Energy of Hydrogen Bond in Tetragonal Pentaerythritol

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Introduction

There appeared already numerous papers dealing with the energy of hydrogen bond. In most of these papers, it is estimated from experimental data of substances in pure liquid or solution state. Generally, in the pure liquid or solution state, the molecular arrangement is not known so accurately that the net contribution of the hydrogen bond cannot be sorted out exactly. On the other hand, the energy of association of some carboxylic acids determined from the temperature variation of equilibrium constant for the hydrogen bond dimerization in the gaseous state(1) would be of unambiguous significance for the derivation of the hydrogen bond energy, since the molecular structure of these dimers have already been determined by the electron diffraction method.(2) In the same sense, the energy data of a crystalline substance, of which the structure is known by the x-ray analysis, will be also useful for this purpose. The only one example of such investigation hitherto carried out is the case of the hydrogen bond energy for ice.(3),(4) Now that the crystal structure of pentaerythritol is completely determined independently by one of the present authors and

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(1) (a) Davies, *Ann. Report Chem. Soc.*, (1947); (b) E. W. Johnson and L. U. Nash; *J. Am. Chem. Soc.*, **72**, 547 (1950).

(2) (a) J. Karle, L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944); (b) V. Schomaker, J. U. O'Gorman, *J. Am. Chem. Soc.*, **69**, 2638 (1947).

(3) Unfortunately, the unit cell of ice is not determined uniquely.

(4) (a) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); (b) T. Ogura, *Busseiron* (in Japanese), No. 12, 1 (1948); (c) A. W. Searcy, *J. Chem. Phys.*, **17**, 210 (1949).

by Cox and his co-workers,(5) this substance may be suitable for the determination of strength of hydrogen bond in the crystalline state. Thus, we attempted to determine the heat of sublimation of this material and compare the results with the calculated values of the lattice energy.

Experimental

The sample used in the present investigation is the product of Kahlbaum Company. It was recrystallized from distilled water and was purified by fractional sublimation under high vacuum (below 1×10^{-5} mm. Hg) at about 130°. By the method of differential thermal analysis, the melting point of the extremely purified sample finally employed for the experiment was determined to be 265.5°(6). The vapor pressures were measured by the effusion method, of which we have already described in a previous paper.(7) The obtained numerical values are summarized in Table 1 and the vapor pressure equation derived from these experimental data is given at the bottom. Some thermodynamical data calculated from it are shown in Table 2.

Table 1

Vapor Pressures of Pentaerythritol

t°C	$P_{\text{mm. Hg}}$ $\times 10^3$	($\log P_{\text{mm. Hg}}$ $+3)_{obs.}$	($\log P_{\text{mm. Hg}}$ $+3)_{calc.}$
123.8	1.70	0.230	0.235
126.1	2.25	0.350	0.345
129.8	3.15	0.498	0.496
132.2	3.93	0.594	0.599
134.5	4.96	0.696	0.697
136.9	6.19	0.792	0.791

$\log P_{\text{mm. Hg}} = 14.525 - 6861.1/T$

Table 2

$\Delta H_s = 31.4 \pm 0.2$ kcal./mole
$\Delta S_s = 53.3 \pm 0.6$ e.u./mole
$\Delta G_{298.1} = 15.5 \pm 0.4$ kcal./mole
ΔH_s : Heat of sublimation
ΔS_s : Entropy of sublimation
ΔG : Free energy of sublimation

Calculation of Lattice Energy

(a) van der Waals Energy.—In a series of papers,(8) we have calculated the lattice energies of more or less complicated crystals and showed empirically that the application of the Slater-Kirkwood formula for the van der Waals interaction may be used within the error of about 10% of the observed values. In these calculations, the contributions of the atoms or atomic groups, into which the molecule is splitted, are summed up. The general agreement between the calculated and the observed values to about 10% may be looked upon as suggesting that the higher order interactions such as Margenau's force are roughly compensated by the repulsive forces.(8a)

In the present case of pentaerythritol, the molecule is splitted into three kinds of force centers; that is, the central C atom, CH_2 and OH groups. According to the Slater-Kirkwood theory the interaction energy between two molecules is given in the form of the following equation:

$$V = -\frac{3}{2}\frac{e\hbar}{m^{1/2}}\sum_{ij}\frac{\alpha_i\alpha_j}{(\alpha_i/n_i)^{1/2}+(\alpha_j/n_j)^{1/2}}\frac{1}{R_{ij}^6} \qquad (1)$$

where e is the elementary charge, m mass of electron, $\hbar = h/2\pi$, n the number of electrons in the outermost electronic shell, α polarizability of an atom or an atomic group, R_{ij} distance between the centers of force, suffix i or j denotes one or the other of the considered pair of the centers.

