Estimation of the Energy of Hydrogen Bonds Formed in Crystals. I. Sublimation Pressures of Some Organic Molecular Crystals and the Additivity of Lattice Energy

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(Received May 25, 1959)

A considerable number of investigations have been done on the problem of hydrogen bonds from both experimental and theoretical points of view, especially since the introduction of the infrared technique in this field of study. Thus, it may safely be said that there is little left to be studied on these topics, so far as they are concerned with hydrogen bondings in solutions of, e. g., phenols, amides and amines in appropriate solvents. One of the questions, however, which is not completely solved as yet, is how to estimate the strength of hydrogen bonds when they are formed in the crystalline state. In this connection, the author has been engaged in the measurement of sublimation pressures of a number of amides and amines with the hope of getting knowledge concerning the relation between the energy of hydrogen bonds in crystals and the heat of sublimation[1].

The principle of estimating the energy of hydrogen bonds in crystals, which has hitherto been adopted by several investigators[1-3], is first to measure the heat of sublimation of a substance in question and then to subtract from it the amount of contribution to the lattice energy due to dispersive and dipolar interaction between molecules in the lattice. Here, the interaction energy due to dispersive force can be calculated theoretically by the Slater-Kirkwood formula[4] if the crystal structure is fully analyzed by X-ray diffraction or by any other methods, while the dipolar interaction can be estimated by the usual procedure or by assuming point charge models.

In case the crystal structure is too complicated to permit theoretical calculation of lattice energy or if it is not analyzed yet, a conventional method has been used in which one assumes the heat of sublimation of a substance, isoelectronic with that in question, as equivalent to the portion of lattice energy due to dispersive and dipolar interaction between molecules in the crystal of a substance forming a hydrogen bond, thereby estimating the energy of the hydrogen bond according to the method already mentioned. A trouble is that an appropriate isoelectronic molecule is not always available to follow the above procedure.

To overcome this difficulty the author has tried first to establish the approximate method of estimating the lattice energy of molecular crystals empirically, assuming its additivity, and then to make use of this method to estimate the energy of hydrogen bonds in crystals of phenols, amides and amines. In this paper, the additivity rule for lattice energy of organic molecular crystals will be examined together with experimental results of sublimation pressure measurement for a number of molecular crystals.

Experimental

Sublimation pressures were measured with a viscosity gauge of the type first designed by Haber[5], Langmuir[6] and later modified by Sasaki[7]. It consists of a Λ shaped fine quartz fiber mounted on a piece of a quartz rod and set in a measuring cell. The diameter of the fiber is 0.1 mm. and the length of the isosceles side of the triangle formed is nearly 10 cm. To facilitate the setting of vibration of the fiber from outside of the cell by a small magnet, a piece of iron wire is attached to the top of the fiber. Samples are fractionally sublimed or distilled under high vacuum and are introduced directly into the cell without allowing them to

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[1] A. Aihara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 855 (1952); ibid., **74**, 437, 631, 634 (1953); ibid., **76**, 492, 495, 497 (1955).

[2] L. Pauling, "The Nature of the Chemical Bnod", Cornell Univ. Press, Ithaca, N. Y. (1945), p. 304—306.

[3] S. Seki et al., This Bulletin, **29**, 127 (1956); ibid., **32**, 137 (1959).

[4] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

[5] F. Haber and F. Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[6] I. Langmuir, *J. Am. Chem. Soc.*, **35**, 107 (1913).

[7] N. Sasaki, " Handbook Experimental Chemistry (Kagaku Jikken Gaku) ", Vol. I—3, Kawade Shobo Co., Ltd., Tokyo (1950), p. 321.

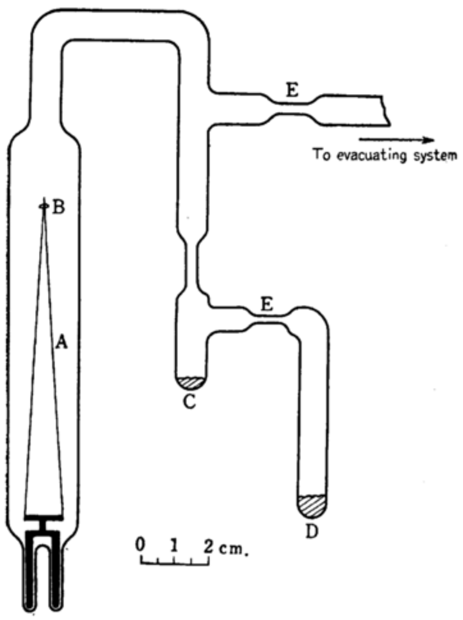

Fig. 1. Viscosity gauge.
A, quartz fiber; B, iron ring
C, sample (purified); D, sample (crude);
E, to be sealed off after evacuation.

make contact with air. The device is shown in Fig. 1[1].

