Vapor Pressures of Molecular Crystals. XIV[1]. *Sulfamide and Diacetylhydrazine*

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The energy of the hydrogen bond can be determined by various methods in vapor, liquid, solution, and crystalline solid. All but one method, that have been reported by the authors and other investigators in cases of liquids and crystals, estimate the energy from the temperature variation of the equilibrium constant for the association-dissociation equilibrium due to hydrogen bonding in vapor or in solution state. Those determinations, however, can not be correlated with the so-called hydrogen bond distances with only one exception for the case of gaseous carboxylic acid dimers, the structure of which could be determined by means of the electron diffraction technique. On the other hand when we deal with crystalline solids, it is possible to determine the hydrogen bond distance by the X-ray investigation although we can not obtain the state, in which only the hydrogen bond ceases to act, other forces such as the dispersion forces and the dipolar forces being unchanged. Usually the compromise has been adopted that the contributions other than the hydrogen bond to be subtracted from the total lattice energy may be estimated by one of the following

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[1] The Report XIII may be found in This Bulletin, **32**, 84 (1959).

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[2] I. Nitta, S. Seki and K. Suzuki, This Bulletin, **24**, 63 (1951).

two methods: (1) the dispersion energy is calculated by using the interatomic distances and the atomic polarizabilities, and the electrostatic energy by assuming the electron density on each atom; (2) the dispersion and the electrostatic energies of the hydrogen-bonded crystal are substituted by the heat of sublimation of the crystal that is isoelectronic with the crystal in question but that possesses no hydrogen bond between molecules[2].

We have here chosen sulfamide and diacetylhydrazine as compounds having NH···O hydrogen bonds in crystals, whose structures were determined[3,4], and we have applied the former method of obtaining the energies of hydrogen bonds.

Experimental

Materials.—Sulfamide $(NH_2)_2SO_2$ was prepared by Goehring's method from liquid ammonia and sulfuryl chloride[5], and purified by fractional sublimation in high vacuum, m. p. 91.9°C (*Anal.* found S 32.84% and N 28.45%.) Diacetylhydrazine $CH_3COHN\text{-}NHCOCH_3$ was supplied by Miss A. Yamaguchi of the University of Tokyo*. This was recrystallized from aqueous solution and dehydrated** and sublimed in high vacuum; m. p. 123°C. The crystal modifications of both substances were checked against the reported crystal structures by X-ray diffractometer.

Apparatus.—The vapor pressures were measured with the apparatus already reported elsewhere[1] except for minor alterations. In the experiments with diacetylhydrazine, it was found that effused vapor condensed on the quartz helical balance which was kept at room temperature, causing a considerable error in the determination of the weight changes. In order to remove this difficulty the balance container was heated with a ribbon heater from outside the glass tubing to maintain the temperature of the balance at about 70°C. The treatment of the quartz balance with dimethyldichlorosilane vapor was also useful in preventing condensation of diacetylhydrazine.

Results and Discussion

The vapor pressures are listed in Table I for both sulfamide and diacetylhydrazine. The experimental values are well reproduced by the equations,

$$\log P = 11.047 - (5300.4/T) \quad \text{(sulfamide)}$$

and

$$\log P = 12.1947 - (5384.4/T) \quad \text{(diacetylhydrazine)}$$

The heat, entropy and free energy changes of sublimation computed by these equations are given in Table II.

TABLE I

VAPOR PRESSURES OF SULFAMIDE CRYSTAL

T°K	P(mmHg) $\times 10^5$	T°K	P(mmHg) $\times 10^5$
347.8_9	6.370	352.7_5	10.43
348.7_0	7.017	354.7_8	12.81
349.7_4	7.960	357.7_9	17.04
350.7_8	8.671		

VAPOR PRESSURES OF DIACETYLHYDRAZINE CRYSTAL (ANHYDROUS)

T°K	P(mmHg) $\times 10^4$	T°K	P(mmHg) $\times 10^4$
342.3_9	2.876	349.6_2	6.100
343.4_8	3.269	350.6_8	6.913
344.9_4	3.946	352.2_5	8.046
347.3_6			

TABLE II

HEATS, ENTROPIES AND FREE ENERGIES OF SUBLIMATION

	ΔH (kcal./mole)	ΔS (cal./deg. mole)	ΔG at 298.16°K (kcal./mole)
Sulfamide	24.25±0.24	37.26±0.68	13.11±0.31
Diacetyl-hydrazine	24.63±0.39	42.60±1.13	11.93±0.51

The heat of sublimation here obtained may be safely regarded as the lattice energy of the crystal*.