The molecular arrangement in the crystal with numbers assigned to molecules for convenience is illustrated in Fig. 1. The lattice constants adopted in the calculation are respectively $a = 6.074$ Å. and $c = 8.877$ Å. at 130°.(9) The polarizabilities of atomic groups are estimated as follows. To obtain the polarizability of CH_2 group, we could make use of either the difference of molecular refractions corresponding to the increase of a CH_2 group in the homologous series of normal hydrocarbons and of normal alcohols or the similar quantities deduced from the symmetrically branched hydrocarbon series.(10)

For the former two series, there are sufficient data of refractive indices for wave lengths of H_α, H_β, H_γ, and D-line, while the data for the latter exist only for the wave length of D-line. Using these values, it is possible to calculate the mean molecular refraction of CH_2 group at infinite wave length, $(M_{\lambda=\infty})$ by application

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(5) (a) F. J. Llewllyn, E. G. Cox, T. H. Goodwin. *J. Chem. Soc.*, 883, **1937**; (b) I. Nitta, T. Watanabé, *Nature*, **140**, 365 (1937); *Sci. Papers. Inst. Phys. Chem. Research*, **34**, 1669 (1938).

(6) Ebert, 260.5°; Mark, 252.5°; Seifert, 252°; Schleede, 257°.

(7) J. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, **71**, 378 (1950).

(8) (a) I. Nitta, S. Seki, *J. Chem. Soc. Japan*, **64**, 475 (1945); (b) S. Seki, H. Chihara, *Sci. Papers. Osaka Univ.* **1**, 1 (1949); (c) I. Nitta, S. Seki, M. Momotani, *J. Chem. Soc. Japan*, **71**, 430 (1950).

(9) These lattice constants are calculated from the experimental data of thermal expansion coefficient determined by x-ray method in this laboratory (unpublished).

(10) We have utilized the refractive indices of $C(CH_3)_4$, $(CH_3)_3C(C_2H_5)$, $(CH_3)_2C(C_2H_5)_2$, $(CH_3)C(C_2H_5)_3$ and of $C(C_2H_5)_4$.

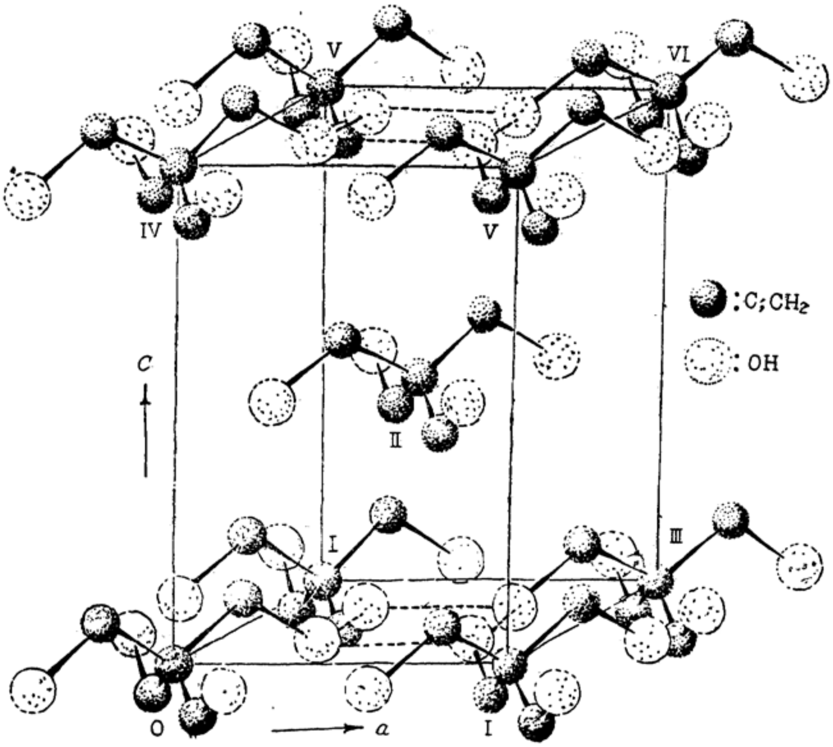

Fig. 1.—Crystal structure of tetragonal pentaerythritol (dotted lines show the hydrogen bonds).

of the Cauchy dispersion formula. In Table 3, there are given mean molecular refraction of a CH_2 group from these three sources.

