of the gas at such sublimation temperature was available considering the gas as vapour of the crystalline enantiomer: the vapour entropy equals the crystal entropy plus the sublimation

**Table 2.** Thermodynamic quantities for ester **1** as a gas at 78.6°C

| $S^{\mathrm{a}}$ | $S_{\mathrm{vib}}$ | $S_{\mathrm{rot}}$ |
|---|---|---|
| $660.6\,\mathrm{J\,K^{-1}\,mol^{-1b}}$ | $213.1\,\mathrm{J\,K^{-1}\,mol^{-1c}}$ | $139.7\,\mathrm{J\,K^{-1}\,mol^{-1d}}$ |
| $E_{\mathrm{vib}}$ | $\nu_{\mathrm{mean}}^{\mathrm{f}}$ | $E_{\mathrm{kin}}$ |
| $835.0\,\mathrm{kJ\,mol^{-1e}}$ | $889.5\,\mathrm{cm^{-1}}$ | $843.7\,\mathrm{kJ\,mol^{-1}}$ |

[a] $S = S(\mathrm{en, cr}) + \Delta_S S$; [b] $S_{\mathrm{tr}} = 307.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ ($p_v = 3.77 \times 10^{-2}$ Pa); [c] deduced from the dependence of the vibrational entropy on temperature by comparison with the *Debye* function for entropy; [d] $I_A I_B I_C = 2.03 \times 10^9\,\mathrm{amu^3\,\mathring{A}^6}$; [e] deduced from the vibrational entropy using the *Debye* functions for entropy and energy, $E^0 = 782.0\,\mathrm{kJ\,mol^{-1}}$; [f] for all vibrational degrees of freedom

entropy (see Tables 1 and 2). The translational entropy of the vapour straightforwardly resulted from the vapour pressure of the crystal at that temperature (Fig. 1) by the formula for the translational entropy of gases in statistical mechanics [11] (see Table 2). The $S_{\mathrm{rot}}^{351.8}$ value is given in Table 2. From this value the product of the three principal moments of inertia of the molecule $(I_A I_B I_C)$ is immediately obtained by the formula for the rotational entropy of the molecule in statistical mechanics [6b]. The resulting $I_A I_B I_C$ value, *i.e.* $2.03 \times 10^9\,\mathrm{amu^3\,\mathring{A}^6}$, is not unreasonable to the extent that it is six times smaller than the value for the homogeneous sphere equivalent to the molecule [9]. The value can be otherwise calculated by *Wilson* and *Hirshfelder*'s method [4b] with the structure of the molecule [9], a method we previously used for much simpler molecules [13], but which we kept from using in this case.

$$S_{\mathrm{rot}} = S - S_{\mathrm{tr}} - S_{\mathrm{vib}} \quad (3)$$

From the found *Debye* temperature for the vibrational motions of the gas molecule the vibrational energy can be arrived at by the *Debye* function for energy, and hence the total energy of the gas by addition of quantity $3RT$ for the translational and rotational motions. However, it was not taken for granted that the vibrational energy would be correct since there was apparently no supporting physical reason why the *Debye* entropy function was suitable for the gas. Moreover, the *Debye* heat-capacity function poorly accounted for the heat capacity. In this respect and from a mathematical point of view it was hopefully considered that energy could be less demanding than heat capacity as it is not a derivative of the entropy $(\mathrm{d}U = T\mathrm{d}S_v, \; C_v = T\mathrm{d}S_v/\mathrm{d}T)$. Such logical defectiveness of *Debye*'s theory in the gas state was dealt with in the following manner.

From the *Debye* temperature and using the *Debye* heat-capacity function, the predicted heat capacity as function of the temperature was worked out ($C_{\text{vib}} = -1.438 \times 10^{-3}T^2 + 3.108T - 442.6$) and matched the actual heat capacity (Fig. 3, $C_{\text{vib}} = C_p - 4R$) in a single point by the middle of the normal temperature interval (the two slanted lines intersected at 310.7 K). It was then assumed that at least in such point the *Debye* heat-capacity function and by extension the energy function would be appropriate in a fundamental manner, and the corresponding energy value was singularly adopted ($E_{\text{vib}} = 818.3\,\text{kJ mol}^{-1}$, $E_{\text{kin}} = 826.0\,\text{kJ mol}^{-1}$). The adequacy of the procedure was subsequently confirmed in the liquid state concerning the liquid racemate. For energy values for temperatures other than such singular temperature the use of the energy function was avoided, and the values were safely reached by means of thermodynamics taking advantage that the kinetic energy of the gas is exactly the internal energy (no cohesion energy, (Eq. (4)): the $\Delta_{310.7}^{T}U$ values were calculated from the heat capacity of the gas (Fig. 3, $\mathrm{d}U = C_v\mathrm{d}T$, $C_v = C_p - R$).