Calculation of the energies of the NH···O hydrogen bonds.—*a) Sulfamide.*—The calculation of the dispersion energy was made by the same procedure as was reported earlier[2]. The summation of r^{-6} (r: interatomic distance) for nonbonded pairs of atoms or atomic groups within 10 Å from a 'central atom' is shown in Table III, which was obtained on the basis of the atomic

TABLE III

SUMMATION FOR SULFAMIDE

Non-bonded pairs	$\sum(1/r^6) \times 10^6$ in Å^{-6}
S∼S	906.63
NH_2∼NH_2	7367.64
O∼O	5962.20
S∼NH_2	6006.26
S∼O	5002.95
NH_2∼O	14792.97*

* The hydrogen-bonded pairs were excluded.

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[3] K. N. Trueblood and S. W. Mayer, *Acta Cryst.*, **9**, 628 (1956) (sulfamide).

[4] R. Shintani and I. Nitta, read before the 4th International Congress of Crystallography, July 1957 (Montreal, Canada); A full paper will be published in *Acta Cryst.* or elsewhere (diacetylhydrazine).

[5] M. Goehring, J. Heinke, H. Malz and G. Ross, *Z. anorg. u. allgem. Chem.*, **273**, 200 (1953).

* The authors are indebted to her for her kindness.

** The monohydrate of diacetylhydrazine is more stable than the anhydrous form at room temperature and humidity.

* Association in vapor can be ignored as the vapor pressure is very low.

parameters determined by Trueblood and Mayer[3]. The atomic polarizabilities were calculated from the molecular refractions R_D for O (in a carbonyl), NH_2 (in a primary amine) and SO_2 (in dialkyl sulfate) compiled by Vogel[6]. The static polarizabilities given in Table IV have been corrected for the dispersion effect by subtracting 3% from the values for the NaD light[7]. The dispersion energy was then computed by using the Slater-Kirkwood formula[8] by summation within the 10 Å sphere and by integration outside that sphere. The summation part contributed 13.71 kcal and the integration part contributed 0.014 kcal. to the dispersion energy. The number of terms included in the summation was 1128. The dipolar interaction energy in sulfamide was obtained by summing up the contribution from each pair of molecules in the crystal by using the value of the dipole moment 3.9 D[9]. The dipolar energy contribution within the 10 Å sphere amounted only to 2.87 kcal. and this was taken as the total electrostatic energy as the integration diverges. The hydrogen bond energy was set equal to the difference between the observed lattice energy and the sum of the dispersion and electrostatic energies; $24.25-(12.08+2.9)=9.30$ kcal./mole. There are two NH···O hydrogen bonds per molecule of sulfamide and therefore the energy of a hydrogen bond is 4.6_5 kcal./mole. Omission of the repulsive potential energy in the calculation may be partly justified by the fact that in many molecular crystals the Margenau potential of r^{-8} factor nearly cancels out the repulsive contribution[10].

TABLE IV

STATIC POLARIZABILITIES

	No. of outer shell electrons	Static polarizability
S	6	1.382×10^{-24} cc.
O	6	0.8162 〃
NH_2	7	1.707 〃

b) *Diacetylhydrazine.* — The summation of r^{-6} and the static polarizabilities are given in Tables V and VI. The dispersion energy is 19.30 kcal./mole for summation within the 10 Å sphere (1064 terms) from "central atoms" and 0.39 kcal./mole for integration outside the sphere. The electrostatic contribtion to the total lattice energy was calculated by point charge model with unbalanced charges on C and O atoms, $\pm2.002\times10^{-10}$ c. g. s. e. s. u., estimated from the bond moment of C=O 2.50 D and the bond length 1.249 Å. The resultant energy was 1.15 kcal./mole, being repulsive. The total hydrogen bond energy is then about 6.06 kcal./mole or 3.03 kcal./mole for each bond.