Table 3

Mean Molecular Refraction of CH_2 Group

	M_γ	M_β	M_D	M_α	$M_{\lambda=\infty}$
From normal alcohols	4.72	4.68	4.64	4.61	4.51
From normal paraffines	4.76	4.68	4.64	4.61	4.51
From branched(*) paraffines	—	—	4.45	—	4.32

* Egloff, "Physical Constants of Hydrocarbon", (1939).

In Table 3 it can be seen that the values derived from the upper two series are in very good agreement with each other, while those from the third is considerably smaller. The $M_{\lambda=\infty}$ value for the last one is estimated by assuming the same relative decrement with wave length as the former. We used the value of 4.32 for calculation, since the situation of CH_2 group in pentaerythritol may rather be approximated to that of the branched chain hydrocarbon series. The molecular refractions of a OH group and the central carbon atom are deduced from the data of normal alcohols and of branched paraffines. From these values of molecular refraction at infinite wave length, we obtain the polarizabilities of the three atomic groups, which are tabulated in Table 4.(11)

Table 4

Molecular Refraction(11) and Polarizabilities

	M_D	$M_{\lambda=\infty}$	$\alpha\times10^{24}$ cc.
CH_2 group	4.45	4.32	1.709
OH group	2.61	2.48	0.981
Central carbon	3.04	2.98	0.928

Inserting these polarizabilities and atomic parameters into the formula (1) and multipling by $N_A/2$ (N_A; the Avogadro number), we obtain the results shown in Table 5.

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(11) The refractive index of this crystal measured by Dr. Kiriyama in this laboratory are $\omega=1.553$ and $\varepsilon=1.515$ for ordinary and extra-ordinary rays, respectively (D-line). Inserting these values in the Lorentz-Lorenz formula, we can obtain the values of $M_\omega=31.27$ and $M_\varepsilon=29.27$. On the other hand, assuming the additivity of atomic refraction, we have obtained from the data listed in Table 4 the value of molecular refraction; $M_D=31.28$ which is in better agreement with the M_ω value given above.

Table 5

Lattice Energy Contributions of Different Atomic Groups and the Numbers of Summation Taken in Calculation

Molecule	Distances from molecule 0	van der Waals interactions between different atomic groups						Total
		C~C	C~CH_2	C~OH	CH_2~CH_2	CH_2~OH	OH~OH	
I	6.073 Å.	4.5	70.0	94.4	269.9	702.2	1332.7	2473.7
II	6.178 Å.	4.0	58.4	48.6	254.3	352.1	71.2	788.6
III	8.590 Å.	0.5	7.8	10.0	24.5	65.8	85.4	194.0
IV	8.881 Å.	0.9	6.3	3.0	20.8	14.2	3.3	48.5
V	10.770 Å.	—	0.8	0.5	3.3	3.4	0.9	8.9
(part of summation)		53.8	797.4	816.4	3280.0	5944.4	6252.8	17144.8
(part of integration)		6	35	23	205	115	95	477
			Total van der Waals energy					17.622 kcal./mole
Numbers of pairs taken for summation		26	94	94	376	376	376	1334

In this calculation, van der Waals interactions between the molecule 0 and the first neighbors (molecules I and II), the second neighbors (molecules III and IV) and the third one (molecule V) are summed up one by one, and for the remaining part of these interactions, summation is replaced by integration, assuming the uniform distribution of the centers of attractive forces. As shown evidently in Table 5, the contribution of OH groups to the van der Waals energy is most predominant. It is also shown that the part due to integration does not exceed more than 3%, indicating the approximation by integration is sufficient for the present purpose.

