Vapor Pressures of Molecular Crystals[1]. *XI. Vapor Pressures of Crystalline Urea and Diformylhydrazine. Energies of Hydrogen Bonds in these Crystals*

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Introduction

Although reliable data about the energy of OH···O type hydrogen bond in crystals have been recently accumulated considerably[1,2,3,4], those for NH···O type are very scanty. The hydrogen bonds of the latter type, however, play an important role in the properties of synthetic polyamide fibres as well as in biological systems generally.

In order to obtain the energy of hydrogen bond with a definite meaning, it is very desirable to investigate a crystalline substance, of which the structure is completely determined and hence the mode of formation of hydrogen bond between molecules is accurately clarified. Recently, the crystal structures of these compounds given in the title have been determined very accurately[5,6], so we have undertaken to determine the energy of hydrogen bond in these materials.

Experimental

A) Apparatus and Procedures.—Vapor pressures were measured by the effusion method. The details of the apparatus and the procedures were reported previously[7].

B) Samples.—i) Urea.—The first-class-grade urea of Wako Pure Chemicals Co. was recrystallized twice from ethyl alcohol solution and then sublimated fractionally under high vacuum (ca. 10^{-5} mmHg). Melting point 132.0–132.5°C.

ii) Diformylhydrazine.—This specimen was given by Mr. Tomiie in our laboratory. It had been kindly sent him by Professor Aston through Dr. Class at the Pennsylvania State University. This material was recrystallized twice from aqueous solution and then sublimed fractionally under high vacuum (ca. 10^{-5} mmHg). Melting point 158.2–158.5°C.

Results and Discussion

Vapor pressure data of urea and diformylhydrazine are given in Tables I and II. Their vapor pressure equations derived from them by the method of least squares are also given

TABLE I

VAPOR PRESSURES OF UREA

t°C	P mmHg×10³
72.88	1.59
76.32	2.18
78.34	2.55
81.68	3.51
86.14	5.10
89.41	6.26
92.49	8.01
95.05	10.2

$$\log P = 10.44 - \frac{4579}{T}$$

TABLE II

VAPOR PRESSURES OF DIFORMYLHYDRAZINE

t°C	P mmHg×10³
97.8	2.13
100.6	2.80
103.4	3.57
106.9	4.61
112.5	7.83
113.7	8.50
120.8	11.8
124.1	14.9
126.7	22.2
129.7	28.8

$$\log P = 11.53 - \frac{5264}{T}$$

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2) I. Nitta and S. Seki, *J. Chem. Soc. Japan*, **69**, 141, 143 (1948).

3) L. Pauling, "Nature of Chemical Bond" (1941).

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5) Urea: P. Vanghan and J. Donohue, *Acta Cryst.*, **5**, 530 (1952).

6) Diformylhydrazine: I. Nitta, Y. Tomiie and C.H. Koo, Presented at the Third Congress of the International Union of Crystallography in Paris (1954).

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

at the bottom of each table. Heats of sublimation (ΔH sub), entropies of sublimation ΔS sub) and standard free energies of sublimation at 25°C ($\Delta G^\circ_{298\cdot16}$) calculated from the vapor pressure equations are given in Table III.

TABLE III

	ΔH(kcal./mol.)	ΔS(e.u)	$\Delta G^\circ_{298\cdot16}$ (kcal./mol.)
Urea	20.95 ± 0.21	34.59 ± 0.59	10.64 ± 0.03
Diformylhydrazine	24.10 ± 0.13	39.60 ± 0.30	12.29 ± 0.03

In order to obtain the energy of the hydrogen bond, it is necessary to derive, first, the lattice energy from the heat of sublimation, which is given by the following equation:

$$\Delta H_{\mathrm{sub}} = L^\circ + W_{\mathrm{G}} + (E^{\mathrm{G}}_{\mathrm{TR}} + E^{\mathrm{G}}_{\mathrm{rot}} - E^{\mathrm{S}}_{\mathrm{L.V.}}) + (E^{\mathrm{G}}_{\mathrm{M.V.}} - E^{\mathrm{S}}_{\mathrm{M.V.}}) + n \cdot \Delta H_{\mathrm{ASSN}}$$