TABLE V

SUMMATION FOR DIACETYLHYDRAZINE

Non-bonded pairs	$\sum(1/r^6)\times10^6$ in $Å^{-6}$
NH∼NH	4286.9
C∼C	3674.0
O∼O	5361.7
CH_3∼CH_3	4126.3
C∼O	11359.2
CH_3∼O	8470.5
NH∼O	9038.3*
C∼CH_3	5110.5
C∼NH	6778.2
CH_3∼NH	3455.5

* H-bond pairs were excluded.

TABLE VI

STATIC POLARIZABILITIES

	No. of outer shell electrons	Polarizability
O	6	$0.816_2\times10^{-24}$ cc.
C	4	1.60 〃
CH_3	7	1.89 〃
NH	6	1.61 〃

Comparison of the energy of NH···O hydrogen bond.—In Table VII are summarized the energies of NH···O hydrogen bonds in crystals hitherto reported. In general the NH···O energies fall in a range of values between 3 and 6 kcal. and are in comparable magnitude with the energies of OH···O bands. However, from the point of view that the energy should decrease with increasing length of the bond, it seems hopeless to correlate the energies with the bond lengths in Table VII. This is partly due to the difference of the method of evaluation of the energy and partly due to relatively small contribution of hydrogen bonding forces to the total lattice forces. The situation is in a sense analogous to the evaluation of the resonance energy of conjugated molecules from the experimental heat of formation and the energy of a Kekulé structure.

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[6] A. I. Vogel, *J. Chem. Soc.*, **1948**, 1833; see also J. R. Partington, "An Advanced Treatise of Physical Chemistry", Vol. IV, Longmans, London (1953), p. 50.

[7] S. Seki and H. Chihara, *Sci. Papers Osaka University*, No. 1 (1949).

[8] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **87**, 684 (1931).

[9] G. Devoto and R. D. Nola, *Gazz. chim. ital.*, **63**, 495 (1953); The gaseous dipole moment of $SO_2(CH_3)_2$ is 4.41D and thus it was assumed that the effect of association of sulfamide in dioxane solution would be small.

[10] I. Nitta and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **64**, 475 (1943).

TABLE VII
ENERGY OF HYDROGEN BONDS

Crystal	N···O length	Energy in kcal./bond	Method	Reference
Diketopiperazine	2.88	5.3	**a**	i
Diformylhydrazine	2.788	6.1	**a**	ii
δ-Valerolactam	—	(7.2)*	**a**	ii
ε-Caprolactam	—	(7.0)*	**a**	ii
Oxamide	—	(4.2)*	**a**	ii
Acetamide	2.89, 2.99	3.0	**a**	ii
Urea	2.99, 3.04	3.5	**a**	ii
Sulfamide	3.02	4.7	**b**	iii
Diacetylhydrazine	2.875	3.0	**c**	iii

i: S. Seki, K. Suzuki and T. Koide, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 346 (1956).
ii: K. Suzuki, S. Onishi, T. Koide and S. Seki, This Bulletin, **29**, 127 (1956).
iii: Present study.
a: Subtraction of the heat of sublimation of the isoelectronic compound possessing no dipole moment.
b: Calculation of the dispersion and the electrostatic energies by use of theoretical formulae (point dipole model).
c: Calculation of the dispersion and electrostatic energies by use of theoretical formulae (point charge model).
* It is uncertain how many bonds there are per molecule.

The method **a** gives the hydrogen bond energy in which the energy required for the rearrangement of molecules from the structure of the isoelectronic crystal to the hydrogen-bonded structure is included. This rearrangement energy is quite analogous to the compression energy[11] and should differ from compound to compound. Thus this type of hydrogen bond energy does not represent the energy localized in the hydrogen bond but includes all the contributions to the change in the lattice energy that would be needed if the hydrogen-bonded structure were transformed into a non-bonded structure, i. e. the energy localized at the hydrogen bonds, the energy of electronic rearrangement within a molecule to make it non-polar within the crystal lattice and the energy for the change of crystal structure[12]. In other words, such "hydrogen bond energy" is a measure of how much gain in stability would result in a crystal as a whole by forming the hydrogen bonds compared with a hypothetical non-bonded structure.