$$E_{\text{kin}}^{T} = E_{\text{kin}}^{310.7} + \Delta_{310.7}^{T}U \qquad (4)$$

The $E_{\text{vib}}$ and $E_{\text{kin}}$ values for the temperature of the experimental energy of sublimation are given in Table 2. The zero-point energy represents a 96–92% of the total energy of the gas at 0–90°C. A mean vibrational frequency for the molecule is gathered in the table. It is the counterpart of the mean frequency for the crystal (Table 1), but this refers to six more vibrational degrees of freedom as occur in the crystal (153 *vs.* 147).

Having the energy of sublimation of the crystalline enantiomer and the kinetic energies for the gaseous phase and the crystal the potential energy of cohesion can be calculated according to Eq. (1). In order to obtain the average for the usual temperature interval, elaborated Eq. (5) was applied to different temperatures. The last two terms in the expression stand for the change in energy of sublimation with the temperature and were calculated from the heat capacities. The average $E_{\text{pot}}$ value was $-47.7 \pm 0.1\,\text{kJ mol}^{-1}$, quite constant in the temperature interval (0–90°C).

$$\begin{aligned}
E_{\text{pot}}^{T} = {} & E_{\text{kin}}^{310.7}(\text{g}) + \Delta_{310.7}^{T}U(\text{g}) - E_{\text{kin}}^{T}(\text{cr}) \\
& - \Delta_s U^{351.8} - \Delta_{351.8}^{T}U(\text{g}) \\
& + \Delta_{351.8}^{T}U(\text{cr})
\end{aligned} \qquad (5)$$

The potential energy of cohesion of the crystal represents only a moderate part of the energy of sublimation, the rest being accounted for by kinetic energy. The share of the kinetic energy is to be attributed in particular to the relatively small decrease in the large zero-point vibrational energy of the gas molecule (Tables 1 and 2), in concomitance with the decrease in mean vibrational frequency and resulting from the dielectric nature of the crystal [4a].

### The Cohesion Potential Energy of the Crystalline Racemate

The heat of melting of racemate **1** is shown in Fig. 4. The heat of formation of the crystalline racemate from the separate crystalline enantiomers was quantitated from the literature heat of melting of the racemic mixture of enantiomers (a conglomerate and eutectic, $\Delta_m H = 33.2\,\text{kJ mol}^{-1}$ [9]) and the heat of melting of the racemate, according to a method we previously reported (Eq. (6) [9]).

$$\begin{aligned}
\Delta_f H^{356.5} = {} & \Delta_m H(\text{congl}) + \Delta_{363.9}^{356.5}H(\text{rac}, l) \\
& - \Delta_{363.9}^{356.5}H(\text{congl}) - \Delta_m H(\text{rac})
\end{aligned} \qquad (6)$$

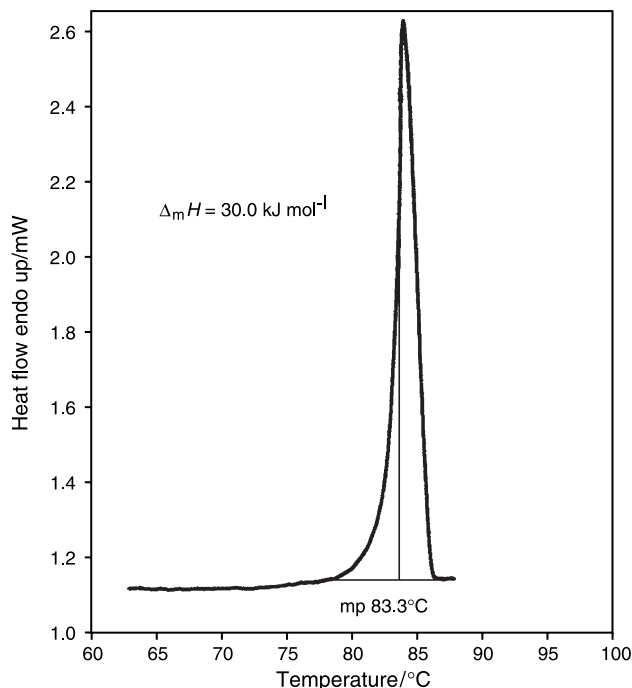The second and third terms in the expression bring the heat of melting of the conglomerate from its