where L° is the lattice energy of solid at absolute zero; W_{G} the work done by evaporation of the vapor ($\approx RT$); $E^{\mathrm{G}}_{\mathrm{TR}}$ the translational energies of gas molecules ($\approx \frac{3}{2} RT$); $E^{\mathrm{G}}_{\mathrm{rot}}$ the rotational energies ($\approx \frac{3}{2} RT$); $E^{\mathrm{S}}_{\mathrm{L.V.}}$, the energy of lattice vibration ($3RT$ for ordinary molecular crystal at ordinary temperatures); $E^{\mathrm{G}}_{\mathrm{M.V.}}$ and $E^{\mathrm{S}}_{\mathrm{M.V.}}$, the energies of intramolecular vibrations in gaseous and crystalline states, respectively; ΔH_{ASSN} the heat of association and n the fraction of associated molecule in gaseous phase, if any. In the above equation the terms in parrentheses are cancelled out with each other approximately and the second term W_{G} can be ignored for the first approximation. Since we measured the heat of sublimation in a region of very low pressures (10^{-2} mmHg or less), the last term may be also ignored*. Thus, we can infer that the heat of sublimation determined experimentally is nearly equal to the lattice energy. Then we may obtain the contribution of the hydrogen bond by subtracting the contribution of van der Waals' energy from the lattice energy. Practically, we may adopt one of the following three methods:

i) If the crystal structure is completely determined and some data of optical properties such as refractive indices, etc. are available, we can calculate the van der Waals' energy by use of some theoretical formulae[1].

ii) If a reference crystal, which is constituted from isoelectronic molecules with similar configuration and at the same time without appreciable permanent dipole moment and any atom or atomic group capable of forming hydrogen bond, could be found, this crystal would have nealy the same amount of contribution as the specimen in respect to the dispersion energy. For instance, we can estimate the energy of the hydrogen bond of ethyl alcohol by comparing its heat of sublimation with that of propane.

iii) By the comparison of the heat of sublimation of the specimen with that of a reference substance composed of isoelectronic molecules having similar configuration and with dipole moment with nearly the same order of magnitude as the specimen, but no ability of intermolecular hydrogen bond formation. For example; comparison of ethyl alcohol with methyl ether.

Each of these three methods of estimation has more or less different physical meaning. In the first method, we calculate the van der Waals' energies on the basis of the intermolecular distances at which the molecules are actually linked together by the hydrogen bonds. The intermolecular distances may become a little larger, however, if there would be no hydrogen bonding between the molecules. Thus, the contribution of the van der Waals' energy calculated by this method may be a little over-estimated in comparison with that of crystal in which molecules are combined together only by the van der Waals' forces.

In this paper we applied the second and the third methods. These two methods seem to be related partly with the difference of the energy of the hydrogen bond. If we define it as including the mutual interaction of molecular permanent dipoles in it, the second one may be more appropriate. On the other hand, the third may be more reasonable, if we consider the hydrogen bond as a special type of binding which does not include the energy of the dipolar interaction.

The suitable reference substances are isobutene[8] (for method ii) and acetone (for method iii) for urea, and 1, 5-hexadiene (ii) and succinic aldehyde (iii) for diformylhydrazine.

As the heats of sublimation of 1, 5-hexadiene and succinic aldehyde are not yet known, we estimated the contribution of the van der Waals' energy and the dipolar energy by

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* Urea molecules would be associated with each other in the gaseous phase in a similar way as acetic acid. The calculated fraction of associated molecules, however, is found to be only 0.02% even at 1×10^{-2} mmHg, if we assume following thermodynamic functions; $\Delta H_{\mathrm{ASSN}} = -14$ kcal./mol., and $\Delta S_{\mathrm{ASSN}} = -36$ e.u. (These data were estimated from the experimental results of acetic acid).

[8] F.D. Rossini, K.S. Pitzer, W.J. Taylor, J.P. Ebert and J. E. Kilpatrick, "Selected Values of Hydrocarbons" (1947).

TABLE IV

HEATS OF VAPORIZATION OF SOME HYDROCARBONS AT THEIR BOILING POINTS* (kcal./mol.)

	ΔH_0		ΔH_1		ΔH_2	$\Delta H_1-\Delta H_0$	$\Delta H_2-\Delta H_1$
ethane	3.517	ethene	3.237	——		−0.3	—
propane	4.487	propene	4.402	——		−0.1	—
n-butane	5.352	1-butene	5.238	butadiene	5.873[9]	−0.1	+0.6
		cis-2-butene	5.480	——		+0.1	—
		trans-2-butene	5.239	——		−0.1	—
iso-butane	5.089	*iso*-butene	5.286	——		+0.2	—
pentane	6.160	——		pentadiene	6.75[10]	—	+0.6
2-methyl-butane	5.809	——		isoprene	6.39[11]	—	+0.6

* All the data except butadiene, pentadiene and isoprene are taken from reference (8).

