Physicochemical Studies of Molecular Compounds. V. Heats of Solution of 1,3,5-Trinitrobenzene, Naphthalene and Anthracene in Benzene. Heats of Solution and Heats of Formation of Molecular Compounds of 1,3 5-Trinitrobenzene with Benzene, Naphthalene and Anthracene

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Introduction

In the two previous papers we have reported the results of our investigations on the vapor pressure[1] and the heat of formation[2] of quinhydrone crystal which is one of the typical colored organic molecular compound. As is well known, on the other hand, there are a large number of organic molecular compounds which are formed between polynitrobenzenes and aromatic polynuclear hydrocarbons. Although phase diagram investigations and spectroscopic studies in the solution state of these molecular compounds have been hitherto accumulated, there is not yet known any energetic investigation in their crystalline state. In this respect, we have undertaken to study the substances mentioned above, to get further insight into the nature of the interaction energy between the component molecules.

Experimental

1) Sample

a) Naphthalene and Anthracene.—These samples were given by the courtesy of Dr. M. Wayaku of the Central Research Institute of Osaka Gas Company. The purity of the sample determined by him was: 99.96% for naphthalene and 99.6% for anthracene.

b) 1, 3, 5-Trinitrobenzene (TNB for brevity).—This material was prepared from 2, 4, 6-trinitrobenzoic acid by the ordinary method[*] and then recrystallized twice from glacial acetic acid, m.p. 125.0–125.5°C.

c) Molecular Compound (MC for brevity) of TNB with Naphthalene in (1: 1) Molar Ratio.—This was prepared by slow evaporation of the solvent from acetone solution containing two components in the 1: 1 molar ratio. The precipitated small crystals on the bottom of the container were picked up. This MC decomposes slowly in the air, so we stored them in a disiccator with a small amount of naphthalene to prevent the preferred evaporation of naphthalene from the MC, m.p. 154.5–155.5°C.

d) MC of TNB with Anthracene in 1: 1 Molar Ratio.—By gradual cooling of the alcoholic solution containing two components in the 1: 1 molar ratio, we obtained this MC, m.p. 162.8–163.3°C.

e) MC of TNB and Benzene in 1 : 1[**] Molar Ratio.—By slow evaporation of benzene solution containing TNB we can obtain the precipitates of MC. This MC decomposed immediately, however, if we picked it up from the mother liquor at ordinary temperature, so we could not obtain pure MC having the 1: 1 ratio. Therefore, we divided the sample into six parts and sealed them as quickly as possible into six small glass bulbs having nearly the same volume. Then, a half of them were used for the analysis to determine the composition just at the beginning of the experiment. In order to determine the chemical composition of these samples, we weighed the sample together with the bulb, then made a small hole on its glass wall and placed it under high vacuum (10^{-5}mmHg) for about eight hours and then weighed it again. As the vapor pressure of TNB is very low at room temperature, we can ascertain by calculation that the loss of TNB during this procedure is negligible. After the decrease of the weight stopped, we confirmed finally by the chemical analysis of the nitrogen-content that the specimens were completely converted into TNB. Accordingly, all the samples employed for experiments are the mixture of MC and TNB (see Table VII).

2) Apparatus and Procedures

The calorimeter used for the determination of the heat of solution is essentially the same as before[2], only with some improvements for making it possible to measure the smaller heat effect. The main thermel for the measurement of temperature difference between the calorimeter

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[1] I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Papers from Osaka Univ.*, No. 29 (1951).

[2] K. Suzuki and S. Seki, This Bulletin, 26, 372 (1953).

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[*] See for example: Gilman, Organic Synthesis, Collected Vol. 1, P. 543.

[**] As to the composition of this MC, there are two alternative views of 1: 1 or 1: 2 molar ratio of TNB and benzene. We have been informed by private communication from Professor C.H. McGillavry at the University of Amsterdam that the 1: 1 compositions are much more reasonable by their preliminary crystal structure determination.

and fluctuation damper was made from 40 junctions of copper-constantan thermocouple. The fluctuation damper was made of a copper block cylinder 4 cm. in diameter and 7 cm. in height, in which 7 narrow wells (2 mm in diameter, 4 cm. in depth) are drilled for the insertion of the junctions of the thermel. By these improvements we could measure the temperature variation of 0.00005°C. When the glass bulb used as the container of the sample was destroyed, it was found that some amounts of heat were absorbed due to the evaporation of the solvent into the free space of the container. Using benzene as the solvent, we deter mined this heat ΔH by employing the empty bulbs of various sizes and found that it is expressed by the following equation,

$$\Delta H(\text{cal.})=0.038v,$$

where v is the volume of the free space in the bulb in cc. All the measurements were carried out at 25°C. In order to check the amount of the heat of dilution, we measured the heats of solution at various concentrations.