Like most of other vapor pressure measuring gauges, the viscosity gauge must be calibrated with an absolute manometer, such as the McLeod or Knudsen gauge. Here, the calibration was made by subjecting the gauge to saturated vapor of carefully purified benzophenone at several temperatures at which the vapor pressure of benzophenone was already known[8]. According to Haber and Kerschbaum[5], the relation between the pressure in the gauge, P, and the damping time rebuired for the amplitude of the vibration of the fiber to decrease to its half value, t, can be expressed as follows; $P\sqrt{M}=b/t-a$. Here a and b are constants of the gauge and M is the molecular weight of the vapor in it. Thus by observing the damping time, t, at several temperatures and putting the corresponding values of vapor pressures into the above equation, the values of a and b can be determined by the method of least squares. An example of the above procedure is shown in Table I. The values of vapor pressure in the last column of the table were calculated by an equation obtained by Nitta and Seki[8]: $\log P= 12.434-4654.3/T$. The constants, a and b, thus obtained are the average values at 30°C, and correction must be made as they vary with $\sqrt{T}$ when measurements are made at different temperatures.

Most of the materials used are commercial products of high grade and are purified several times by fractional sublimation or distillation under high vacuum. Their melting points are shown in the following tables together with sublimation pressure obtained.

Table I. Relation between the damping time and the vapor pressure of benzophenone at several temperatures

T°C	t sec.	P(mmHg)$\times 10^4$
20.3	351	3.78
23.0	261	5.26
25.4	197	7.03
28.1	144	9.91
30.5	110	12.8
33.2	81.7	17.7
36.0	59.1	25.2
38.8	44.1	32.9

$a=5.66\times 10^{-4}$, $b=2.00$

Results

The observed sublimation pressures of biphenyl, diphenylmethane, dibenzyl, triphenylmethane, benzil, benzoylacetone, naphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, 2-acetylnaphthalene,

Table II. Sublimation pressure of biphenyl

T°K	P(mmHg)$\times 10^3$	T°K	P(mmHg)$\times 10^3$
279.3	0.972	290.6	3.51
281.7	1.28	292.7	4.61
282.8	1.49	295.9	6.16
285.8	2.11	297.5	7.04
288.1	2.59	299.1	8.43
289.7	3.23		

$\log P(\mathrm{mmHg})=11.168-3959.4/T$: m. p. 69.5°C

Table III. Sublimation pressure of diphenylmethane

T°K	P(mmHg)$\times 10^3$	T°K	P(mmHg)$\times 10^3$
277.9	1.26	288.4	4.52
279.3	1.48	290.8	5.70
280.9	1.79	292.3	6.44
282.6	2.22	294.4	7.75
284.1	2.71	296.0	9.16
286.4	3.57	297.9	10.26

$\log P(\mathrm{mmHg})=12.594-4307.8/T$: m. p. 26.8°C

Table IV. Sublimation pressure of dibenzyl

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
286.6	7.77	295.0	23.6
288.6	10.1	298.5	31.8
290.7	12.7	299.6	36.3
293.1	16.8	301.4	44.0
294.3	19.8	307.4	83.7

$\log P(\mathrm{mmHg})=12.194-4386.0/T$: m. p. 53.2°C

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[8] I. Nitta and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 71, 378 (1950).

acenaphthene, and *p*-acetylanisole are shown in Tables II—XIII, respectively. Vapor pressure equations for these substances, obtained by the method of least squares, are also shown together with their melting points.

