Thermochimica Acta, 99 (1986) 27–32
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MEAN MOLAR HEAT CAPACITIES OF SUGARS. HEAT CAPACITY CONTRIBUTIONS OF THE PYRANOSE RING WITH DIFFERENT CONFORMATIONS

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(Received 9 August 1985)

ABSTRACT

This paper presents the results of calorimetric measurements of mean molar heat capacity for the following sugars: methyl-2,3,4-tri-*O*-benzyl-*β*-D-galactopyranoside; 6-*O*-acetyl-2,3,4-tri-deoxy-*α*-DL-glycero-hex-2-enopyranose; methyl-2,3-anhydro-4-deoxy-*α*-DL-ribo-hexopyranoside; 6-*c*-(2-furyl)-1,2:3,4-di-*O*-isopropylidene-*α*-D-glycero-D-galacto-hexopyranose; 1,2:3,4-di-*O*-isopropylidene-6-*O*-*p*-toluene-sulfonylo-*α*-D-galactopyranose. Heat capacity contributions of the pyranose ring in these sugars confirm the existence of different energy levels found previously from semi-empirical calculations for different conformations of the pyranose ring.

INTRODUCTION

Conformational calculations performed for several six-membered saccharide rings of sugars, whose crystalline structures have been determined by X-ray diffraction methods, have shown that these rings adopt mainly deformed or even hybrid conformations. As shown previously [1], a ring of tetrahydropyrane may theoretically adopt six different basic conformations derived from cyclohexane models.

Some earlier X-ray investigations on unsaturated sugar derivatives allowed us to establish the conformation of dihydropyrane rings as a deformed half-chair (H) [2] and as a hybrid half-chair + sofa (H + E) [3]. Similarly, mixed (E + H) or deformed (H) conformations were found for 2,3-anhydropyranose rings [4,5].

On the other hand, the saturated pyranose rings in diacetonogalactose derivatives may be characterised by the hybrid conformations twist + boat (T + B) [6], screw + twist (S + T) [7] or a deformed twist (T) [8].

The occurrence of deformed or mixed conformations in pyranose rings of crystalline sugars may be partly elucidated by the results of intramolecular strain energy (E_s) calculations made for particular models of cyclohexane and tetrahydropyrane in various conformations [8]. The most energetically favourable sequence is found to be C, T, B, H, E, the chair (C) being the most favoured conformation.

Nevertheless, the small E_s differences between H and E conformations (~ 1 kcal mol^{-1}) as well as between B and T (~ 2 kcal mol^{-1}) indicate that the interconformational energy barriers are probably low. Thus, various intermolecular interactions, such as of Van der Waals, dipole–dipole or hydrogen-bonding type, may introduce energy increments sufficient to cause conformational deformations or even hybridisations of pyranose rings.

Thermochemical investigations have been undertaken in order to obtain experimental support for the conformationally favoured sequence in pyranose rings found previously from semi-empirical calculations. In this paper we present mean molar heat capacities ($\bar{C}_p$) of some sugar crystals with both structure and conformation established. The results, in the form of contributions of the isolated pyranose ring to the heat capacity of particular sugars, are compared with the strain energy values reported earlier on the basis of semi-empirical calculations.

MATERIALS

All substances were synthesized at the Department of Natural Products, Institute of Organic Chemistry, Polish Academy of Sciences. The sugars were the same as used previously for the structural analysis. Table 1 gives the full chemical names of the substances investigated, their numbers (for the purpose of this paper) and references for the determination of structures.

EXPERIMENTAL

Several dozen milligrams of each substance, which we had at our disposal, suggested the use of a temperature-controlled scanning calorimeter for heat