(b) Electrostatic Energy. — In the calculation of electrostatic interaction between free molecules, the dipole model is usually employed. However, for the molecular interaction in the crystalline state, the point charge model would be more adequate than the dipole model, for the intermolecular distance is much smaller here. In the present work, we used the point charge model, putting an effective charge $+\mathcal{E}$ on the nuclear position of the carbon atom in CH_2 group, $-(\mathcal{E}+\mathcal{E}')$ on the oxygen atom and $-\mathcal{E}'$ on the hydrogen atom in OH group. Exact estimation of such formal charges is of course difficult. In the present case, following the usual method, the charge $\mathcal{E}$ is deduced from the bond moment 0.8 D for C—O by dividing this value by the corresponding bond distance 1.46 Å. This comes out to be 0.551×10^{-10} e.s.u., which corresponds to 11.5% ionic character of this bond. The value of $\mathcal{E}'$ can be estimated in the same way. However, the cyclic formation of hydrogen bonds will cause further elongation of the bond length as well as the increase of charge distribution of O—H bond. Taking this circumstances into account, we may use for trial three bond moments of 1.66 D, (bond moment of the free OH group in aliphatic alcohols), 1.79 D and 1.93 D, on the assumption of the normal bond length of 0.96 Å. These three values correspond respectively to the ionic character of 36%, 39% and 42%. The formal charges derived from these values are $\mathcal{E}'=1.726$, 1.870 and 2.015×10^{-19} e.s.u. respectively. However, for the reason mentioned above, the latter two values will be preferable. The electrostatic potential V_{el} is expressed by the following equation:

$$V_{el}=\sum_{ij}\frac{\mathcal{E}_i\mathcal{E}_j}{R_{ij}} \tag{2}$$

where $\mathcal{E}_i$ is the formal charge of the i-th atom, $\mathcal{E}_j$ that of the j-th atom and R_{ji} is the distance between these point charges. We have used this equation only for the first and the second neighbors and the remaining part has been calculated approximately in the following manner.

We can rewrite equation (2) as follows:

$$V_{el}=\sum_{R}\sum_{ij}\frac{\mathcal{E}_i\mathcal{E}_j}{|\vec{R}-\vec{r}_i+\vec{p}_j|}=\sum_{R}\sum_{ij}\frac{\mathcal{E}_i\mathcal{E}_j}{|\vec{R}+\vec{\sigma}_{ij}|},$$
$$\vec{\sigma}_{ij}=\vec{p}_j-\vec{r}_i \tag{3}$$

where $\vec{r}_i$ is the radius vector of the i-th point charge from the center of the molecule 0 (see Fig. 1) and p_j is that of the j-th point charge from the molecular center which is situated at $\vec{R}$ from the center of the molecule 0. For the contribution of the molecules of the third neighbors and of the molecules lying farther than these, the interation energies become

$$\Delta E=\sum_{R}{}'\sum_{ij}\frac{\mathcal{E}_i\mathcal{E}_j}{|\vec{R}+\vec{\sigma}_{ij}|} \tag{4}$$

where $\sum_{R}'$ implies the summations excluding the first and the second neighbors. Using the relation $R \gg \sigma$ this can be expanded by the Taylor theorem. In terms of components of these vectors ΔE becomes,

$$\Delta E \doteqdot \sum_{X}'\sum_{Y}'\sum_{Z}'\sum_{ij}\frac{1}{4!}\left(x_{ij}\frac{\partial}{\partial X}+y_{ij}\frac{\partial}{\partial Y}+z_{ij}\frac{\partial}{\partial Z}\right)^4\frac{\varepsilon_i\varepsilon_j}{(X^2+Y^2+Z^2)^{1/2}}$$

$$=\sum_{X}'\sum_{Y}'\sum_{Z}'\{3(X^4+Y^4)+8Z^4+6X^2Y^2-24Z^2(X^2+Y^2)\}/(X^2+Y^2+Z^2)^{9/2}\times\frac{3}{16}\sum_{ij}(r^2_{xi}+r^2_{yi}-2r^2_{zi})(p^2_{xj}+p^2_{yj}+p^2_{zj})\varepsilon_i\varepsilon_j \qquad (5)$$

where X, Y, Z; x_{ij}, y_{ij}, z_{ij}; r_{xi}, r_{yi}, r_{zi} and p_{xj}, p_{yj}, p_{zj} are the three cartesian components of the vectors $\vec{R}$, $\vec{\sigma}_{ij}$ and $\vec{p}_j$. Cutting off the higher term than the sixth, it is found that the terms involving the first, the second, the third and the fifth derivatives vanish on account of the symmetry properties.