**Fig. 4.** DSC trace of melting of racemate **1**

$$C = -0.0112T^2 + 10.18T - 1554$$
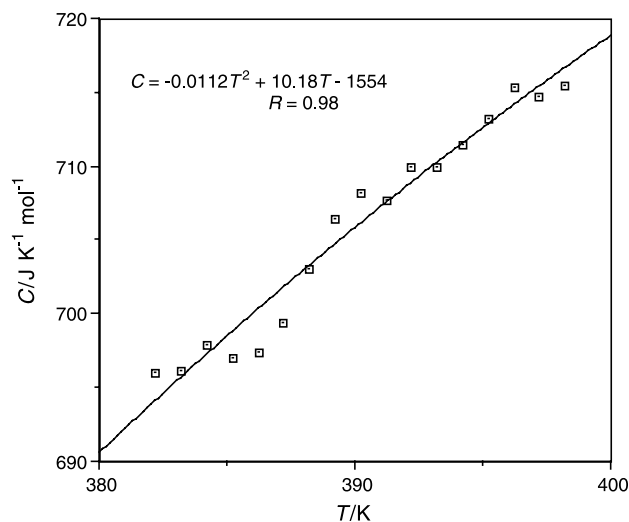$$R = 0.98$$

**Fig. 5.** Experimental heat capacity of racemate **1** in the liquid state

melting point to the melting point of the racemate as the available temperature for the heat of formation. The values of such terms were calculated by integration using the heat capacities in Figs. 2 and 5 ($dH = C_p dT$). The resulting $\Delta_f H^{356.5}$ value was 3.0 kJ mol$^{-1}$. The approximate value we previously reported [9] is incorrect inasmuch as the heat of melting of the racemate was mistaken. The entropy of formation of the racemate was obtained in the same way, using the equation for entropy fully analogous to Eq. (6). The resulting value (Table 3) is close to the value for the ideal solid solution of the enantiomers, merely the spatial entropy of mixing of the enantiomers, *i.e.* $\Delta_f S = R\ln 2 = 5.76$ J K$^{-1}$ mol$^{-1}$. This suggests that the racemate is a solid solution with a slight deviation from ideality rather than truly a racemic compound. The value of *Gibbs* free enthalpy of formation of the racemate ($\Delta_f G = \Delta_f H - T\Delta_f S$) is 0.72 kJ mol$^{-1}$. From the $\Delta_f S$ value the total entropy of the crystal was obtained adding the known entropy of the crystalline enantiomer (see Tables 1 and 3).

The heat capacity of the crystalline racemate could not be obtained with the DSC technique on account of the small amount of racemate available, which precluded to obtain the kinetic energy for the crystal from the heat capacity by *Debye*'s theory, as to the crystalline enantiomer. Hence a single $E_{kin}$ value was obtained from the only value for the entropy of the crystal by means of the *Debye* function for entropy ($S = Nf_S(T_D/T)$, $N = 51$) [12], solving the $T_D$ value by the tabulated function and then applying it to the *Debye* energy function. As it was assumed that the racemate was a solid solution such entropy value was beforehand reduced by quantity $R\ln 2$, only leaving the thermal entropy for a proper use of the *Debye* functions (the fact that the racemate consists of two components is of no concern). The $E_{kin}$ value as well as the $\nu_{mean}$ value are given in Table 3. The reliability of the $E_{kin}$ value is contingent on the suitability of *Debye*'s theory for the crystal, which could not be tested because heat-capacity data were lacking as mentioned.

