Vapor Pressure and Liquid Heat Capacity of Perhydroacenaphthylene and Perhydrophenanthrene

Vladislav Roháč,[†] Miroslav Čenský,[†] Diana Zala,[‡] Vlastimil Růžička,*[,†] Květoslav Růžička,[†] Karel Sporka,[§] and Karel Aim[||]

Department of Physical Chemistry and Department of Organic Technology, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic, Ecole polytechnic fédérale de Lausanne, Ecublens, CH - 1015 Lausanne, Switzerland, and E.Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6 - Suchdol, Czech Republic

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Saturated vapor pressures and liquid heat capacities have been measured for liquid perhydroacenaphthylene and perhydrophenanthrene by comparative ebulliometry over an approximate pressure range from (8 to 100) kPa and by heat conduction calorimetry over a temperature range from about (305 to 335) K. The obtained results for vapor pressures and for heat capacities have been represented within experimental uncertainties by the Antoine and the Cox equations and by an empirical polynomial equation, respectively, and compared with the data available in the literature.

Tricyclic perhydroaromatic substances have been of interest for a long time to organic chemists, as they occur widely in substances of nature.[1−4] Cyclic substances originating by hydrogenation of aromatic hydrocarbons are important as intermediates for the synthesis of chemical specialties,[5,6] as potential aircraft and missiles fuels,[7] and as substitutes for aromatic solvents because of increasingly strict environmental legislation.[8] The complete hydrogenation of the aromatic skeleton can be accomplished by using metal catalysts.[9]

The industrial significance of perhydroacenaphthylene became more important recently when production of new adamantane-based pharmaceuticals was initiated. A series of reaction pathways begins with perhydroacenaphthylene, leads to 1,3-dimethyladamantane as an intermediate, and finally gives a desired pharmaceutical. As an isomerization of a mixture of stereoisomers of perhydroacenaphthylene results in 1,3-dimethyladamantane, it is ineffective to separate individual stereoisomers.

In addition to finding suitable chemical reaction pathways for synthesizing polycyclic perhydrohydrocarbons, it is also desirable to determine their basic physicochemical properties. Vapor pressure belongs to properties required for phase equilibria calculations as well as for modeling the fate and distribution of substances in the compartments of the environment.

This work has been concerned with measurement of vapor pressure and liquid heat capacity of a mixture of stereoisomers of tricyclo[7.2.1.0^{5,12}]dodecane (perhydroacenaphthylene) and of a mixture of stereoisomers of tricyclo-[8.4.0.0^{2,7}]tetradecane (perhydrophenanthrene).

Experimental Section

Chemicals. Perhydroacenaphthylene was prepared by hydrogenation of 1,2-dihydroacenaphthylene (product of DEZA a.s., Valašské Meziříčí, minimum purity of 99%) in cyclohexane solution on a commercial nickel catalyst (Ni−NiO/Al_2O_3 catalyst type 6524, Leuna, Germany) at a maximum temperature of 180 °C and pressure of 8 MPa. Under these reaction conditions 1,2-dihydroacenaphthylene was completely hydrogenated to perhydroacenaphthylene. A detailed description of the hydrogenation procedure has been given.[10] The product of hydrogenation was analyzed using the GC-MS technique and contained the following mixture of stereoisomers: 70% cis,trans,trans, 7% trans,trans,trans, 5% cis,cis,trans, and 18% cis,cis,cis, respectively, cis,trans,cis. It was reported[7] there were six possible stereoisomers of perhydroacenaphthylene. Three of them were synthesized, and MS spectral data were reported.[7]

Perhydrophenanthrene was prepared by hydrogenation of phenanthrene (product of DEZA a.s., Valašské Meziříčí, original purity of 90.5%) thoroughly purified by repeated recrystallization. Hydrogenation was carried out in a cyclohexane solution on a commercial nickel catalyst (Ni−NiO/Al_2O_3 catalyst type 6524, Leuna, Germany) at a maximum temperature of 250 °C and pressure of 4 MPa. Under these reaction conditions phenanthrene was completely hydrogenated to perhydrophenanthrene. The product of hydrogenation was analyzed by a GC-MS technique. The mass spectral data showed the product contained a mixture of five species with an identical molar mass of 192. These species were assigned to stereoisomers of perhydrophenanthrene, and their relative amounts were as follows: 47% of isomer A, 21% of isomer B, 29% of isomer C, 3% of isomer D, 1% of isomer E. It has been reported[1] that there were six stereoisomers of perhydrophenanthrene. As we found no spectral data for any of these, it was impossible to identify the stereoisomers in the mixture obtained in this work. However, the reaction conditions used in this work determine uniquely the stereoisomeric composition of the synthesized perhydrophenanthrene.