TABLE 1

List of substances investigated

No.	Chemical name	Ref.
1	Methyl-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside	7
2	6-*O*-Acetyl-2,3,4-trideoxy-α-DL-glycero-hex-2-enopyranose	3
3	Methyl-2,3-anhydro-4-deoxy-α-DL-ribo-hexopyranoside	5
4	6-*c*-(2-furyl)-1,2:3,4-di-*O*-isopropylidene-α-D-glycero-D-galacto-hexopyranose	6
5	1,2:3,4-Di-*O*-isopropylidene-6-*O*-*p*-toluene-sulfonylo-α-D-galactopyranose	8

capacity determination. Unfortunately, the reproducibility of results was not satisfactory and we therefore decided to use the drop method with an isothermal calorimeter instead. The calorimeter (UNIPAN 600 [9]) was set at 323.15 K. The samples of sugars dropped into the calorimeter were previously embedded in aluminium pans and thermostated at room temperature. The aluminium pans were selected so as to have the same mass. The calorimeter was calibrated with benzoic acid samples embedded in similar aluminium pans to the substances under study. Values of the heat capacity of benzoic acid as function of temperature have been taken from Moriya et al. [10]. The reproducibility of results was this time about 1%, which is satisfactory for the purpose of the present study.

RESULTS AND DISCUSSION

The values of mean molar heat capacities, $\bar{C}_p$, of the substances under study are given in Table 2. The values were obtained by division of the molar enthalpy change of the substance, measured in the calorimeter, by the temperature difference between the calorimetric cell and the temperature of the substance prior to dropping into the calorimeter. The mean temperature value was 308.7 K.

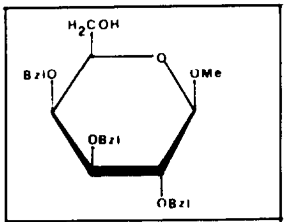
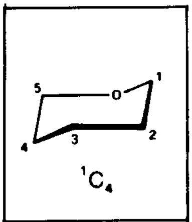
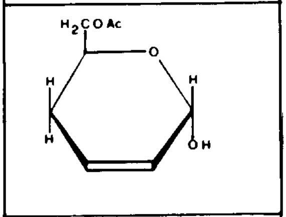
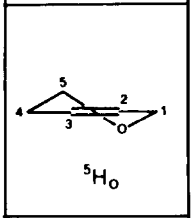
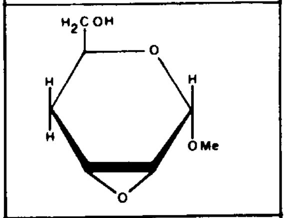
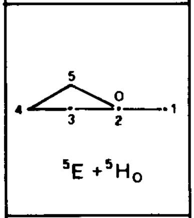
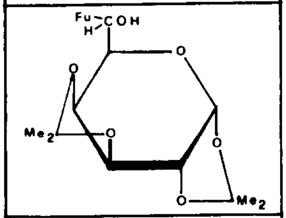
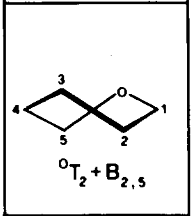
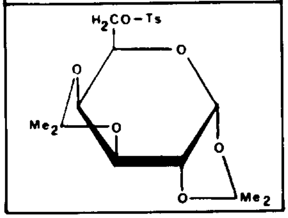
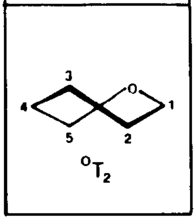
Table 2 also presents heat capacity contributions, C_p^*, of the isolated pyranose ring in different conformations. Conformations of the pyranose ring in different sugars are presented on the basis of previous investigations (see in Table 1). Heat capacity contributions, C_p^*, have been determined according to the following equation

$$C_p^* = \bar{C}_p - (\Sigma a + \Sigma bT + \Sigma cT^2 + \Sigma dT^3)$$

where $T = 308.7$ K. The summations are made over all atomic groups of a sugar except the ring itself. The values of coefficients a, b, c and d for the particular groups have been taken from Rihani and Doraiswamy [11]. In the case of sugar 5, for which there is a lack of data on coefficient values of the sulfonyl group, calculations were divided into two groups of –O– and one –S–, which could obviously cause errors. However, the main limitation of the method is a lack of data on all coefficient values in the solid state. The values given by Rihani and Doraiswamy [11] are concerned with the gas phase. Therefore, the absolute values of heat capacity contributions, C_p^*, given in Table 2 include an error. It is assumed, however, that this error has a similar value for all sugars under study in the crystalline state. If this assumption is correct, it would not influence the shape of a relationship between the heat capacity contribution of the ring, C_p^*, and its conformation. Figure 1 gives a graphic presentation of a relationship between the heat capacity contribution of the ring, C_p^*, and a puckering parameter, q_2 [12] (curve 1). For comparison, Fig. 1 presents the results of intra-molecular