TABLE V. SUBLIMATION PRESSURE OF TRIPHENYLMETHANE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
325.6	4.04	336.2	13.2
327.3	4.93	336.6	13.7
329.0	5.75	340.0	19.4
330.0	6.61	344.3	30.2
333.0	8.99	349.3	48.7

$\log P(\text{mmHg}) = 12.661 - 5227.9/T$: m. p. 94.0°C

TABLE VI. SUBLIMATION PRESSURE OF BENZIL

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
318.7	3.83	328.1	10.9
321.1	5.07	329.7	12.8
322.4	5.89	333.1	18.2
324.1	6.92	336.1	25.7
325.2	7.83	340.1	41.1

$\log P(\text{mmHg}) = 12.708 - 5140.8/T$: m. p. 95.5°C

TABLE VII. SUBLIMATION PRESSURE OF BENZOYLACETONE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
278.6	4.12	288.8	14.9
280.4	5.28	290.5	18.6
282.8	7.06	294.4	28.4
284.6	8.88	296.6	36.2
286.7	11.3	299.5	51.0

$\log P(\text{mmHg}) = 12.317 - 4374.6/T$: m. p. 58.3°C

TABLE VIII. SUBLIMATION PRESSURE OF NAPHTHALENE

T°K	P(mmHg)$\times 10^3$	T°K	P(mmHg)$\times 10^3$
275.9	6.63	281.1	11.6
277.8	8.32	283.2	14.1
279.5	9.47		

$\log P(\text{mmHg}) = 10.376 - 3462.6/T$: m. p. 81.7°C

TABLE IX. SUBLIMATION PRESSURE OF 2,3-DIMETHYLNAPHTHALENE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
278.5	3.32	287.4	9.91
280.4	4.27	290.0	13.5
282.6	5.59	291.6	15.9
283.0	5.80	293.8	20.5
283.7	6.31	295.4	24.3
284.9	7.44	297.3	29.7
285.6	7.89	301.3	45.9
286.3	8.55		

$\log P(\text{mmHg}) = 11.510 - 4172.6/T$: m. p. 105.3°C

TABLE X. SUBLIMATION PRESSURE OF 2,6-DIMETHYLNAPHTHALENE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
279.0	2.72	289.3	10.2
280.5	3.32	290.5	11.7
282.1	4.13	293.7	16.9
283.8	5.17	296.7	24.2
285.6	6.55	299.7	33.8
286.8	7.44	303.8	52.2

$\log P(\text{mmHg}) = 12.165 - 4386.4/T$: m. p. 106.2°C

TABLE XI. SUBLIMATION PRESSURE OF 2-ACETYLNAPHTHALENE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
295.1	3.95	305.5	13.3
297.2	5.16	309.5	21.3
299.3	6.59	315.8	41.4
302.5	9.49		

$\log P(\text{mmHg}) = 12.153 - 4589.9/T$: m. p. 55.8°C

TABLE XII. SUBLIMATION PRESSURE OF ACENAPHTHENE

T°K	P(mmHg)$\times 10^3$	T°K	P(mmHg)$\times 10^3$
291.1	1.03	298.3	2.40
292.2	1.20	301.0	3.22
292.9	1.29	304.4	4.64
293.8	1.44	307.3	6.20
295.8	1.79	310.6	8.54
297.3	2.09		

$\log P(\text{mmHg}) = 11.758 - 4290.5/T$: m. p. 95.0°C

TABLE XIII. SUBLIMATION PRESSURE OF *p*-ACETYLANISOLE

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
275.8	4.53	287.4	18.1
277.7	5.72	289.1	21.9
280.3	7.78	293.1	33.9
282.0	9.76	296.4	48.3
284.4	12.8	298.8	61.6
285.1	13.8	300.4	72.4

$\log P(\text{mmHg}) = 11.367 - 4056.1/T$: m. p. 38.4°C

Some of the results of the measurements of sublimation pressure of biphenyl, published previously by several investigators[9-11], are compared in Fig. 2 with the author's. As can be seen in the figure, the author's result is in good agreement with that of Seki and Suzuki, while the others show considerable deviations from the author's, Bradley's data being too high and Bright's too low. The fact that the results obtained by different methods, i. e., a method using viscosity gauge by the

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9) N. F. H. Bright, *J. Chem. Soc.*, **1951**, 624.

10) S. Seki and K. Suzuki, This Bulletin, **26**, 209 (1953).

11) R. S. Bradley, *J. Chem. Soc.*, **1953**, 1690.