Apparatus and Procedure for Vapor Pressure Measurement. A modified ebulliometer and an apparatus based on comparative ebulliometry have been used for the vapor pressure measurements. The experimental arrange-

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* Corresponding author. E-mail: vlastimil.ruzicka@vscht.cz.

[†] Department of Physical Chemistry, Institute of Chemical Technology.

[‡] Ecole polytechnic fédérale de Lausanne. On leave as an IAESTE fellow.

[§] Department of Organic Technology, Institute of Chemical Technology.

[||] Academy of Sciences of the Czech Republic.

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Table 1. Vapor Pressure of Perhydroacenaphthylene

		Antoine, eq 1			Cox, eq 5		
T/K	p^{exp}/kPa	ΔT/K	Δp/kPa	$100\Delta p/p$	ΔT/K	Δp/kPa	$100\Delta p/p$
422.072	8.449	0.010	−0.006	−0.07	−0.007	0.004	0.05
430.559	11.210	0.015	−0.013	−0.12	0.015	−0.013	−0.12
437.807	14.089	−0.001	0.001	0.01	0.006	−0.007	−0.05
443.983	17.002	−0.010	0.014	0.08	−0.001	0.002	0.01
444.006	17.000	−0.017	0.024	0.14	−0.009	0.012	0.07
450.351	20.527	−0.008	0.014	0.07	0.000	0.000	0.00
457.082	24.847	−0.016	0.036	0.14	−0.011	0.025	0.10
463.527	29.719	−0.003	0.007	0.02	−0.001	0.003	0.01
469.800	35.193	0.014	−0.047	−0.13	0.012	−0.039	−0.11
469.963	35.187	−0.023	0.076	0.21	−0.024	0.084	0.24
475.900	41.181	0.012	−0.048	−0.12	0.007	−0.027	−0.07
475.900	41.172	0.010	−0.041	−0.10	0.005	−0.020	−0.05
482.070	48.101	0.020	−0.098	−0.20	0.012	−0.062	−0.13
491.890	60.822	0.009	−0.060	−0.10	0.001	−0.009	−0.01
501.290	75.424	0.006	−0.053	−0.07	0.002	−0.018	−0.02
511.580	94.172	−0.016	0.180	0.19	−0.011	0.125	0.13
513.930	99.173	−0.003	0.035	0.04	0.005	−0.059	−0.06
mean absolute deviation		0.011	0.044	0.11	0.008	0.030	0.07
standard deviation		0.014	0.068	0.13	0.011	0.051	0.11

ment has been described in detail,[11,12] and thus only a brief characterization is given below.

Two very similar ebulliometers essentially of the classical Swietosławski design have been used. A reference ebulliometer was filled with water as a reference fluid of known vapor pressure and partly enclosed in a box that shielded it from temperature fluctuations of the surroundings. The measuring ebulliometer (all made of quartz) was filled with about 60 cm^3 of the investigated substance and placed in an air thermostat, whose temperature was kept constant to ±1 K at a value about 15 K below the actual boiling temperature. Both ebulliometers were connected in parallel via cold traps to the pressure-controlling assembly, whose main parts were two buffer reservoirs (connected in series by a pneumatic resistor) and an air-thermostated mercury manostat. The pressure control assembly made it possible to maintain the pressure in the ebulliometric system constant within less than ±3 Pa at a series of evenly spaced pressure values in the range from 3 kPa to over 100 kPa.

The boiling temperatures (of water and of a substance investigated) in the two ebulliometers at a given pressure were measured simultaneously by two 2850D-type probes of the Hewlett-Packard quartz thermometer (Model HP-2801A). Both probes had been repeatedly calibrated against a Leeds & Northrup standard platinum 25 Ω resistance thermometer (Model 8163-B) coupled in a four-wire connection with a precision resistance bridge Model F17A (Automatic Systems Laboratories, Milton Keynes, U.K.). Overall accuracy in the measured boiling temperatures is estimated to be better than ±0.01 K within ITS-90 over the whole investigated range.