TABLE 2

Mean molar heat capacities ($\bar{C}_p$) of sugars and heat capacity contributions (C_p^*) of the isolated pyranose ring in different conformations (cal K^{-1} mol^{-1}; 1 cal = 4.184 J)

No.	Formula	$\bar{C}_p$	Conformation	C_p^*
1		167.8		70.4
2		54.1		26.7
3		51.7		26.8
4		98.6		30.3
5		124.3		31.0

strain energy (E_s) calculations made for particular models of both cyclohexane (curve 2) and tetrahydropyrane (curve 3) in various conformations [8]. It can be seen from Fig. 1 that both sets of results are consistent: the most stable chair conformation, $^{1}C_{4}$, has the lowest strain energy value and the

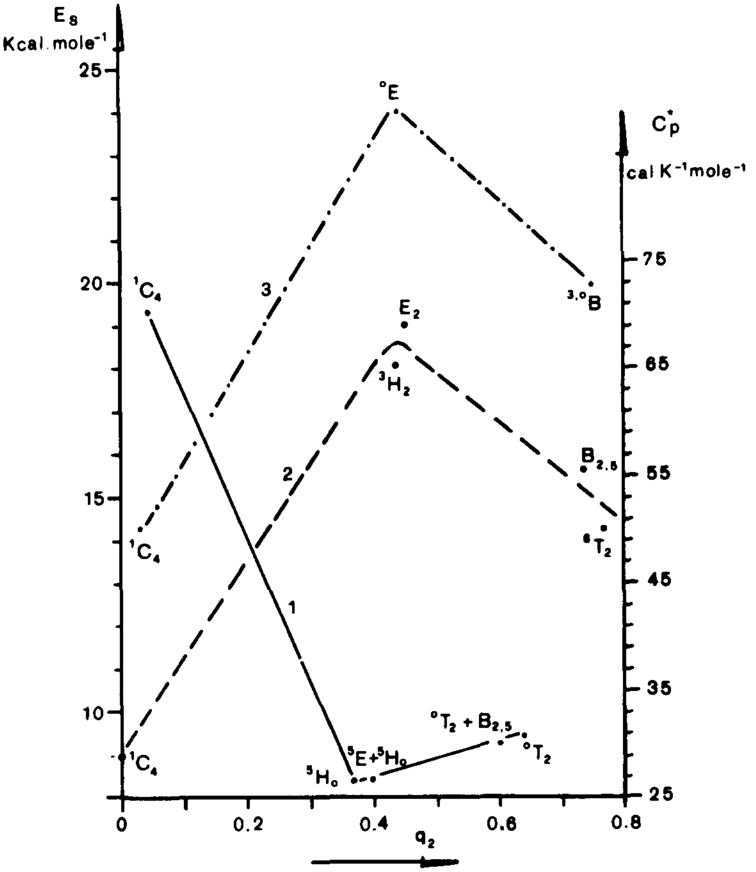


Fig. 1. Graphical presentation of relationship between the puckering parameter, q_2 [12], and heat capacity contributions, C_p^*, of the isolated pyranose ring in different conformations (curve 1, present study), strain energies, E_s, in cyclohexane conformations (curve 2), and tetrahydropyrane in various conformations (curve 3) [8].

largest heat capacity contribution and, oppositely, conformations with the highest strain energy values have the lowest heat capacity contributions; conformations with intermediate values on the strain energy scale also have intermediate values on the heat capacity contribution scale.

CONCLUSIONS

Calorimetric measurements of the mean molar heat capacity of sugars with different conformations of the pyranose ring have confirmed the existence of different energy levels of these rings found previously from semi-empirical calculations.

ACKNOWLEDGEMENTS

The authors are grateful to Drs. A. Banaszek and S. Jarosz for providing the sugar samples. Financial support from programs 03.10.1.7.2 and MR-I.12 is acknowledged.

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