Results and Discussion

The heats of solution of the components as well as those of MC's are all given in Tables I∼VI. It may be noticed here that the heats of solution of TNB decrease with the increase of the concentration of the solution, while those of naphthalene behave oppositely. For naphthalene and TNB (Table I and II) the extrapolated values to the infinite dilution are also given. They were calculated by assuming the following linear equation,

$$\Delta H_{\text{soln.}}(C)=\Delta H^{\infty}_{\text{soln.}}+C\Delta H_{\text{diln.}}$$

where $\Delta H_{\text{scln.}}(C)$ stands for the heat of solution at the concentration C, $\Delta H^{\infty}_{\text{soln.}}$ the heat of solution at infinite dilution, and $\Delta H_{\text{diln.}}$ the heat of dilution. The heats of solution of the other sub-

TABLE I

HEATS OF SOLUTION OF TNB

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar Ratio		ΔH kcal./mol.
		initial	final	
1	1.3048	0.00000	0.00114	2.593
1′	1.3261	0.00000	0.00134	2.572
2	1.4032	0.0017	0.00234	2.560
2′	1.3718	0.00134	0.00256	2.572
3	1.4964	0.00230	0.00306	2.527
		Extraporated to zero concentration		2.601±0.011

TABLE II

HEATS OF SOLUTION OF NAPHTHALENE

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar Ratio		ΔH kcal./mol.
		initial	final	
1	0.8507	0.00000	0.00134	4.212
2	0.8958	0.00134	0.00277	4.214
3	0.8486	0.00277	0.00420	4.272
4	0.8520	0.00420	0.00555	4.233
5	0.9100	0.00554	0.00690	4.257
6	0.8582	0.00690	0.00826	4.296
		Extraporated to zero concentration		4.205±0.013

TABLE III

HEATS OF SOLUTION OF ANTHRACENE

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar Ratio		ΔH kcal./mol.
		initial	final	
1	0.6402	0.00000	0.00036	5.768
2	0.6693	0.00036	0.00130	5.858
3	0.6664	0.00130	0.00187	5.870
4	0.6738	0.00187	0.00266	5.853
		Average		5.812±0.020

TABLE IV

HEAT OF SOLUTION OF (1:1) MC OF NAPHTHALENE AND TNB

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar Ratio (MC/Benzene)		ΔH kcal./mol.
		initial	final	
1	1.2016	0.00000	0.00063	7.893
2	1.4030	0.00062	0.00136	7.950
3	1.0532	0.00136	0.00206	7.957
4	1.1775	0.00207	0.00263	7.905
		Average		7.926±0.011

TABLE V

HEAT OF SOLUTION OF (1:1) MC OF ANTHRACENE AND TNB

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar Ratio (MC/Benzene)		ΔH kcal./mol.
		initial	final	
1	0.8850	0.00000	0.00040	8.785
2	0.8647	0.00040	0.00080	8.770
3	0.8523	0.00080	0.00119	8.689
	0.4912	0.00119	0.00142	8.772
		Average		8.754±0.015

TABLE VI

HEAT OF SOLUTION OF THE MIXTURE OF TNB AND OF (1 : 1) MC OF BENZENE AND TNB

No.	Weight of the Sample used. (g)	Concentration of Solution in Molar ratio (MC/Benzene)		ΔH cal./g.
		initial	final	
1	1.6800	0	0.00141	12.73
2	1.1809	0	0.00081	12.02
3	1.3164	0	0.00089	13.10
		Average		12.74±0.18

stances are independent of the concentrations within the experimental errors, so the average value for each material may be looked upon directly as the heat of solution at infinite dilution. Among these results, only that of naphthalene is known.[3] This reported result, however, is less accurate and without any description of the concentration and temperature at which the experiment was carried out, so we do not compare it with ours.