The total internal energy of the racemic crystal (that pertinents to changes of state for the crystal) can be expressed in terms of available experimental quantities and the known internal energy of the gaseous phase ($E_{kin}$) by Eq. (7). The $U$ value is given in Table 3. The potential energy of cohesion of the crystal follows subtracting the value of kinetic energy ($U = E_{kin} + E_{pot}$), resulting in $-44.2$ kJ mol$^{-1}$.

$$U^{356.5}(\text{rac}) = \Delta_f U^{356.5}(\text{rac}) - \Delta_s U^{351.8}(\text{en}) + \Delta_{351.8}^{356.5} U(\text{en}) + E_{kin}^{351.8}(\text{g}) \quad (7)$$

The decrease in cohesion on formation of the racemic crystal from the crystalline enantiomers amounts to 3.5 kJ mol$^{-1}$, as it follows from the potential energies of cohesion of the racemic crystal and the crystalline enantiomer. That quantity is more or less the same as the internal energy of transformation of 3.0 kJ mol$^{-1}$. Thus the potential energy accounts for the energy of this transformation in

**Table 3.** Thermodynamic quantities for the racemic crystal of racemate **1** at 83.3°C

| $\Delta_f U^a$ | | $\Delta_f S^a$ | | $S^c$ |
|---|---|---|---|---|
| 3.0 kJ mol$^{-1b}$ | | 6.4 J K$^{-1}$ mol$^{-1b}$ | | 325.1 J K$^{-1}$ mol$^{-1}$ |
| $E_{kin}$ | $\nu_{mean}^e$ | | $U$ | $E_{pot}$ |
| 773.5 kJ mol$^{-1d}$ | 758.4 cm$^{-1}$ | | 729.3 kJ mol$^{-1}$ | $-44.2$ kJ mol$^{-1}$ |

[a] Formation of the crystal from the crystalline enantiomers; [b] experimental value; [c] $S = S(\text{en, cr}) + \Delta_f S$; [d] value derived from the $S$ value by means of the *Debye* functions for entropy and energy, $E^0 = 693.9$ kJ mol$^{-1}$; [e] for all vibrational motions

the solid state, according to the way that the vibrational energies for the crystals are very similar and offset (Tables 1 and 3). This outcome is in striking contrast with that which happens in the sublimation of the enantiomer as discussed above. When the racemic crystal was treated as a racemic compound rather than a solid solution a cohesion energy of $-39.2\,\text{kJ}\,\text{mol}^{-1}$ resulted with a decrease in cohesion on formation of the crystal of $8.5\,\text{kJ}\,\text{mol}^{-1}$, which does not coincide at all with the actual energy of transformation. For this reason the former value of cohesion energy was preferred.

### The Entropy, Kinetic Energy, and Overall Potential Energy of the Liquid Racemate

In order to find the kinetic energy for the racemate in the liquid state the harmonic-oscillator model (above referred to) was first tried for suitability to the experimental heat capacity of the liquid (given in Fig. 5) withdrawing the translational and rotational heat capacities. The translational contribution of the molecule in the liquid to heat capacity is the same as in the gas, *i.e.* $3R/2$, in the same manner that the translational energy in the liquid is the same as in the gas in spite of the existence of cohesion forces ($3RT/2$) [16]. For the rotational contribution free rotation of the molecule in the liquid was assumed, thus subtracting $3R/2$. Applying the model the vibrational frequency for the harmonic oscillator representative of the vibrations in the molecule was constant within $\pm0.95\%$ in a temperature interval of 48 degrees. This accommodation of the model to the molecule in the liquid was not weighed sufficiently for the required accurate deduction of the vibrational energy. It was however an improvement over the gas molecule as commented above.

Since the *Debye* function for entropy had been suitable to the vibrational entropy of the gas, it was used for the vibrational entropy of the liquid. However, the vibrational entropy was treated together with the rotational entropy as the method itself turned out to provide this joint entropy in the case of the liquid. So the added-up vibrational and rotational entropy of the liquid racemate can be expressed as a function of temperature by Eq. (8), in reference to the yet unknown $S_{\text{vib}+\text{rot}}$ value for the liquid racemate at its temperature of solidification to the conglomerate. The equation was deduced making use of

the heat capacity of the liquid (Fig. 5, $\mathrm{d}S_{\text{vib}+\text{rot}} = C_{\text{vib}+\text{rot}}\mathrm{d}T/T$, $C_{\text{vib}+\text{rot}} = C_v - 3R/2$).