From the boiling temperature of water the corresponding equilibrium pressure in the system was calculated at each point by using the accurate vapor pressure equation.[13] The accuracy in pressure determined in this manner is estimated to be better than ±0.1% of the measured pressure value over the entire range studied. Nevertheless, due to the fact that the samples investigated were mixtures of stereoisomers rather than pure chemical species, certain fluctuations in both temperature and pressure were observed during the measurements. Accordingly, the uncertainties assigned to the measured quantities had to be larger compared to those used in our previous studies.[14,15] Their values are specified below in the paragraphs describing the vapor pressure data processing.

Apparatus and Procedure for Heat Capacity Measurement. Saturation heat capacities in the liquid phase were measured with a commercial heat-conduction C-80 Setaram calorimeter equipped with standard cells having the inner volume of 9.5 cm^3 reduced by a raised bottom. In a typical heat capacity experiment, the temperature was increased in steps of 10 K with a heating rate of 3.3 mK·s^{-1}. The average heat capacity C for a given temperature step T was obtained from the time integrals of the differential thermopile signal for the filled and empty sample cells. As the vapor pressure of all studied substances was below 5 kPa at all experimental temperatures, it was not necessary to apply any correction for sample vaporization. The temperature dependence of heat capacity for both studied substances was close to linear; then the average heat capacity over the individual temperature step could be considered directly as the true heat capacity relating to the mean temperature of the interval. The calorimeter was calibrated with synthetic sapphire (α-Al_2O_3), NIST Standard Reference Material 720. The accuracy of heat capacity measurements estimated from calibration and test experiments with several substances of well-known heat capacity values is ±1% of the measured value. As all experimental heat capacities determined in this work lie about 100 K below the normal boiling temperature, the reported saturation heat capacities are identical to isobaric heat capacities.

Results and Discussion

Measured vapor pressures of perhydroacenaphthylene and of perhydrophenanthrene are presented in Tables 1 and 2 together with the results of their representation by the Antoine and the Cox equations.

The Antoine equation was employed in the form

$$\log(p/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C] \qquad (1)$$

where p and T denote the saturated vapor pressure and temperature, respectively, and A, B, and C are adjustable parameters characteristic of a substance.

The parameters A, B, and C in eq 1 were evaluated from the experimental vapor pressure data by the method of maximum likelihood,[16,17] allowing for the fact that both the measured variables are subject to experimental uncertainties. A symmetric maximum likelihood objective function was used in the form

$$S = \Sigma[(\Delta T_i)^2(\sigma_{T,i})^{-2} + (\Delta p_i)^2(\sigma_{p,i})^{-2}] \qquad (2)$$

where the index in the summation runs over all experi-

Table 2. Vapor Pressure of Perhydrophenanthrene

		Antoine, eq 1			Cox, eq 5		
T/K	p^{exp}/kPa	ΔT/K	Δp/kPa	$100\Delta p/p$	ΔT/K	Δp/kPa	$100\Delta p/p$
454.684	8.292	−0.073	0.045	0.55	−0.037	0.022	0.27
455.090	8.438	−0.037	0.023	0.27	−0.003	0.002	0.02
463.522	11.208	0.058	−0.052	−0.47	0.056	−0.049	−0.43
463.710	11.207	0.005	−0.004	−0.03	0.000	0.000	0.00
471.070	14.087	0.019	−0.023	−0.16	0.000	0.000	0.00
471.140	14.085	−0.001	0.001	0.00	−0.020	0.023	0.16
477.110	16.999	0.097	−0.142	−0.84	0.074	−0.110	−0.64
477.570	17.005	−0.016	0.023	0.13	−0.038	0.056	0.33
483.870	20.522	0.058	−0.106	−0.52	0.039	−0.070	−0.34
484.220	20.532	−0.021	0.039	0.19	−0.041	0.074	0.36
490.960	24.860	0.036	−0.085	−0.34	0.025	−0.059	−0.24
491.250	24.845	−0.033	0.077	0.31	−0.044	0.103	0.41
497.710	29.718	0.042	−0.122	−0.41	0.040	−0.118	−0.40
498.110	29.718	−0.042	0.121	0.41	−0.042	0.123	0.42
498.120	29.709	−0.046	0.134	0.45	−0.047	0.136	0.46
504.380	35.185	0.039	−0.139	−0.40	0.048	−0.171	−0.48
504.790	35.185	−0.042	0.148	0.42	−0.033	0.115	0.33
510.950	41.188	0.014	−0.061	−0.15	0.032	−0.136	−0.33
511.210	41.186	−0.035	0.150	0.36	−0.017	0.073	0.18
517.730	48.109	−0.021	0.110	0.23	0.002	−0.013	−0.03
528.150	60.846	−0.021	0.140	0.23	0.004	−0.025	−0.04
528.150	60.857	−0.019	0.132	0.22	0.005	−0.035	−0.06
538.120	75.413	−0.010	0.085	0.11	0.001	−0.014	−0.02
548.840	94.142	0.019	−0.232	−0.25	−0.001	0.012	0.01
551.610	99.533	0.028	−0.357	−0.36	−0.004	0.049	0.05
mean absolute deviation		0.033	0.102	0.31	0.026	0.064	0.24
standard deviation		0.042	0.136	0.38	0.036	0.088	0.33