The results calculated by equations (2) and (5), multiplied by $N_A/2$, are tabulated in Table 6.

Table 6

Electrostatic Energies of First and Second Neighbors

Sort of molecule	Number of molecule	Energies per one pair		
		A	B	C
I	4	−3.28	−3.79	−4.35
II	8	−0.72	−0.79	−0.87
III	4	+1.84	+2.08	+2.33
IV	2	+0.25	+0.24	+0.23

Electrostatic Energy Contributions of Different Parts

	A	B	C
First neighbors (molecules I and II)	−18.88	−21.48	−24.36*
Second neighbors (molecules III and IV)	+ 7.86	+ 8.80	+ 9.78*
Outer part	+ 0.05	+ 0.07	+ 0.08**
Total	−10.79	−12.61	−14.50

Case A, B and C correspond to the 36 %, 39 % and 42 % ionic character of OH bond. Unit is kcal./mole.

* Calculated by Eq. (2). ** Calc. by Eq. (5).

It is seen that the electrostatic forces of the second neighbors and of the outer part are as a whole contributing repulsively. This is evident from the symmetry and arrangement of the molecules in the crystal.

Discussion of Results

Adding the van der Waals energy to the electrostatic one, we obtain three values for the total energy; 28.59, 30.33, and 32.12 kcal./mole respectively, corresponding to the three degrees of the ionic characters 36 %, 39 % and 42 % of the OH-bond. These values are in general agreement with the experimental value: 31.4 ± 0.2 kcal./mole. By the reason mentioned in the preceding section the latter two of the calculated values may be more reasonable. Evidently, to calculate the interaction energy more exactly, we must take into account the repulsive energy, the energy due to the induction effects, the higher order van der Waals energy and the resonance energy. However, as described at the beginning of the third section, we have seen in many examples that the van der Waals energies calculated by the Slater-Kirkwood formula come out nearly equal to, or somewhat larger than, the experimental values. These facts seem to show empirically that the repulsive energy is nearly cancelled by the higher order van der Waals energies. It may be supposed also that the contribution of the induction effects will be small. In the above calculation, the increment of formal charge of the OH bond may be said to take this effect partly into account in a certain sense. As to the so-called resonance energy of the hydrogen boad, it is estimated from the deuterium and other effects that its contribution for the present bond length of hydrogen bond is very small as compared with the electrostatic contribution. Hence, it may be neglected without introducing any serious error.

For the estimation of the energy of hydrogen bond, it should be remarked that the definition of the energy of hydrogen bond is rather ambiguous and depending on the methods of determination. For example, in the case of dimerization of carboxylic acids, the energy of hydrogen bond is determined from the temperature dependence of equilibrium constant by the application of the van't Hoff isochore. Therefore, the energy obtained in this way involves that of reorganization of the dissociated molecules and does not correspond exactly to the hydrogen bond energy in the state of dimeric association.

Furthermore, it is uncertain whether we should take into consideration the interaction energy only of the atoms directly concerned with hydrogen bonding, or, in addition to it, the energy due to the remaining atoms. It is actually known that the effect of hydrogen bond upon the state of the remaining atoms will modify the interaction energy.

For the estimation of the magnitude of hydrogen bond energy in this crystal, neglecting the energy of reorganization, there may be considered, for the present, following three cases. Of these the simplest may be such energy defined as interaction energies only between OH groups which are directly linked together by the hydrogen bond. From Tables 5 and 6, this is found to be 5.1 or 5.7 kcal./mole one hydrogen bond, according to whether we adopt the case B or C. The second estimation is as follows. The molecules in this crystal form distinct layers, in each of which they are linked together by the hydrogen bonds (Fig. 1). Thus, the work necessary to separate all the molecules of such a layer may be a second definition of the hydrogen bond energy. Following this definition, it comes out to be about 4.5 or 4.8 kcal./mole. Thirdly, it can be seen in Tables 5 and 6 that, although the intermolecular distances of molecules I and II from the molecule 0 are nearly equal, both the van der Waals and electrostatic energies are considerably different (Table 7). This difference may be looked upon as due to the effect of hydrogen bonding, for the molecule I is hydrogen-bonded with molecule 0, while the molecule II is not. From this point of view, we obtain as the approximated hydrogen bond energy the value of 4.68 or 5.16 kcal./mole.