The methods **b** and **c** are less unambiguous than the method **a** in that the former give the energy values in the approximation, the origin of which is less obscure. The estimation of the electrostatic energy is always a hard thing to do correctly; the point dipole model would be a very rough approximation in short-range interaction as in crystals and the charge distribution in crystal is rarely known except in cases of fully refined analysis of the crystal structures. Although the resultant contribution of the electrostatic energy to the total lattice energy is usually small, it is still so large as to affect the hydrogen bond energy value significantly.

The precision with which the dispersion energy is estimated by use of the Slater-Kirkwood formula depends primarily on the choice of the values for the static polarizability of atoms or atomic groups. We have some ground for believing that the calculated dispersion energy is a good measure to the actual interaction energy because we obtained relatively good agreement with the experimental heats of sublimation of nonpolar compounds as is shown in Table VIII. The difference between the calculated and the observed energies still amounts to a few kcal./mole which can not be ignored in comparison with the energy of a hydrogen bond. It may be concluded that the method of evaluating the energy of hydrogen bonds by subtracting contributions of other sources than the hydrogen bonds from the total lattice energy may be applied only to those crystals in which the hydrogen bonding plays an overwhelmingly important role in determining the crystal structure such as ice.

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[11] C. A. Coulson, "Valence", Clarendon Press, Oxford (1953), p. 236.

[12] H. Chihara, *J. Japanese Chem.* (*Kagaku no Ryoiki*), **10**, 31 (1956).

TABLE VIII

CALCULATED AND OBSERVED LATTICE ENERGIES OF NONPOLAR COMPOUNDS (kcal./mole)

	Calculated	Observed	Reference
Tin tetraiodide SnI_4	20.6	18.1	(10)
Titanium tetraiodide TiI_4	16.4	14.9	(10)
Iodine, I_2	15.5	14.8	(10)
Benzene, C_6H_6	10.7	9.2	(13)
Naphthalene, $C_{10}H_8$	18.2	15.9	(10)
Anthracene, $C_{14}H_{10}$	27.2	22.8	(10)
Hexamethylbenzene $C_6(CH_3)_6$	19.4	19.3	(7)

The lattice forces in relation to the crystal structure.—Only one of two hydrogen atoms in each NH_2 group participates in hydrogen bonding in sulfamide crystal. The closest approach between molecules is through the hydrogen bonds but their distance is longer than in diformlyhydrazine. Diformylhydrazine is probably the crystal possessing the shortest NH⋯O hydrogen bonds (2.788Å) ever known* and its closest approach in the crystal is through hydrogen bonds and not at the contact CH⋯O between neighboring molecules (the non-bonded closest distance CH⋯O is 3.69 Å, which is longer than the sum of the van der Waals radii 3.4 Å). Therefore the equilibrium distance in the system NH⋯O would be 2.788 Å**. In sulfamide also, there is nothing hindering the neighboring molecules from approaching nearer and nevertheless its hydrogen bond is longer than in diformlyhydrazine. This may be explained by the difference in electronic configuration in these two compounds. In fact the infrared absorption spectrum of sulfamide, recorded with Hilgar Model H800 spectrometer, showed NH stretching absorptions at 3338 and 3248 cm^{-1} by the Daifloil mull method in comparison with about 3100 cm^{-1} in diformylhydrazine[14].

Sulfamide is a polar crystal with parallel orientation of molecular dipoles in the direction of the *c* axis. This may plausibly give rise to the spontaneous polarization of the crystal unless twinning masks the effect. An estimation of the spontaneous polarization gives about 44226 e. s. u. by using the dipole moment 3.9 D. This is surprisingly large polarization being in comparable magnitude with the case of ferroelectric barium titanate $BaTiO_3$ (the saturation polarization 48000 e. s. u.). The measurement of the polarization should give the value of the dipole moment of a molecule in the crystal, and a study along this line is now going on.