The results of analysis on the composition of the MC between TNB and benzene are given in Table VII. As is evident, the residue, after the evacuation, consists completely of pure TNB. In spite of the special care taken to avoid the preferred evaporation of benzene, it was found that the sample for the experiments was decomposed already to a considerable extent.

TABLE VII

BENZENE CONTENTS OF THE SAMPLES IN TABLE VI

Amount of benzene determined by the loss of weight on evaparation:	18.7±0.4% (average of three samples)
Amount of benzene in residue*:	0.0±0.05%

*Chemical analysis of N_2 in the residue:	observed value	19.63%
	calculated value (TNB)	19.72%

Now, the heats of formation ΔH_f^c, of MC from the components in their crystalline state except that between benzene and TNB, can be calculated as the difference of ΔH^{∞}_{soln} of MC and the sum of those of component crystals, since at the infinite dilution the interactions between solute molecules may be negligible. In the above-mentioned case of MC of benzene and TNB pure MC can not be obtained, so that the data given in Table VI should correspond to the heats of the solution of the mixture of MC and TNB. The heat of formation ΔH_f^l of pure MC (1: 1) from TNB and liquid benzene may be, therefore, calculated by the following relation

$$\Delta H_f^l = \{Q-(1-x)Q_o\}/(x/M_B)$$

where Q is the observed heat of solution of the specimen in the unit of cal./g, Q_o the heat of solution of pure TNB in the same unit, x the weight fraction of benzene in the specimen and M_B the molecular weight of benzene. The heats of formation ΔH_f^g from the gaseous components or the lattice energies of the crystalline MC's, were calculated from ΔH_f^c (or ΔH_f^l) and the heats of sublimation (or vaporization) of each component.

The heats of formation of the three MC's measured by us are given in Table VIII, together with the binding energies of the MC's in the solution determined by Briegleb et al. for reference.[4] In this table, the heat of formation of MC between benzene and TNB from the component crystals ΔH_f^c was calculated by subtracting the heat of fusion of benzene (2.351 kcal./mol.)[5] from the $\Delta H_f^l = 3.05 \pm 0.26$ kcal./mol. As shown in this table, ΔH_f^g, the total interaction energies increase with the order of benzene, naphthalene and anthracene while ΔH_f^c the specific interaction energy between the component molecules, empirical net MC formation energy, is largest for the MC of TNB and naphthalene. As to the latter fact, we shall discuss later more in detail.

On examining the Table 8 it is worth while noticing the following two facts that (i) our values of heat of formation of these MC's determined above are different from those for solution and that (ii) binding energies in solution depend on solvents used and even their relative order of

TABLE VIII

HEAT OF FORMATION OF MC IN CRYSTALLINE AND IN SOLUTION STATES (kcal./mol.)

State		Benzene-TNB MC	Naphthalen-TNB MC	Anthracene-TNB MC
Heat of Formation of MC from gaseous molecules	ΔH_f^g	−34.9	−40.7	−46.9
Heat of Formation of MC from component crystals	ΔH_f^c	−0.70±0.26	−1.120±0.035	—0.341±0.046
Heat of Formation in Solution				
CCl_4 Solution*		− 0.6	− 3.45	− 4.4
$C_2H_2Cl_4$ Solution		——	——	− 3.6
Ether Solution*		——	− 0.99	− 2.1
Benzene Solution*		——	− 1.90	− 0.98

* see ref. (4)

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3) G. Gehlhoff, *Z. Physik. Chem.*, 98, 252 (1921). $\Delta H = 4.42$ kcal./mol.

4) G. Briegleh and T. Schachowsky, *Z. Physik. Chem.*, B19, 255 (1932).

5) F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert and J. F. Kilpatrick, Selected Values of Properties of Hydrocarbons (1947).

magnitude for the naphthalene MC and anthracene MC for different solvents shows a different trend. Although the latter fact (ii) seems to be a little unreasonable at first sight, it is natural if we consider the meaning of this binding energy more in detail. In the solution, all the solute molecules are not isolated as they are in the gaseous state, but surrounded by many solvent molecules, forming a kind of cluster with their neighbouring solvent molecules. Therefore, these energies do not correspond to the genuine binding energies of MC's, but to the heats of reaction of the following equation,

$$\text{Hydrocarbon (solvent) } z_{\mathrm{H}} + \text{TNB}\cdot\text{(solvent) } z_{\mathrm{T}}$$
$$= \text{MC}\cdot\text{(solvent) } z_{\mathrm{M}} + (Z_{\mathrm{H}} + Z_{\mathrm{T}} - Z_{\mathrm{M}}) \text{ solvent}$$