$$S^T_{\text{vib}+\text{rot}} = -5.6\times10^{-3}T^2 + 10.18T - 1566.4\ln T + S^{363.9}_{\text{vib}+\text{rot}} \quad (8)$$

Then the $S^{363.9}_{\text{vib}+\text{rot}}$ value was scanned for a coincidence of Eq. (8) with the *Debye* entropy function for an interval of 48 degrees (366.2–414.2 K), using the *Debye* function jointly to the vibrational and rotational degrees of freedom (*i.e.* with $N-1$ (50), $S = (N-1)f_{\mathbf{S}}(T_D/T)$). A maximal and nearly perfect coincidence of the two functions was reached with an $S^{363.9}_{\text{vib}+\text{rot}}$ value of $345.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, the $T_D$ value being thus constant within $\pm0.014\%$ for the temperature interval ($T_D = 1409.8 \pm 0.2$ K). The increased fitness of the *Debye* entropy function for the liquid with respect to the gas was not surprising in view of the better suitability of the harmonic-oscillator model to the liquid. The involvement of the rotational motions in the *Debye* vibrational function suggested that molecular rotation in the liquid was not free, but this represented an issue beyond the theoretical level in the work.

From the $T_D$ value the *Debye* heat capacity was derived ($C_{\text{vib}+\text{rot}} = -3.352\times10^{-3}T^2 + 4.446T - 522.9$) and equalled the actual heat capacity (Fig. 5, $C_{\text{vib}+\text{rot}} = C_v - 3R/2$) at a temperature close to the mean for the relevant temperature interval: the two lines slightly oblique to each other intersected at 388.6 K. The *Debye* energy for this point of correspondence between theory and observation was taken (Table 4, $E_{\text{vib}+\text{rot}}$). The $E^0$ value is an 86% of the

**Table 4.** Thermodynamic quantities for racemate **1** in the liquid state

| $\Delta_m U$ (90.7°C)[a] | $\Delta_m S$ (90.7°C)[a] | $S$ (90.7°C)[c] |
|---|---|---|
| $33.2\,\text{kJ}\,\text{mol}^{-1}$[b] | $91.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$[b] | $422.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ |
| $S_{\text{vib}+\text{rot}}$ (90.7°C) | $E_{\text{vib}+\text{rot}}$ (115.4°C) | $\nu^{\text{f}}_{\text{mean}}$ |
| $345.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$[d] | $763.4\,\text{Kj}\,\text{mol}^{-1}$[e] | $735.2\,\text{cm}^{-1}$ |
| $E_{\text{kin}}$ (115.4°C) | $U$ (115.4°C) | $E_{\text{pot}}$ (115.4°C) |
| $768.2\,\text{kJ}\,\text{mol}^{-1}$ | $781.2\,\text{kJ}\,\text{mol}^{-1}$ | $13.0\,\text{kJ}\,\text{mol}^{-1}$ |

[a] Relative to the solid racemate as a conglomerate; [b] Ref. [9]; [c] $S = S(\text{en},\ \text{cr}) + \Delta_m S$; [d] deduced from the dependence of the joint vibrational and rotational entropy on temperature by comparison with the *Debye* function for entropy, $S_{\text{tr}} = 77.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$; [e] deduced from the joint vibrational and rotational entropy using the *Debye* functions for entropy and energy, $E^0 = 659.5\,\text{kJ}\,\text{mol}^{-1}$ (for the vibrational and rotational motions, see text); [f] for the vibrational and rotational degrees of freedom (see text)

total kinetic energy of the liquid. The corresponding $\nu_{\text{mean}}$ value is summarized in Table 4.

