

SHORT COMMUNICATIONS

VAPOUR PHASE SPECTRUM AND ENTHALPY OF SUBLIMATION OF NAPHTHACENE*†

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The determination of the enthalpy of sublimation of organic compounds is of interest to us as this thermodynamic quantity enables a comparison to be made between the lattice energies of the various members of the phthalocyanine series. Most organic compounds have sufficiently high vapour pressures to permit the use of diffusion techniques, but the extremely small vapour pressures of the phthalocyanines¹ restrict the range of measurements to temperatures at which decomposition is known to occur^{1,2} at a measurable rate. These difficulties were overcome by using an optical technique similar to that used by Stafford,³ Jortner,⁴ and Stevens.⁵ However, it was considered necessary to demonstrate the applicability of the method by measuring the enthalpy of sublimation of some standard organic compound over a temperature range in which the vapour pressures were comparable to those of the phthalocyanines. Naphthacene was used as the standard and we publish the result here as there appears to be some controversy in the literature⁶ over the most probable value. It was necessary to record the vapour phase spectrum and it is considered that this is of interest as previously unresolved⁷ structure is now apparent.

An excess of naphthacene was introduced into a 50-cm absorption cell in such a way that it remained in the section which was normally in the coolest portion of the furnace. This Pyrex glass cell had optically flat windows and it was sealed off at the pump after baking and outgassing. A Sunvic proportional controller maintained the selected temperature to $\pm 0.5^\circ$ and the windings of the heater coils were adjusted to ensure that the ends of the tube were always $6-10^\circ$ higher than the section in which the naphthacene sample was located. The intensity of the transmitted radiation was recorded continuously during an experiment and the record showed that equilibrium was attained 40 min after each change in temperature. The light source, monochromator, and detector have been described elsewhere;² in this experiment a collimated beam of light was passed through the cell and brought to a focus at the entrance slit of the monochromator. The zero and 100% transmissions were

* Supported by a grant from the Australian Institute of Nuclear Science and Engineering.

† Manuscript received May 15, 1964.

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¹ Lawton, E. A., *J. Phys. Chem.*, 1958, **62**, 384.

² Fielding, P. E., and Mackay, A. G., *Aust. J. Chem.*, 1964, **17**, 750.

³ Stafford, F. E., *J. Chem. Ed.*, 1963, **40**, 249.

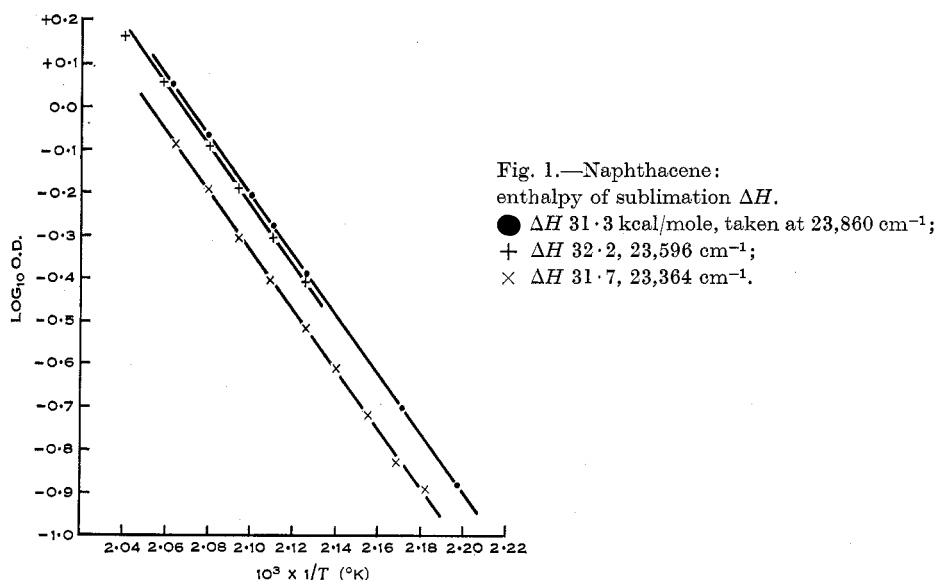
⁴ Jortner, J., Wilson, E. G., and Rics, S. A., *J. Amer. Chem. Soc.*, 1963, **85**, 814.

⁵ Stevens, B., *J. Chem. Soc.*, 1953, 2973.

⁶ Bradley, R. S., and Cleasby, T. G., *J. Chem. Soc.*, 1953, 1691.