TABLE V

Substances			A			B		
			Diformyl-hydrazine	δ-Valero-lactam	ε-Capro-lactam	Acetamide	Oxamide	Urea
Heat of sublimation (kcal./mol.)	Observed		24.10	17.81[12]	19.86[12]	13.6[13]	27.0[14]	20.95
	Contribution from the energy of	dispersion effect*	12.0**	10.6	12.9***	7.6	10.1**	7.6
		dipolar interaction	2.2†	2.1††	2.1††	3.3†††	3.6※	3.3†††
		hydrogen bond (ii)	12.1	7.2	7.0	6.0	16.9	13.4
		hydrogen bond (iii)	9.9	5.1	4.9	2.7	13.3	10.1
Hydrogen Bond	Number of hydrogen bond per molecule		2[5]	(1)	(1)	2[22]	(4)	4[5]
	Energy of one hydrogen bond (ii) (kcal./mol.)		6.1	(7.2)	(7.0)	3.0	(4.2)	3.5
	〃 (iii)		5.0	(5.1)	(4.9)	1.4	(3.3)	2.5
	Hydrogen bond distance (Å)		2.787[6]	—	—	2.83[22] 2.99	—	2.99[5] 3.04
	Number of donated hydrogen atoms per molecule		2	(1)	(1)	2	(4)	4
	Number of hydrogen accepting atoms per molecule		2	(1)	(1)	1	(2)	1
	Hydrogen atom-Hydrogen acceptor ratio		1	(1)	(1)	2	(2)	4

* Heats of sublimation of the reference substances are obtained by adding the heats of fusion and those of vaporization near the melting point the latters of which are calculated from the vapor pressure equations. hexane ($\Delta H_F=3.11,^{(8)}$ $\Delta H_v=8.31^{(8)}$) for diformylhydrazine; methylcyclohexane ($\Delta H_F=1.613,^{(15)}$ $\Delta H_v=8.94^{(8)}$) for δ-valerolactam; iso-butene ($\Delta H_F=1.42,^{(8)}$ $\Delta H_v=6.19^{(8)}$) for urea and acetamide; 2,3-dimethylbutane ($\Delta H_F=0.19,^{(16)}$ $\Delta H_t=1.55,^{(16)}$ $\Delta H_v=7.73^{(8)}$). For 2,3-dimethylbutane we have taken into account the heat oftransition for estimating the heat of sublimation.

** Heat of sublimation of the reference substances plus effect of conjugated π-electrons (0.6 kcal).

*** Heat of sublimation of methylcyclohexane plus increment of the heat of sublimation of CH_2 group; see ref. (17).

† Difference of the heats of sublimation of *p*-quinone ($\Delta H_{sub}=16.4^{(18)}$) and *p*-xylene ($\Delta H_{sub}=\Delta H_v^{\cdot\cdot}$ (at 25°; $10.1^{(8)})+\Delta H_F(4.1^{(8)})$).

†† Difference of the heats of vaporization of cyclohexanone ($\Delta H_v=11.05^{(2)}$) and methylcyclohexane. (we used this difference in place of that of their heats of sublimation, since the solid phase of cyclohexanone just below the melting points belongs to the so-called plastic crystal.)

††† Difference of the heats of sublimation of acetone ($\Delta H_{sub}=9.5$ (ΔH_v at the melting point$^{(19)}$)$+1.36$ ($\Delta H_F{}^{(20)}$)) and iso-butane.

※ Difference of the heats of vaporization of glyoxal ($\Delta H_v=9^{(21)}$) and 2,3-dimethylbutane.

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9) J.G. Aston and G.F. Szasz, *J. Am. Chem. Soc.*, **69**, 3108 (1947).

10) K. Kuchinskaya, *Chem. Abst.*, **34**, 3147 (1940).

11) Roth's data taken from Landolt-Börnstein's Physikalisch-Chemisches Tabellen (II'er Erg. Band).

12) A. Aibara, *J. Chem. Soc. Japan*, **74**, 631 (1953).

13) A. Aibara, *J. Chem. Soc. Japan*, **73**, 955 (1952).

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15) D.R. Douslin and H.M. Huffman, *J. Am. Chem. Soc.*, **68**, 173 (1946).

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19) W.A. Felsing and S.A. Durban, *J. Am. Chem. Soc.*, **48**, 2893 (1926).

20) G.S. Parks and K.K. Kelley, *J. Phys. Chem.*, **32**, 1739 (1928).