where Z_{H}, Z_{T} and Z_{M} are the numbers of solvated molecules on a molecule of the aromatic hydrocarbon, TNB and MC, respectively. Accordingly, to obtain a genuine binding energy of MC, all the heats of solvation in the equation must be known. At present, however, it is impossible to find out an adequate way of estimating the heat of solvation for the MC's, so we should be contented with the prediction that the contribution of these energies would not be ignored. The energies of solvation for the component molecules can be estimated by the following relation,

$$\Delta H^{\infty}_{\mathrm{solv.}} = \Delta H^{\infty}_{\mathrm{soln.}} - \Delta H_{\mathrm{sub.}},$$

where $\Delta H^{\infty}_{\mathrm{solv.}}$ and $\Delta H^{\infty}_{\mathrm{soln.}}$ the heats of solvation and of solution at infinite dilution, $\Delta H_{\mathrm{sub.}}$ the heat of sublimation, respectively. $\Delta H^{\infty}_{\mathrm{solv.}}$ obtained by this way are given in Table IX. Data for diphenyl and α-mononitronaphthalene are also given for reference. We can realize that the amount of $\Delta H^{\infty}_{\mathrm{solv.}}$ is much larger than Briegleb's apparent binding energy between component molecules in MC, so that only a slight change in the number of the solvating molecules, which should occur on the MC formation from the component molecules, would cause a change of energy presumably amounting to a few kcal./mol. We must, therefore, discuss with sufficient precaution the meaning of apparent binding energy in solution state.

TABLE IX

SOLVATION ENERGY DENSITIES AND SOME RELATED DATA OF SOME AROMATIC COMPOUNDS

	ΔH_{sub}	$\Delta H^{\infty}_{\mathrm{soln}}$	$\Delta H^{\infty}_{\mathrm{solv}}$	ρ	V	$\Delta H^{\infty}_{\mathrm{solv/V}}$
Benzene			-8.09[8]	1.08	72.2	0.112
Naphthalene	15.8[6a]	4.205	-11.6	1.158	110.6	0.105
Anthracene	22.8[6b]	5.812	-17.0	1.245	143.1	0.119
Diphenyl	17.9[6c]	4.31 [7]	-13.6	1.165	132.2	0.103
TNB	23.8[6d]	2.601	-21.2	1.687	126.4	0.168
α-mononitro-naphthalene	25.6[6d]	5.38 [7]	-20.2	1.331	130.1	0.155

ρ: density. V: molecular volume in c.c. ΔH: kcal./mol.

In this connection, we should like to refer to the mode of the interaction between solvent and solute molecules at infinite dilution. For this purpose, we may define the quantity $\Delta H^{\infty}_{\mathrm{solv.}}/V$ in which V stands for the molecular volume of the solute in crystalline state*. This may be called the solvation energy density. In other words, this may be useful as one of the measures of the deviation from the ideal solution. In the last column of Table IX we can see that these quantities for the aromatic hydrocarbons are nearly equal, whreas those for nitro compounds are larger than those for hydrocarbons and increase with the number of nitro groups. This fact will indicate that the interactions between nitrocompounds and hydrocarbons should be discussed with cautions.

Finally a few remarks may be given below on the nature of the specific binding energy which appears on the formation of these MC's.

i) In comparison with the heat of formation $\Delta H^{\mathrm{c}}_{\mathrm{f}}$ of quinhydrone which comes out 5.387 kcal./mol., those of the present materials are much smaller. In the former, the energy contribution due to the enhancement of the strength of the hydrogen bond on the formation of the molecular compound and also the electrostatic force due to the migration of changes as suggested by Murakami might play a more or less important role. Judging from the order of magnitude of the heats of formation of the present MC's, we may conclude that the nature of the interaction in these MC's can neither be of a covalent bond nor of an ionic one, but rather it seems to be a kind of weaker interaction given by the theory of quantum-mechanical second order perturbation such as the induction or the intermolecular charge transfer forces.

ii) Diamagnetic properties[9] of these MC's indicate that the constituent molecules have no unpaired electron and the normal states of these molecules are in one of the singlet states. This fact excludes the possibility of any type of free radical with ion pair such as TNB^{-} and $\mathrm{anthracene}^{+}$.