⁷ Williams, R., and Goldsmith, G. J., *J. Chem. Phys.* 1963, **39**, 2008.

checked before and after a run and the zero was also monitored during a run. As a check on the method it was decided to measure the enthalpy of sublimation by



recording the variation of optical density with temperature for three different absorptions at 23,810, 23,595, 23,365 cm^{-1} (see Fig. 1). The results shown in Figure 1

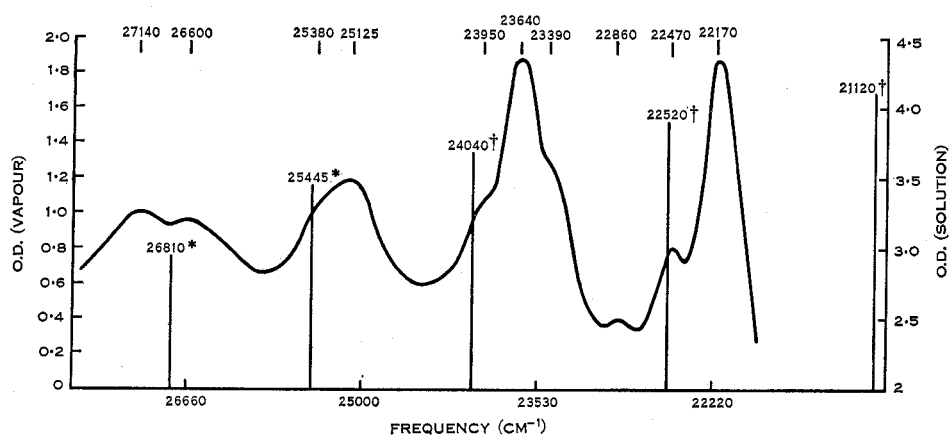


Fig. 2.—Naphthalene vapour (219°) and solution (in benzene; from Clar⁸) spectra. Vertical lines represent positions of absorption maxima in solution. * Clar⁸; † present work.

give a mean value of 31.7 ± 0.6 kcal mole⁻¹ for the enthalpy of sublimation (ΔH). This is to be compared with Inokuchi's⁹ value of 27.1 kcal mole⁻¹ at the same temperature (186°).

⁸ Clar, E., "Aromatische Kohlenwasserstoffe," p. 233. (Springer-Verlag: Berlin 1952.)

⁹ Inokuchi, H., Shiba, S., Handa, T., and Akamatu, H., *Bull. Chem. Soc. Japan*, 1952, 25, 299.

The vapour phase spectrum (Fig. 2) is very similar to that recently reported by Williams and Goldsmith⁷ except for a slight difference in the relative intensities of the peaks. More structure is resolved as the vapour was at 219° whereas the above workers used 320°. The absorption spectrum of naphthacene in benzene is included for comparison. A displacement of about 1100 cm⁻¹ to the red occurs on going from the vapour to solution.

TABLE 1
LATTICE ENERGIES ΔE
 ΔE in kcal mole⁻¹

Compound	No. of Carbon Atoms <i>n</i>	Bradley and Cleasby ⁶				Inokuchi <i>et al.</i> ⁹			
		Temp.	ΔE	$\Delta E/n$	Ref.	Temp.	ΔE	$\Delta E/n$	Ref.
Benzene	6	5°	10.6	1.77	10	—	9.2	1.53	12
Naphthalene	10	6–20°	17.3	1.73	6	15–33°	15.3	1.53	12,13
Anthracene	14	65–80°	24.4	1.74	6,11	92°	21.3	1.52	8
Naphthacene	18	180–210°	30.6	1.70	*	186°	27.1	1.51	8

* Present work.

The lattice energies (ΔE) for various aromatic compounds are given in Table 1 and the data fall into two groups; those listed under the heading of "Bradley and Cleasby" are thought to be the more reliable.¹⁴ We have placed our value of 30.6 kcal mole⁻¹ under this as the lattice energy per carbon atom is in good agreement with those for the other members of the group. Inokuchi *et al.*⁹ have remarked that their value was lower than the figure of 29.7 kcal mole⁻¹ obtained by Magnus *et al.*¹⁵ from heats of solution measurements.

¹⁰ Milazzo, G., *Annali Chim.*, 1956, **46**, 1105.

¹¹ Sears, G. W., and Hopke, E. R., *J. Amer. Chem. Soc.*, 1949, **71**, 1632.

¹² Wolf, K. L., and Weghofer, H., *Z. phys. Chem. B*, 1938, **39**, 194.

¹³ Zil'berman-Granouskaya, A. A., *Zhur. Fiz. Khim. U.S.S.R.*, 1940, **14**, 759.

¹⁴ Westrum, E. F., and McCullough, J. P., in "Physics and Chemistry of the Organic Solid State." (Eds. D. Fox, M. M. Labes, and A. Weissberger.) p. 114. (Interscience: New York 1963.)

¹⁵ Magnus, A., Hartmann, H., and Beeker, F., *Z. physik. Chem.*, 1951, **197**, 75.