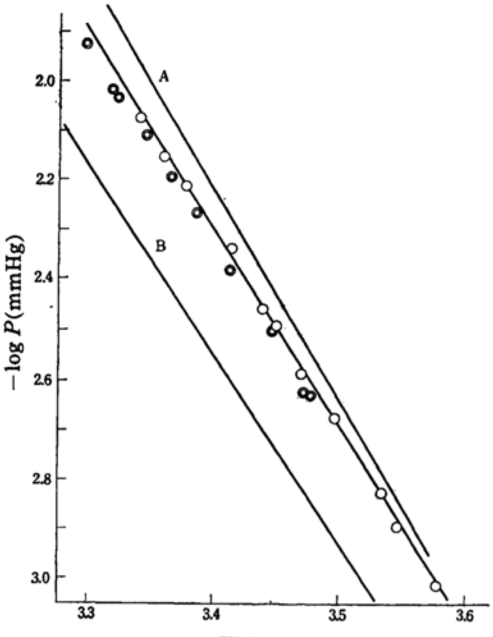


Fig. 2. Sublimation pressure of biphenyl.
○, Aihara; ◎, ▲ Seki & Suzuki;
A, Bradley; B, Bright.

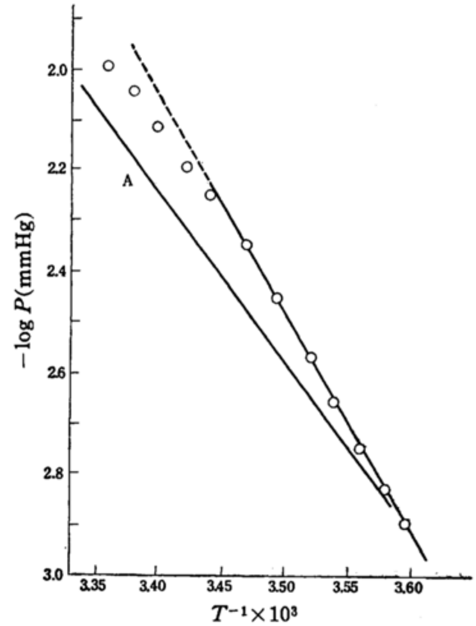


Fig. 3. Sublimation pressure of diphenylmethane.
○, Aihara; A, Bright.

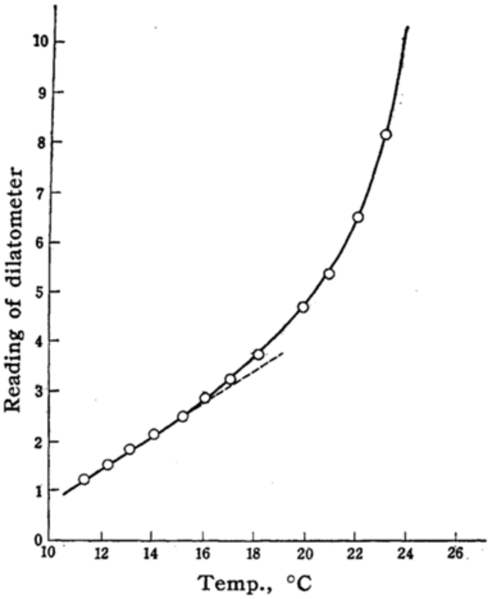


Fig. 4. Dilatometry of diphenylmethane. Reading of dilatometer is in an arbitrary scale.

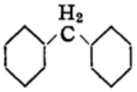
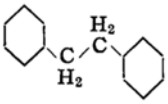
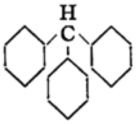
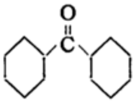
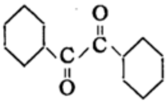
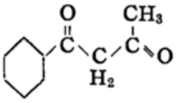
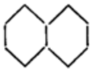
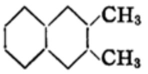
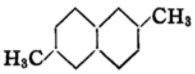
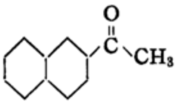
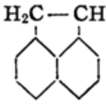
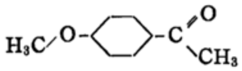
author and an effusion method by Seki and Suzuki, give a good agreement, clearly shows the reliability of these data.