Now the internal energy of the liquid racemate at the correspondence temperature is given by Eq. (9). The equation addresses to the internal energy of the liquid racemate at its temperature of solidification to the conglomerate ($U^{363.9}$), and the $\Delta_{363.9}^{388.6}U$ term which connects this temperature with the correspondence temperature was calculated from the experimental heat capacity of the liquid (Fig. 5). The detailed expression for $U^{363.9}$ is analogous to the expression for the internal energy of the racemate as a solid, which was given in Eq. (7). For the new $\Delta_m U(\text{congl})$ term the literature value was used (gathered in Table 4) [9]. The final value is given in Table 4 ($U$). The potential energy of the liquid follows from subtracting the value of kinetic energy ($U = E_{\text{kin}} + E_{\text{pot}}$) resulting in $13.0\,\text{kJ mol}^{-1}$. Desiring to obtain the average for the temperature interval, $E_{\text{kin}}$ values for temperatures other than the correspondence temperature were worked out from the *Debye* temperature (thus overusing *Debye*'s theory), eventually resulting in the same value of $13.0 \pm 0.1\,\text{kJ mol}^{-1}$.

$$U^{388.6} = U^{363.9} + \Delta_{363.9}^{388.6}U$$
$$= \Delta_m U(\text{congl}) - \Delta_s U^{351.8}(\text{en}) + \Delta_{351.8}^{363.9}U(\text{en})$$
$$+ E_{\text{kin}}^{351.8}(\text{g}) + \Delta_{363.9}^{388.6}U \qquad (9)$$

The positive value for the potential energy in the liquefaction of the racemate indicates that the increase in electronic potential energy resulting from the strong dielectric character of the liquid is larger than the cohesion of the liquid ($E_{\text{pot}} = E_{\text{pot}}(\text{coh}) + \Delta E_{\text{pot}}(\text{el})$). A measure of the molecular electronic energy is the potential energy of dissociation of the gas molecule into the constituent atoms, which amounts to $22142.7\,\text{kJ mol}^{-1}$ (the method of calculation is given in Experimental). So, supposing a cohesion energy of a matter of $-20\,\text{kJ mol}^{-1}$ for the liquid, the variation of electronic energy by *ca.* $33\,\text{kJ mol}^{-1}$ on the liquefaction is as little as 0.15%. The two kinds of potential energy cannot be separately reached by the methods herein described. For the cohesion energy of the liquid it may be necessary to obtain the configuration integral for the liquid [6b] by higher statistical mechanics (Eq. (10)).

$$E_{\text{pot}}(\text{coh}) = RT^2 \left( \frac{\partial \ln Q_{\text{conf}}}{\partial T} \right)_v \qquad (10)$$

## Conclusion

A method was devised to find out the potential energy of cohesion of the crystal of enantiomer **1** from the heat of sublimation, and using the heat capacities of the gaseous phase and the crystal for finding the values of kinetic energies for the gas and the crystal. The method does not require force potentials or the crystal structure. The vibrational energy of the gas was derived from the dependence of the vibrational entropy on temperature (from the heat capacity) and utilizing the *Debye* functions for entropy and energy. The kinetic energy for the crystal was obtained by *Debye*'s theory of heat capacities. The cohesion energy was $-47.7 \pm 0.1\,\text{kJ mol}^{-1}$, as determined for the interval of 0–90°C. For complete reliance on experimental data the procedure lacked the actual heat capacity of the vapour of the crystal, which was approached by an estimation method. The cohesion energy of the racemic crystal of racemate **1** was found to be $-44.2\,\text{kJ mol}^{-1}$. The change in potential energy from the enantiomer crystal to the racemic crystal accounted for the heat of formation of the racemic crystal of $3.0\,\text{kJ mol}^{-1}$ in the solid state.

## Experimental

A racemic mixture of the crystalline enantiomers of **1** as a conglomerate and the racemate of **1** in the form of a crystalline solid were available [5]. The apparatus for sublimation was equipped with a sublimation chamber, which contained an effusion cell with the effusion orifice ($0.347 \pm 0.002\,\text{mm}^2$) on a tenuous metallic membrane (actual thickness $0.021 \pm 0.004\,\text{mm}$, correcting *Clausing* coefficient [17] $0.980 \pm 0.004$). The chamber was kept evacuated by a high-vacuum system ($1 \times 10^{-4}\,\text{Pa}$), and its temperature was controlled by a thermoregulated water bath ($\pm 0.1°\text{C}$). DSC: Perkin-Elmer Pyris 1 calorimeter, samples contained in sealed aluminum pans, heat capacities determined with the scan technique [8]. Weighing: Mettler AT21 microbalance. Errors stated in the text refer to the average deviation.