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[6] (a) K.L. Wolf et al, *Z. Physik. Chem.*, **B29**, 194 (1938); A.A. Zilberman and Granovskaya, *Chem. Abst.*, **35**, 3867 (1941). (b) I. Nitta, S. Seki and M. Momotani, *J. Chem. Soc. Japan*, **71**, 430 (1950). (c) S. Seki and K. Suzuki, This Bulletin, **26**, 209 (1953). (d) I. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, **71**, 378 (1950).

[7] International Critical Table.

[8] Heat of vaporization of benzene taken from ref (5).

* Strictly speaking, we must use the molecular volumes for the solutions at infinite dilution. However, they are not yet known at present.

[9] R.C. Sahney, S. L. Aggarwal and M. Singh, *J. Indian. Chem. Soc.*, **23**, 335 (1946).

iii) Nakamoto[10] measured the absorption spectrum of the crystalline anthracene-TNB MC and found that the absorption of light with electric vector perpendicular to the molecular plane is much stronger than that of the light with parallel vector. On the basis of this intensity ratio, two types of assignment for this absorption band may be possible, i.e. intermolecular charge transfer[11] and $n \rightarrow \pi$ transition spectra.[12] If we examine the intensity relation closely, however, the former seems to be more plausible. For, the order of magnitude of the absorption due to the $n \rightarrow \pi$ transition is ordinarily not so strong. In fact, the absorption due to the $n \rightarrow \pi$ transition of most of nitrobenzene derivatives has not been detected in crystalline state because of the overlapping with more intense absorption due to $\pi \rightarrow \pi$ transition[13]. From this point of view, the mechanism of intermolecular charge transfer may be more probable for the explanation of the interaction of these MC's.

iv) If we assume that the origin of interaction in this MC consists of an induction effect of polarizable electrons of aromatic hydrocarbons caused by the strong field of dipole moment of NO_2 groups as proposed by Briegleb[14], then we may expect the order of the relative strength of the interaction in *s*- trinitro- and *m*- dinitro benzene MC's as follows:

anthracene-TNB > naphthalene-TNB >
benzene-TNB
and
anthracene-DNB > naphthalene-DNB >
benzene-DNB

However, the magnitudes of the heats of formation of the MC's of TNB found by us do not go parallel with the above order and, moreover, in the latter series we can isolate only the MC of naphthalene-DNB as a stable crystal[15]. Accordingly it seems to be inappropriate to explain the origin of these MC's only by this view at least in the crystalline state.

For the discussion of the relative strength of interaction from the viewpoint of intermolecular charge transfer mechanism, data of ionization potential of these hydrocarbons are highly desirable. Unfortunately, the data for anthracene is not yet known, so we will not carry on the present discussion further.*

In conclusion the authors wish to express their sincere thanks to Professor Nitta for his kind suggestions and encouragement throughout this work and to Dr. Wayaku of the Central Research Laboratory of Osaka Gas Company for his gift of pure naphthalene and anthracene and also for pertinent data on them. Appreciation should be also expressed to Professor C. H. McGillavry for her kind information on the cell dimension of the Benzene-TNB MC in advance of publication and to Mr. Ônishi for his collaboration in the work of measurement. The expense of this research was partly defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the thanks of the present authors are due.

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[10] K. Nakamoto, This Bulletin, **26**, 70 (1953).

[11] R.S. Mulliken. *J. Phys. Chem.*, **56**, 801 (1952).

[12] K. Nakamoto and K. Suzuki, *J. Chem. Phys.*, **20**, 1971 (1952),

[13] K. Nakamoto, *J. Chem. Soc. Japan*, **71**, 621 (1949).

[14] G. Briegleb, *Z. Physik. Chem.*, **B26**, 63 (1934).

[15] See Landolt-Börnstein's Table.

* Recently, people calculated theoretically the ionization potentials of these unsaturated hydrocarbons; benzene, 9.76 e.v., naphthalene, 8.28 e.v. and anthracene, 7.38 e.v. (*Trans Faraday Soc.*, **49** 1375 (1953)). If we utilize his results, we can find that the order of the strength of interaction energies of these MC's can not be explained on the basis of the mechanism of intermolecular charge transfer, so far as we take only the ionization potential into consideration. We are indebted to Dr. Nagakura for his kind information on the reference given above.