The heat of sublimation of diacetylhydrazine is by about one kcal./mole smaller than would be predicted by the additivity of lattice energies; the heat of sublimation of diformylhydrazine is 24.1 kcal./mole and an increment of about one kcal./mole may be predicted for the addition of a CH_2 unit*. The melting point 132°C and the density 1.35 are lower than 158°C and 1.59 of diformylhydrazine. Diacetylhydrazine is very hygroscopic and changes to the monohydrate in air under ordinary condition within an hour. Such properties are reflected on relatively weak hydrogen bonds in diacetylhydrazine. The fact that the electrostatic interaction is acting as repulsive** is somewhat surprising result

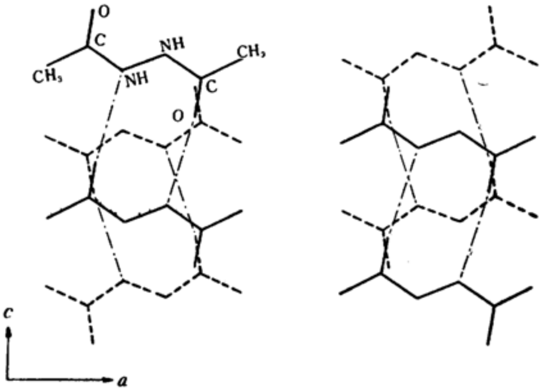

Fig. 1. The arrangement of diacetylhydrazine molecules projected along the *b* axis. Full line shows the molecules lying on *c* plane and dotted line shows molecules displaced halfway in *b*-direction. Hydrogen bonds are represented by chain lines.

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13) J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).

* 2.75Å for NH⋯O bond was reported for amino acids or peptides (cf. H. L. Yakel and E. W. Hughes, *Acta Cryst.*, **7**, 291 (1954); R. A. Pasternak, L. Katz and R. B. Corey, ibid., **7**, 225 (1954)) but these are the bonds, $N^+H\cdots O^-$, between zwitterions.

** In ice and in solid and gaseous hydrogen fluoride there is nothing that hinders the molecules from getting nearer exceptthe inherent potential energy along the hydrogen bonds, so that the actual distances found 2.76Å and 2.55Å would correspond to the shortest approach in linear OH⋯O and FH⋯F systems, respectively, if other effects like conjugation do not greatly modify the electronic structure of the molecules. In other words the single minimum OH⋯O bond will not exist unless the hydrogen bond is very strongly conjugated with the molecular network.

14) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **76**, 341 (1955).

* Mr. Hiroshi Suga of our laboratory has found a lambda-type phase transition of diacetylhydrazine at about 50°C with the heat of transition of probably less than one kcal./mole. In comparing the heats of sublimation of these two compounds the heat of transition must be considered and then the discrepancy would be much smaller. This transition, however, does not affect much the discussion on the hydrogen bond energy.

** Solid carbon dioxide is another example of repulsive electrostatic energy.

in view that the molecules are packed in layers so that C=O bonds are directing antiparallel, one over another (see Fig. 1). This is only a deceptive appearance in the arrangement and actually the lattice is mainly constructed by the dispersion forces.

Summary

The vapor pressures of crystalline sulfamide and diacetylhydrazine were measured between 347°K and 358°K and between 342°K and 353°K, with the results, $\log P = 11.047-(5300/T)$ and $\log P = 12.195-(5384/T)$, respectively. The heats of sublimation were found to be 24.25±0.24 kcal./mole and 24.63±0.39 kcal./mole, respectively. The hydrogen bond (NH···O) energies were evaluated by subtracting from the observed heat of sublimation the contribution of the dispersion energy (by Slater-Kirkwood formula) and the contribution of the electrostatic interaction energy. The latter contribution was obtained by adopting the point dipole model with the dipole moment 3.9 D (for sulfamide) and by adopting the point charge model with the charges ±2.002 e.s.u. at C and O atoms diacetylhydrazine). The NH···O energies were 4.7 kcal. and 3.0 kcal., respectively. The electrostatic interaction in diacetylhydrazine is repulsive. Critical discussions are given on the significance of the hydrogen bond energy values obtained by various methods. The inter-relation between the lattice forces and the packing of molecules in the crystals is discussed on the basis of the calculation of separated contributions to the lattice energy and it is shown that the principal forces, acting between diacetylhydrazine molecules are the dispersion forces and the antiparallel arrangement of C=O dipoles in crystal is only a deceptive appearance. It is suggested that the nearest approaches in the linear systems OH···O and FH···F are 2.76 Å and 2.55 Å, respectively, unless very strong conjugation with the molecular network occurs. The NH stretching modes of vibration in sulfamide absorb at 3338 and 3248 cm^{-1}.

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