Crystal Structure and Lattice Energy of i-Erythritol. II. Lattice and Hydrogen Bond Energies for i-Erythritol

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There have been already reported many studies on the lattice energy of crystalline substances, but most of them are dealing with crystals which are composed of ions. Viewed from the standpoint of the fact that the most powerful force capable of holding ions together is the electrostatic one, this situation seems to be very natural. On the other hand, there have been reported few studies on the lattice energy of crystals composed of more or less complicated molecules. Among these studies, a detailed calculation of the lattice energy has been already carried out for pentaerythritol[1], which gave a satisfactory result in comparison with the observed heat of sublimation. Of *i*-erythritol ($CH_2OH \cdot C^*HOH \cdot C^*HOH \cdot CH_2OH$), which is also a member of tetrahydric alcohols, various physical properties have been already reported and related to those of pentaerythritol[2,3]. Now that the crystal structure of *i*-erythritol has recently been determined by X-ray analysis[4], it was attempted to calculate the lattice energy and compare it with the observed heat of sublimation[2].

Calculation of the Lattice Energy.—The crystal of *i*-erythritol was found to belong to the tetragonal system with $a=12.81$ Å, $c=6.81$ Å and the space group $C_{4h}^6-I4_1/a$[5]. There are eight centro-symmetrical molecules in the unit cell. The structure projected on the (001) plane is shown in Fig. 1, in which the Roman numerals are given for the sake of convenience in the following calculations. The interesting feature of this structure is that two different types of hydrogen bonds, as shown in Fig. 1, link all the molecules firmly in a three-dimensional way*. One of these two types of the hydrogen bond, with a distance 2.77 Å, connects two CHOH groups of adjoining molecules while the other, with a distance 2.66 Å, connects two CH_2OH groups of adjoining molecules. The coordinates of atoms determined by X-ray analysis[4] were used in the following calculations.

The calculations of the lattice energy was carried out in the same way as in the case of pentaerythritol. This energy was supposed to be composed mainly of the van der Waals and electrostatic energies. Slater-Kirkwood's formula was applied to get the former energy, splitting the molecule into three kinds of force center; they are the CH, the CH_2 and the OH group. The polarizability α of each atomic group used in Slater-Kirkwood's formula is shown in Table I. They were

TABLE I
MOLECULAR REFRACTION AND POLARIZABILITY

Group	M_∞	$\alpha \times 10^{24}$ cc.
OH	2.48	0.981
CH	3.41	1.350
CH_2	4.32	1.709

esimated from the molecular refractions M_∞ at infinite wave length[1]. As for the molecules the centers of which lie within about 10 Å from the molecule 0 at the origin, the minus sixth power of distance between force centers was computed one by one and summed up. As for the molecules lying apart beyond 10 Å from the molecule 0, the summation was replaced by integration, assuming the uniform distribution of the force centers. The result of calculation is given in Table II, showing that the contribution of the integral part is found to be very small. The obtained value 20.42 kcal./mol. is somewhat greater than that of pentaerythritol (17.62 kcal./mol.) and this is possibly related to the

1) I. Nitta, S. Seki and K. Suzuki, This Bulletin, **24**, 63 (1951).
2) I. Nitta, S. Seki, M. Momotani, K. Suzuki and S. Nakagawa, *Proc. Japan Acad.*, **26**, (10) 11 (1950).
3) S. Seki and K. Suzuki, This Bulletin, **26**, 63 (1953).
4) A. Shimada, This Bulletin, **32**, 325 (1959).
5) For a detailed explanation of the crystallographic data, see "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England (1952).

* A preliminary infrared study on *i*-erythritol crystal shows that there is no marked band at the frequency of the unbonded OH stretching mode (3700 cm^{-1}), but at 3210cm^{-1} is observed a broad band which can be ascribed to the stretching modes of the hydrogen-bonded OH. Further study is now in progress.