The sublimation pressure of diphenylmethane measured by Bright[9] is again lower than the author's result, the linear relation between $\log P$ and T^{-1} showing a smaller inclination compared with the author's. (Fig. 3). Plotting the experimental values of $\log P$ against T^{-1}, it is noticed in the author's measurement that there occurs a change in the linear relation between $\log P$ and T^{-1} at about 15°C and upward. Roughly speaking, the relation between $\log P$ and T^{-1} after this change goes almost parallel with that of Bright's. Also a simple dilatometric measurement revealed the occurrence of a change in the expansion coefficient of diphenylmethane at about 15°C. (Fig. 4). Although the nature of this transitional change is not clear as yet, it is likely that Bright missed it, putting too much weight on observed values of sublimation pressure above 15°C. The vapor pressure equation shown in Table III is, thus, valid for the temperature range below 15°C.

Bright's[9] result on the sublimation pressure of dibenzyl deviates similarly from the author's as was seen in the two cases mentioned above: the vapor pressure equation and the heat of sublimation obtained by Bright are, $\log P=9.86-3783/T$, $\Delta H=17.3$ kcal./mol., while the author's are $\log P=12.194-4386.0/T$ and $\Delta H=20.07$ kcal./mol.

Of the other substances dealt with in this paper, mention should be made of the

TABLE XIV. VALUES OF THERMODYNAMIC FUNCTIONS

Compounds	ΔH_{obs} kcal./mol.	ΔH_{calc} kcal./mol.	$\Delta G^{298.2°K}$ kcal./mol.	ΔS cal./deg. mol.
	18.12±0.14	18.0	6.81±0.28	37.9±0.5
	19.71±0.15	20.0	6.45±0.31	44.5±0.5
	20.07±0.11	22.0	7.36±0.22	42.6±0.4
	23.92±0.14	29.0	10.58±0.26	44.8±0.4
	21.30 [8]	21.5	8.26 [8]	43.7 [8]
	23.52±0.27	25.0	10.11±0.55	45.0±0.9
	20.02±0.10	20.0	7.14±0.21	43.2±0.4
	15.84±0.54	15.5	5.61±1.12	34.3±1.9
	19.09±0.07	19.5	7.31±0.14	39.5±0.2
	20.07±0.09	19.5	7.40±0.18	42.5±0.3
	21.00±0.10	21.0	8.35±0.20	42.4±0.3
	19.63±0.10	19.5	7.52±0.21	40.6±0.4
	18.56±0.05	18.5	6.98±0.11	38.8±0.2

result of sublimation pressure of naphthalene. There are plenty of data on the sublimation pressure of naphthalene published already in literatures[11-13], but strangely none of them coincide with one another. The author's value of sublimation pressure lies between those of Bradley[11]* and Andrews[13], while $\Delta H=15.84$ kcal./mol. by the author agrees well with Zilberman-Granovskaya's[12] value, $\Delta H=15.7$ kcal./mol., and Wolf's[14] value, $\Delta H=15.9$ kcal./mol. The differences between the various results must be due to different degrees of purity of the samples with which the determinations were made, and also due to the inaccuracy of the methods of determination.

The values of some thermodynamic functions of the substances derived from vapor pressure equations are shown in Table XIV.

Additivity of Lattice Energy

Inspection of the relation between the heats of sublimation and the molecular structures of the compounds listed in Table XIV suggests that an additivity rule may be applied to the lattice energies of these crystals, at least as a first approximation. Now let it be assumed that each constituent group of a molecule, such as methyl, carbonyl, phenyl, etc., makes a contribution to the lattice energy independently. Then, if we allot an appropriate energy to each group, it should be possible to get a "calculated lattice energy" of a compound in question. The third column of Table XIV shows the values of lattice energies thus calculated for compounds dealt with in this paper, with the following values of allotted lattice energies for constituent groups. (Table XV). Notwithstanding the approximate nature of the method of calculation, the agreement between observed and calculated values of lattice energies, i. e., ΔH_{obs} and ΔH_{calc}, is quite satisfactory, as can be seen in Table XIV. Disagreement noticed in a few cases, such as dibenzyl, triphenylmethane and benzil, can be ascribed to the bulky structure of the molecules which prevents the close approach of constituent groups to each other, thus decreasing the amount of contribution to the lattice energy to some extent.