21) F. Rossini, "Selected Values of Chemical Thermodynamic Properties", (1952).

comparing the heat of sublimation of *n*-hexane with those of some other substances. In Table IV, it is seen that the heats of vaporization of *n*-paraffines and of corresponding monoolefines are nearly equal, whereas those of conjugated olefines are by ca. 0.6 kcal./mol. larger than those of corresponding paraffines. As the molecule of diformylhydrazine has conjugated π-electrons, it may be reasonable to assume that the van der Waals' energy of diformylhydrazine is larger than that of *n*-hexane by an amount of ca. 0.6 kcal./mol. For the third method, we used the difference of the heats of sublimation of *p*-benzoquinone and *p*-xylene for estimating the contribution of the dipole-dipole interaction.

All the observed heats of sublimation and the contributions from the various kinds of energies, i. e. the dispersion energy, the dipole-dipole interaction and the energy of the hydrogen bonds (derived by use of the methods (ii) and (iii)) of the present materials are given in Table V.

In this table corresponding data for δ-valero-lactam, ε-caprolactam, acetamide and oxamide are also calculated for reference.

As the number of hydrogen bonds per molecule of urea[5], diformylhydrazine[5] and acetamide[22] are already known by the X-ray methods (see the sixth row of Table V), the energies per one hydrogen bond for these substances are calculated as shown in the seventh and eighth rows. The numbers of hydrogen bonds for the other substances in this table are not yet determinede experimentally, so the energies of the hydrogen bonds are estimated by assuming appropriate number of the hydrogen bonds. (They are shown in parentheses.)

From these results, we may derive the following several conclusions:

(1) The energy of NH···O type hydrogen bond in crystal is not always so small as the value given by Davies[23] (2 kcal./mol. for aniline-benzophenone). This may be one of the reasons for the fact that almost all the substances with -NHCO- groups show rather high melting points.

(2) It is usually supposed that the shorter the distance of the hydrogen bond the larger the energies become. But, this does not always hold. For instance, if we compare urea, diformylhydrazine and acetamide with each other, then we can see that diformylhydrazine with the shortest NH···O distance have the largest hydrogen bond energy, whereas urea with the longest N-H···O distance gives larger energy of hydrogen bond than that of acetamide with a little shorter bond distance. So it seems to be rather dangerous to estimate the relative strength of the hydrogen bond only from the knowledge of the distance of the hydrogen bond, though it may be useful for a rough estate of its strength.

(3) The energies of the NH···O type hydrogen bonds show rather scattered values (7.0–3.0 kcal./mol. from the method (ii); 5.1–1.4 kcal./mol. from the method (iii)) in comparison with those of the OH···O type in which the energies are limited in the region of 4.5*–6.0** kcal./mol. (method (ii) or (i)).

As one of the reasons for such scattering as mentioned above, we may point out the varieties of the ratio of the number of donated hydrogen atoms to those of accepting oxygen atoms. In fact, we can see in Table V that for the substances of the A-class having larger energies of the hydrogen bond, i.e. for diformylhydrazine, δ-valerolactam and ε-caprolactam, this ratio is 1, whereas it is 2 or 4 for substances of the B-class with smaller energies of the hydrogen bond, i. e. acetamide, oxamide and urea. When this ratio increases, the steric hindrance between the donated hydrogen atoms surrounding the same acceptor atom will become larger. As the result, this effect may cause a considerable difference between the energies of the hydrogen bond of the classes A and B. On the other hand, in the case of the OH···O type hydrogen bond this ratio is mostly one. So, the energies of the OH···O type hydrogen bond are not so divergent as those of the NH···O type one.

The other factors, for example, the changes of electron densities of oxygen or nitrogen atoms due to the conjugations of the π-electrons, may also contribute to some extent to the energies of hydrogen bonds. This effect, however, seems less important than the effect of hydrogen atom-hydrogen acceptor ratio, at least in the crystalline state.

These conclusions mentioned above will give some contribution for the elucidation of complex structures and phenomena found in some synthetic fibers as well as in some biological systems.

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[23] Davies, *Ann. Report*, **1946**, 5.

* Value for phenol, see ref. (2).

** Values for carboxylic acid dimer in the vapor; that is the heat of association of their dimer minus contribution of dispersion effect, see ref. (1).

sample of diformylhydrazine, and also to Mr. Y. Tomiie for his kind discussion. The expense of this research is partly defrayed from the Scientific Reseach Grant from the Ministry of Education as well as from the fund of Taniguchi Kôgyô-Shyôreikai to which the authors' thanks are due.

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