349. *The Vapour Pressure and Lattice Energy of Some Aromatic Ring Compounds.*

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The vapour pressures, lattice energies, and entropies of vaporisation have been determined for naphthalene, anthracene, phenanthrene, fluorene, diphenyl, and pyrene by an effusion method.

DATA on the vapour pressures and lattice energies of the polycyclic aromatic hydrocarbons are in general discrepant or scanty. The lattice energies are of interest in view of the problem of interaction of conjugated systems which has been studied by de Boer (*Trans. Faraday Soc.*, 1936, **32**, 10), by Seki and Chihara (*Coll. Papers Fac. Sci. Osaka Univ.*, Series C, Chemistry, 1943—49, **11**, 1), and more recently by Coulson and Davies (*Trans. Faraday Soc.*, 1952, **48**, 777).

EXPERIMENTAL

The vapour pressures were considerably higher than those studied by the authors in their work on hydrogen-bonded crystals (*J.*, 1953, 1681), and it was not necessary to use a sensitive balance. A silica helical balance of the McBain–Bakr type was used to determine the rate of effusion of vapour from a small vessel, a cold finger cooled by acetone and solid carbon dioxide being used to condense the vapour. The apparatus was similar to that used by Bradley and Care (preceding paper): it was placed in a thermostat at the required temperature and, after assembly, was evacuated down to 1 mm. and left for 30 min. The pressure was then reduced to 10^{-5} cm., the cooling agent was added, and deflection–time readings were taken. Errors due to incorrect ratio of effusion hole size to mean free path, self-cooling, and radiation cooling were shown to be negligible. Benzophenone was used to calibrate the effusion vessels. Hydrocarbons were purified by recrystallisation from solution and by vacuum sublimation. The constants of the vapour-pressure equation and the entropies of vaporisation and lattice energies are given for all the compounds studied in Table 8, the equation being written as $\log_{10} p_{\text{cm. Hg}} = -A/T + B$. In no case was a curvature observable in the plot of log p against $1/T$.

Results for naphthalene are given in Table 1. Values given in the literature are surprisingly discrepant, as is seen from Table 2.

TABLE 1. *Vapour pressures (cm.* Hg) *of naphthalene.*

	Effusion vessel 1.								Effusion vessel 2.		
T	20·70°	18·70°	17·55°	17·35°	15·65°	13·85°	12·30°	8·10°	16·85°	12·70°	6·70°
V. p. × 10^3 ...	5·34	4·38	3·83	3·82	3·20	2·63	2·22	1·41	3·50	2·35	1·22

TABLE 2. *Comparison of published vapour pressures* (× 10^3; *cm.* Hg) *of naphthalene.*

Ref.	0°	5°	10°	15°	20°	Lattice energy (cal. mole⁻¹)	Ref.	0°	5°	10°	15°	20°	Lattice energy (cal. mole⁻¹)
1	0·708	1·17	1·95	3·16	5·13	15,700	5	0·6	1·0	2·1	3·5	5·4	17,900
2	0·430	—	1·30	—	4·10	17,900	6	2·3	—	—	—	6·4	8,000
3	—	—	1·74	—	6·48	19,600	7	—	—	1·54	—	6·4	—
4	2·2	3·4	4·7	6·2	8·0	11,000	8	—	0·993	1·73	2·96	4·92	17,300

References.—(1) Zilbermann-Granovskaya, *J. Phys. Chem. U.S.S.R.*, 1940, **14**, 759; calculated from $\log_{10} p = 9{\cdot}40 - 3429/T$. (2) Andrews, *J. Phys. Chem.*, 1926, **30**, 1497. (3) Swan and Mask, *J. Amer. Chem. Soc.*, 1925, **47**, 2112. (4) Allen, *J.*, 1900, **77**, 400. (5) Schlumberger, *J. Gasbeleuchtung*, 1912, **55**, 1257. (6) Barker, *Z. physikal. Chem.*, 1910, **71**, 235. (7) Sears and Hopke, *J. Amer. Chem. Soc.*, 1949, **71**. 1632. (8) This paper.

Sears and Hopke represent their result by an Antoine equation and consider that there is an unusual curvature in the plot of log p against $1/T$ in the region of 20°. We have not detected this curvature in our results over the range 6·7—20·7°, which show that the variation of lattice energy with temperature is negligible over this range.

Results for anthracene, phenanthrene, fluorene, diphenyl, and pyrene are given in Tables 3—7, respectively. Our results for anthracene agree with those of Sears and Hopke (*loc. cit.*) within ±3%.