TABLE XV. ALLOTMENT OF LATTICE ENERGIES TO GROUPS

Groups	Energy kcal./mol.	Groups	Energy kcal./mol.
CH, CH_2, CH_3	2.0	O-CH_3	4.0
NH, NH_2	2.0	C_6H_5	9.0
OH	2.0	$C_{10}H_7$	15.5
C=O	3.5	*t*-Butyl	5.5

In Table XV, the value for phenyl group, 9.0 kcal./mol., was determined by dividing the heat of sublimation of biphenyl, 18.1 kcal./mol., by two: this value is very close to the heat of sublimation of benzene obtaind by Trieschmann, 9.2 kcal./mol.[15] The value for naphthyl group, 15.5 kcal./mol. is close to the average of the heat of sublimation of naphthalene determined by the author, Wolf[14], and Zilberman-Granovskaya[12]. As to the increment of lattice energy due to a methyl (or methylene) group, several investigators have published the following values: 2.3 kcal./mol. by Müller[16], 1.5 kcal./mol. by Inokuchi[17], 1.7~2.2 kcal. mol. by Moelwyn-Hughes[18], 1.1~1.7 kcal./mol. by Davies[19]. The author's value, 2.0 kcal./mol., is the average of the above values and those obtained by analyzing the data in Table XIV. The same value is assigned to amino and hydroxyl groups as that of a methyl group, because these molecules are all isoelectronic. The validity of assigning the same value to these groups will be confirmed in succeeding papers where the lattice energies of phenols, amides and amines will be discussed. Also Bondi and Simkin[20] have discussed this problem. The value for a carbonyl group, 3.5 kcal./mol., was obtained by analyzing the heats of sublimation of benzophenone, benzoylacetone, 2-acetylnaphthalene and some other compounds having a carbonyl group. The value for a *tert*-butyl group was derived from the heat of sublimation of 1, 4-di*tert*-butylbenzene[21]. 4.0 kcal./mol. for

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12) Zilberman-Granovskaya, *J. Phys. Chem.* (*U.S.S.R.*), **14**, 759 (1940):

$$\log P=10.41-3429/T,\ \Delta H=15.7\ \text{kcal./mol.}$$

13) M. R. Andrews, *J. Phys. Chem.*, **30**, 1497 (1926):

$$\log P=12.275-4000/T,\ \Delta H=18.28\ \text{kcal./mol.}$$

* Bradley's data:

$$\log P=11.597-3783/T,\ \Delta H=17.3\ \text{kcal./mol.}$$

14) K. L. Wolf and H. Weghofer, *Z. physik. Chem.*, **B39**, 194 (1938).

15) H. G. Trieschmann, Dissertation, Kiel (1935).

16) A. Müller, *Proc. Roy. Soc.* (*London*), **A154**, 124 (1936).

17) H. Inokuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 552 (1951).

18) E. A. Moelwyn-Hughes, "Physical Chemistry", Pergamon Press, London (1957), p. 682.

19) M. Davies, private communication.

20) A. Bondi and D. J. Simkin, *J. Chem. Phys.*, **25**, 1073 (1956).

21) E. R. Hopke and G. W. Sears, *J. Chem. Phys.*, **19**, 1345 (1951).

a methoxyl group was determined by subtracting the allotted lattice energies for methyl and carbonyl groups from the heat of sublimation of *p*-acetylanisole.

It must be admitted that the treatment of lattice energies of organic molecular crystals discussed above is quite rough and could not be applied to more complicated cases without further refinement. Still, an orthodox way of calculating lattice energies, such as by Slater-Kirkwood formula[4] or by other ways, does not necessarily give a satisfactory agreement between calculated and observed lattice energies, as has been pointed out by Seki and his collaborators[22]. Therefore, it would be helpful, at the present stage, to have an approximate way of estimating lattice energies of molecular crystals empirically, as is proposed in this paper. This procedure will be used later to get the energy of hydrogen bond in crystals of phenols, amides and amines.

Summary

Sublimation pressures of a number of organic molecular crystals were measured by a viscosity gauge. The heats of sublimation of these compounds were examined in relation to their molecular structures, and it was concluded that an additivity rule could be applied to the lattice energies of these crystals as a first approximation.

The author wishes to thank Professor M. Davies, the University of Wales, for informing the author about some of his results prior to publication. The cost of the work was partly defrayed by the financial support of the Ministry of Education to which the author's thanks are due.

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