### *Heat of Sublimation of an Enantiomer of 1*

The conglomerate (*ca.* 120 mg) contained in the effusion cell of the sublimation apparatus was subjected to controlled sublimation at fixed increased temperatures (70.8–86.4°C). Before and after each sublimation period (320–498 min) the effusion cell was weighed to know the amount of conglomerate sublimed (0.869–7.42 mg). With the temperature and rate of sublimation for each stage together with the area of the effusion aperture the vapour-pressure value for each temperature was obtained by the formula for effusion in the kinetic theory of gases [6a]. The vapour-pressure values for a single enantiomer are half the experimental values as the conglomerate is a juxtaposition of the two independent solid enantiomers. The values are

presented in Fig. 1. With the $p_v - T$ pairs and *Clausius-Clapeyron* equation [11] the values of heat of sublimation for the successive temperature intervals were obtained and were adequately constant. The average, referred to the mean temperature of the full temperature interval, is shown in Fig. 1.

*Heat of Melting of Racemate 1*
The racemate (0.805 mg) was heated in the calorimeter for melting and at a constant heating rate (2.5°C min$^{-1}$). The trace of melting on the temperature scale (corresponding with the time scale) is shown in Fig. 4; the area under the peak (power × time) corresponds to the heat of melting specific of the sample.
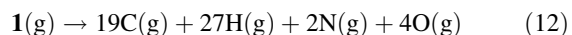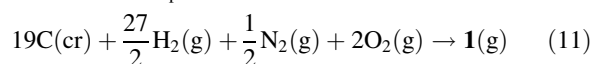
*Heat Capacities of one Enantiomer of 1 in the Solid State and Racemate 1 in the Liquid State*
The conglomerate (2.328 mg) was heated in the calorimeter below the onset of melting to obtain the heat capacity of an enantiomer of **1** as a function of the temperature (heating rate 10°C min$^{-1}$). A sample of synthetic sapphire as a standard was heated under the same conditions to check the calorimeter deviation. The process was repeated for another sample of the conglomerate, the heat-capacity values being concordant within ±2%. The average values are represented in Fig. 2.

The heat capacity of the racemate in the liquid state, formed by melting the conglomerate in the calorimeter, was obtained by the preceding procedure. The data is presented in Fig. 5.

*Potential Energy of Atomic Dissociation of Molecule 1*
The standard enthalpy of formation of ester **1** (Eq. (11), 298 K, $1.01 \times 10^5$ Pa) was estimated by *Benson*'s group-contribution method [18a]: $\Delta_f H° = -661.7$ kJ mol$^{-1}$. From this value the enthalpy of atomic dissociation (Eq. (2)) was obtained by *Hess*'s law, using the enthalpy of sublimation of graphite (the reference state for carbon) to atomic carbon [19] and the enthalpies of dissociation of hydrogen, nitrogen, and oxygen [18b]: $\Delta_d H° = 21635.3$ kJ mol$^{-1}$. The corresponding value of internal energy was obtained subtracting quantity $\Delta_d pV$, equal to $50RT$ (298.2 K): $\Delta_d U° = 21511.3$ kJ mol$^{-1}$. From this value the potential energy of atomic dissociation was obtained by Eq. (13). The $\Delta_d E_{tr}$ term amounted to $150RT/2$ (counting $3RT/2$ for each species), and the $\Delta_d E_{rot}$ term equalled $-3RT/2$ (for ester **1**). The value of vibrational energy of the ester molecule (corresponding to $-\Delta_d E_{vib}$ and including the zero-point energy) was obtained in the manner described in text: $E_{vib} = 813.6$ kJ mol$^{-1}$ (298.2 K). The $\Delta_d E_{pot}$ value was 22142.7 kJ mol$^{-1}$.

$$19C(cr) + \frac{27}{2}H_2(g) + \frac{1}{2}N_2(g) + 2O_2(g) \rightarrow \mathbf{1}(g) \qquad (11)$$

$$\mathbf{1}(g) \rightarrow 19C(g) + 27H(g) + 2N(g) + 4O(g) \qquad (12)$$

$$\Delta_d E_{pot} = \Delta_d U - \Delta_d E_{tr} - \Delta_d E_{rot} - \Delta_d E_{vib} \qquad (13)$$

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