Table 7

Difference of Interaction Energy between Molecule I and II

Molecule	van der Waals energy	Electrostatic energy		Total	
		B	C	B	C
I	−2.47	−3.79	−4.35	−6.26	−6.82
II	−0.79	−0.79	−0.87	−1.58	−1.66
Difference	−1.68	−3.00	−3.48	−4.68	−5.16

Comparing the energy of hydrogen bond with the total lattice energy, it is found that in any case the contribution of hydrogen bonding amounts to approximately two-thirds of the total energy.(12) It can be seen also in Table 7, as an instance, that, although the electrostatic contribution makes larger part of the whole energy, the van der Waals energy is not at all negligible.

To show such a situation by another example, we calculated in the same way as above, the hydrogen bond energy of formic acid dimer. Moelwyn-Hughes(13) has already calculated the electrostatic part of this energy, adopting the dipole model and neglecting the contribution of the van der Waals energy. His results are 8.6 and 13.1 kcal./mole corresponding to the O−H···O distances of 2.85 and 2.55 Å., respectively. On the other hand, Davies(14) has calculated the electrostatic contribution of this energy using the point charge model, and the induction energy by the use of the dipole model. The sum of these energies amounts to 13.4 kcal./mole for the hydrogen bond distance of 2.67 Å. These results seem, at first sight, to give good agreements with the experimental value of 14.13 kcal./mole.(1b) However, they are both not satisfactory in such regards that the former used the dipole model and hydrogen bonds distance which do not correspond to the actual case, and both authors do not take into account the contribution of the van der Waals energy. Thus, we recalculated the electrostatic energy due to the point charge model, and the van der Waals energy, using the numerical values of the polarisabilities of atomic groups and the ionic character of each bond shown in Table 8. In this case, the revised molecular configuration recently determined by Brockway and others(2a) is used. The obtained results are summerized in Table 9.

Table 8

Atom or atomic group	$\alpha\times10^{24}$	Bond	Bond moment	Ionic character		
				A	B	C
O	0.630	C=O	2.50D	42%	44%	46%
OH	0.981	C−O	0.8 D	12%	14%	16%
CH	1.350	O−H	1.66D	36%	39%	42%
		C−H	0.4 D	7%	7%	7%

Case A is corresponding to the observed dipole moment.

Table 9

van der Waals energy (O−H··O)	1.36
ibid. (excluding O−H····O)	1.37
Electrostatic energy	A, 12.15; B, 13.77; C, 15.17
Total	14.88 16.50 17.89 kcal./mole

It is shown that in this molecule the contribution of van der Waals energy is not so

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(12) At 187.7°, the tetragonal pentaerythlitol transforms into the cubic modification. This phase transition is intimately related to the breaking of the hydrogen bond. I. Nitta, S. Seki, M. Momotani, Proc. Japan Acad., **26** (1950) (9) 25; I. Nitta, S. Seki, H. Momotani, K. Suzuki S. Nakagawa, Ibid. **26** (1950) (10) 11; I. Nitta, T. Watanabé, S. Seki, M. Momotani, Ibid. **26** (1950) (10) 19.

(13) Moelwyn-Hughes, *J. Chem. Soc.*, **1938**, 1243.

(14) Davies, *Trans. Faraday Soc.*, **36**, 333 (1940).

much as in the case of pentaerythritol, and still it amounts to about 15% of the whole.

Comparing this result with the experimental value, the model A is apparently in best agreement. However, as already pointed out, it should be taken into account that the experimental value must contain the energy of reorganization of the dissociated monomer molecules. It is recognized that in the monomer state the *cis*-form is more stable by ca. 7 kcal./mole than the *trans*-form.(9) As the shape of a single molecule in the dimer association state is a midform *cis* and *trans*, that it will be less stable by a few kcal./mole than the *cis*-form.(15) If we assume that almost all dissociated monomer molecules take the *cis*-form at the temperature of experiment, we must compare the calculated value with the experimental one with an addition of a few kcal./mole for such energy of reorganization. Thus, it is seen that again the case B or C is rather in better agreement with the observed value.

After all, the energy of hydrogen bond for this substance may be estimated to be about 8 kcal./mole, which is somewhat larger than that of pentaerythritol.

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(15) We cannot estimate this energy difference exactly, because of the change of molecular structure and interatomic distances on dissociation of the dimer into monomer.