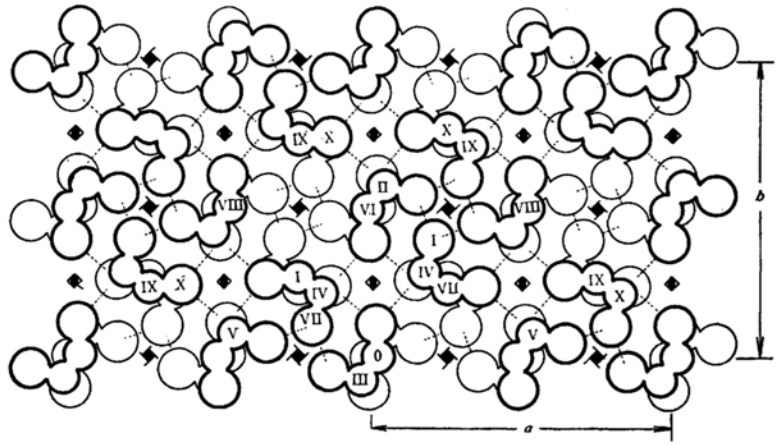

Fig. 1. View of molecular arrangement projected on (001) plane. The upper half of the centro-symmetrical molecule is shown by the broad outline, the large circle standing for OH group and the small one for CH and CH_2 groups. Dashed line indicates the hydrogen bond between the molecules.

TABLE II

VAN DER WAALS ATTRACTION ENERGY BETWEEN DIFFERENT ATOMIC GROUPS

Sort of molecule	van der Waals energy (cal./mol.)						
	CH∼CH	CH_2∼CH	CH_2∼CH_2	OH∼CH	OH∼CH_2	OH∼OH	Total
I	409.0	732.2	406.0	2393.7	3090.4	6168.9	13200.2
II	33.9	113.5	153.5	84.4	133.5	114.2	633.0
III	41.5	182.5	188.5	205.5	534.3	219.0	1371.3
IV	62.7	427.0	821.5	514.9	990.6	356.9	3173.6
V	35.5	102.4	59.4	273.7	264.2	376.4	1011.6
VI	7.6	27.5	22.6	23.8	45.6	36.7	163.8
VII	6.9	16.3	10.3	31.3	37.1	38.1	140.0
VIII	10.1	25.5	22.2	36.5	58.1	54.3	206.7
IX	1.4	14.3	11.1	25.2	35.5	27.7	115.2
Part of sum	608.6	1641.2	1695.1	3589.0	5189.3	7292.2	20015.4
Part of integral	38.1	48.1	59.6	64.4	81.3	112.0	403.5
			Total van der Waals energy:				20418.9

TABLE III

ELECTROSTATIC ENERGY BETWEEN DIFFERENT MOLECULES, USING DIFFERENT NET CHARGES

Sort of molecule	Distance from molecule 0 (Å)	Number of molecules	Electrostatic energy (kcal./mol.)		
			A	B	C
I	4.74	4	−16.687	−19.199	−21.711
II	6.41	2	− 1.260	− 1.809	− 2.344
III	6.81	2	0.166	0.192	0.226
IV	6.83	4	− 3.174	− 3.655	− 4.033
V	7.25	4	1.654	1.781	2.045
VI	9.35	4	− 0.412	− 0.769	− 1.065
VII	9.64	4	0.165	0.231	0.403
VIII	9.68	8	7.894	8.803	9.966
IX	9.94	8	− 0.522	− 0.531	− 0.545
X	11.05	8	0.364	0.435	0.508
		Total:	−11.812	−14.521	−16.550

difference of the packing in the two compounds (molecular volume: *i*-erythritol 84.2 cc./mol. and pentaerythritol 97.5 cc./mol. at room temperature).

In the calculation of electrostatic energy for this crystal, the point charge model was adopted, putting a net charge ε on the nuclear positions of the carbon atoms in CH and CH_2 groups, ε' on the hydrogen atoms in OH groups and $-(\varepsilon+\varepsilon')$ on the oxygen atoms. The positions of hydrogen atoms in OH groups were assumed to lie approximately on the line connecting two oxygen atoms at a distance 0.96 Å from the oxygen atom. A value 0.551×10^{-10} e. s. u. was assigned to the charge ε, and values 1.726 (Case A), 1.870 (Case B) and 2.015 (Case C) $\times10^{-10}$ e. s. u. were given for the charge ε', as in the case of pentaerythritol. These three cases correspond respectively to the three degrees of ionic characters 36, 39 and 42% of the OH bonds. The result of calculation is shown in Table III. In this calculation, the summation is taken over a sphere with its origin at the center of the molecule 0 and a radius of about 11 Å. The contribution of the outer part is neglected, in consideration of a possibility that it will decrease at least with the third power of distance. In fact, it can be shown by the Taylor's theorem that the electrostatic energy between each pair of molecules with no resultant permanent dipole moment will decrease at least with the fifth power of distance, and the number of pairs of molecules will increase with the second power of distance. Summing up the van der Waals and the electrostatic energies, the following three values are obtained, 32.23, 34.94 and 36.97 kcal./mol., corresponding respectively to the case A, B and C. The first value is in good agreement with the experimental value: 32.3± 0.2 kcal./mol[2]. It will be seen that for *i*-erythritol a good agreement is obtained for the case A, whereas the case B or C stands good for the case of pentaerythritol.