TABLE 3. *Vapour pressures (cm.* Hg) *of anthracene.*

	Effusion vessel 3.					Effusion vessel 4.				
T	79·95°	77·25°	73·55°	69·91°	65·7°	80·40°	72·20°	71·25°	68·75°	67·10°
V. p. × 10^4	3·67	2·81	1·94	1·25	0·86	3·93	1·67	1·56	1·18	1·05

TABLE 4. *Vapour pressures (cm.* Hg) *of phenanthrene.*

	Effusion vessel 5.						Effusion vessel 6.				
T	48·80°	48·80°	46·70°	42·60°	39·85°	36·70°	49·65°	46·70°	44·62°	42·10°	39·15°
V. p. × 10^4	2·25	2·23	1·85	1·20	0·89	0·64	2·41	1·82	1·45	1·11	0·81

TABLE 5. *Vapour pressures (cm.* Hg) *of fluorene.*

	Effusion vessel 7.					Effusion vessel 8.				
T	49·25°	45·00°	40·30°	37·20°	33·30°	49·55°	47·75°	42·45°	38·45°	34·85°
V. p. × 10^4	8·18	5·43	3·43	2·50	1·64	8·33	7·08	4·16	2·81	1·95

TABLE 6. *Vapour pressures (cm.* Hg) *of diphenyl.*

	Effusion vessel 9.			Effusion vessel 10.					Effusion vessel 11.			
T	24·70°	20·70°	15·05°	40·55°	37·90°	35·10°	35·05°	32·45°	35·90°	31·25°	26·50°	23·05°
V. p. × 10^3	0·919	0·584	0·312	5·02	3·87	2·91	2·90	2·23	3·10	1·91	1·15	0·77
T				29·15°	27·05°	24·10°	24·00°					
V. p. × 10^3				1·54	1·20	0·888	0·887					

TABLE 7. *Vapour pressures (cm.* Hg) *of pyrene.*

	Effusion vessel 12.							Effusion vessel 13.				
T	85·00°	82·65°	81·70°	78·20°	78·05°	74·15°	68·90°	85·25°	82·70°	78·90°	75·85°	71·75°
V. p. × 10^4	3·79	3·07	2·92	2·06	1·97	1·41	0·86	3·80	3·04	2·16	1·67	1·08

TABLE 8. *Summary of vapour-pressure data.*

Hydrocarbon	Range of temp.	A	B	Lattice energy, cal. mole^{-1}	Entropy of vaporisation, cal. degree^{-1} mole^{-1}
Naphthalene	6·70—20·70°	3783	10·597	17,300	40·0
Anthracene	65·70—80·40	5320	11·638	24,400	44·7
Phenanthrene	36·70—49·65	4519	10·388	20,700	38·9
Fluorene	33·30—49·55	4324	10·325	19,800	39·1
Diphenyl	15·05—40·55	4262	11·282	19,500	43·0
Pyrene	71·75—85·25	4904	10·270	22,500	38·4

DISCUSSION

The lattice energy of benzene and of these hydrocarbons should be made up of two terms only, quantum-mechanical dispersion energy and energy of repulsion. The first approximation to the former, the molecule being taken as a whole and allowance made for the anisotropy of polarisability, gives for benzene far too small a result. In the next approximation the molecules are imagined to interact in units in the manner envisaged by de Boer (*loc. cit.*), who obtained good agreement with the experimental lattice energy of benzene, following the crystal-structure determined by Cox (*Proc. Roy. Soc.*, 1932, **135**, *A*, 491), and by using the Slater–Kirkwood approximation to the dispersion energy. However, energy of repulsion and higher terms in the dispersion energy have been neglected, and as London has pointed out, these conjugated systems give rise to induced dipoles in which the separation between positive and negative charges is large. His suggestion that the interaction should be studied in terms of monopoles does not lend itself readily to calculation. Coulson and Davies (*loc. cit.*) have therefore begun a study of intermolecular forces in conjugated chain compounds based on molecular-orbital theory. It would be of interest if the packing of the zig-zag type for benzene could be shown to have the lowest energy, and if the angle of the plane of the rings to the axis could be determined theoretically. It would also be of interest to relate the lattice energy to the virial coefficient of the vapour, which has recently been determined accurately (Allen, Everett. and Penny, *Proc. Roy. Soc.*, 1952, *A*, **212**, 149; Casado, Massie, and Whytlaw-Gray, *ibid.*, *A*, **207**, 483).

For the three similar compounds, benzene, naphthalene, and anthracene, it is remarkable that the lattice energy per carbon atom is very nearly the same (1·78, 1·73, and 1·74 kcal., respectively). Phenanthrene and pyrene are less symmetrical and do not fit into this series. The lattice energies of diphenyl and of fluorene are nearly the same, as might be expected from the molecular form, but the entropy of vaporisation of the former is 43·0 as against 39·1 cal. degree^{-1} mole^{-1} for the latter, in agreement with the possibility of rotation about the central " single " bond for diphenyl in the vapour phase. The entropy of vaporisation of anthracene and the heat of vaporisation are greater than the corresponding quantities for the isomeric phenanthrene, in agreement with the closer packing and more symmetrical structure of the former (densities, anthracene 1·25, phenanthrene 0·98 at room temperature).

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