Estimation of the Hydrogen Bond Energy.—A part of the lattice energy may be attributed to the four hydrogen bonds, which are formed between a molecule of *i*-erythritol and its nearest neighbors. However, it is not easy to define and calculate that part of energy in this case, because in this complicated structure are appreciable the contributions of distant neighbors especially to the electrostatic energy and, furthermore, there is a rather even distribution of the hydrogen bonds, in contrast to the case of pentaerythritol where the hydrogen bonds connect the molecules to construct a typical layer lattice. Hence, in this case, the hydrogen bond energy is tentatively defined as the interaction energy between two OH groups directly linked together by the hydrogen bond. The van der Waals energies for the hydrogen bonds between two CHOH and two CH_2OH groups come out to be 1.35 and 1.65 kcal./mol. respectively. The corresponding electrostatic energies are computed, for the case A, to be 2.90 and 4.73 kcal./mol. Summing up these values, the hydrogen bond energies are to be 4.3 and 6.4 kcal./mol. The average value of these energies (5.4 kcal./mol.) seems to be somewhat larger than that of pentaerythritol (4.68 kcal./mol. for the case B or 5.16 kcal./mol. for the case C), although the definition of the hydrogen bond is somewhat different between these two compounds[1]. However, it is noteworthy to point out that a reasonable correlation of hydrogen bond energies (4.3 and 6.4 kcal./mol.) with hydrogen bond distances (2.77 and 2.66 Å) has been found in this calculation on the ground of rather simple model, while the model suggested by Lippincott[6] gives the values of hydrogen bond energies, 4.2 and 6.7 kcal./mol., corresponding to these two hydrogen bond distances.

Suzuki et al.[7] suggested another way for estimating hydrogen bond energy. This is to compare the heat of sublimation of the hydrogen-bonded substance with that of a reference substance, which is composed of isoelectronic molecules having similar configuration but no ability of hydrogen-bonding. This method was also applied to the cases of *i*-erythritol and pentaerythritol. The suitable reference substance chosen were 3,4-dimethylhexane and 3,3-diethylpentane each for these two compounds. The heat of sublimation of the reference substance was obtained by adding the heat of fusion[8] and that of vaporization. Since the heat of fusion of 3,4-dimethylhexane is not yet known, it was estimated by adding the difference between the heat of fusion of 2,3-dimethylbutane (0.194 kcal./mol.) and that of

6) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1099 (1955).

7) K. Suzuki, S. Ōnishi, T. Koide and S. Seki, This Bulletin, **29**, 127 (1956).

8) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimental, "Selected Values of Physical and Thermodynamical Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh, U. S. A. (1953).

n-butane (1.114 kcal./mol.) to that of *n*-hexane (3.114 kcal./mol.). The heat of vaporization was calculated from the temperature variation of vapor pressure[8] near the melting point. Table IV gives the latent heats associated with the phase

TABLE IV
HEAT OF PHASE CHANGE FOR THE REFERENCE SUBSTANCE (kcal./mol.)

	Reference substance	
	3,4-Dimethyl-hexane	3,3-Diethyl-pentane
Heat of fusion	2.19	2.35
Heat of vaporization	9.53	10.50
Heat of sublimation	11.7	12.9

changes for the reference substances. From these values, the hydrogen bond energies of 5.2 and 4.6 kcal./mol. have been estimated for *i*-erythritol and pentaerythritol respctively. These values are found to be in good agreement with the average values mentioned in the preceding paragraph.

At any rate, it seems likely that the average hydrogen bond energy for *i*-erythritol is larger than that for pentaerythritol, since the two methods of calculation gave parallel results. The values obtained above can be compared with those obtained on other alcohols[9]. Although in the calculation of the lattice energy mentioned above certain assumptions are involved, and the repulsive and other higher terms are ignored[10], it is noteworthy that the reasonable values for the lattice and hydrogen bond energies are obtained, based on the crystal structure.

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9) I. Nitta and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **69**, 143 (1948).

10) In the case of iodine crystal, these two terms were found to cancel out with each other. The agreement of the observed heat of sublimation with the lattice energy calculated by the use of Slater-Kirkwood's formula in many examples seems to indicate that these two terms cancel out with each other. See, I. Nitta and S. Seki, ibid., **64**, 475 (1943).