Table 3. Parameters of the Antoine Equation (Eq 1)

	A	B	C	T_b/K
perhydroacenaphthylene	5.957 216	1710.212	82.12819	514.93
perhydrophenanthrene	5.480 736	1433.463	140.2354	552.74

mental observations and $\sigma_{T,i}$ and $\sigma_{P,i}$ are estimated standard deviations in measured temperature and pressure for the i-th observation, respectively. For computations with the original data presented in this work, these were assigned the values $\sigma_{T,i} = 0.02$ K and $\sigma_{p,i} = 0.001 p_{\mathrm{exp},i}$ for perhydroacenaphthylene and $\sigma_{T,i} = 0.04$ K and $\sigma_{p,i} = 0.002 p_{\mathrm{exp},i}$ for perhydrophenanthrene, respectively, for all observations as a priori estimated from the properties of the experimental setup and substances investigated, as well as from the observations made during the measurements (as described above). The parameters of the correlating eq 1 and the calculated values $T_{\mathrm{calc},i}$ and $p_{\mathrm{calc},i}$ corresponding to each observation were evaluated by minimizing the objective function, as defined by eq 2, by a robust iterative procedure (using the simplex method in each of the alternating steps).

The resulting parameters of the Antoine equation (eq 1) obtained for the present vapor pressure data on perhydroacenaphthylene and perhydrophenanthrene are given in Table 3 along with the calculated normal boiling temperatures. Tables 1 and 2 display also the corresponding characteristics of the fit, namely the deviations

$$\Delta T_i = T_{\mathrm{calc},i} - T_{\mathrm{exp},i} \quad \text{and} \quad \Delta p_i = p_{\mathrm{calc},i} - p_{\mathrm{exp},i}$$

evaluated at the minimum of the objective function. The deviations in percent of pressure are also displayed, since the second term in the objective function (eq 2), with $\sigma_{p,i}$ specified as a constant multiple of the i-th pressure value, just minimizes the percent deviations in pressure. Also given in Tables 1 and 2 are the mean absolute deviations a_T and a_p, given by

$$a_X = \Sigma|X_{\mathrm{calc},i} - X_{\mathrm{exp},i}|/n, \quad X = T \text{ and } p \qquad (3)$$

and the standard deviations s_T and s_p, defined by

$$s_X = [\Sigma(X_{\mathrm{calc},i} - X_{\mathrm{exp},i})^2/(n - m)]^{1/2}, \quad X = T \text{ and } p \qquad (4)$$

where m is the number of parameters in the correlating eq 3 and n is the number of experimental observations. It is seen from the tables that the Antoine equation represents the experimental vapor pressure data within the estimated experimental errors.

The Antoine equation is generally considered to be the most appropriate for correlating vapor pressures over the so-called medium-pressure region that spans the range approximately from 1 kPa to 200 kPa. It should be noted, however, that the Antoine equation is unsuitable for extrapolation below the lower limit of experimental data due to its low flexibility.[18] We present the Antoine equation parameters here, as it is often used in many different standard program packages for the calculation of vapor pressures close to the normal boiling temperature.

Since all studied substances are high-boiling, our concern was to use for data fitting another relationship exhibiting good extrapolation capability in the direction toward the triple point and not requiring use of critical parameters. Our previous tests have shown[18] that the Cox equation is a convenient option:

$$\ln\left(\frac{p}{p_0}\right) = \left(1 - \frac{T_0}{T}\right) \exp\left(\sum_{i=0}^{2} A_i T^i\right) \qquad (5)$$

where T_0 and p_0 relate to a reference temperature and to the corresponding vapor pressure, respectively. In this work, the normal boiling temperature T_0 was used as a reference point and was determined by a fit of the vapor pressure data with eq 5, in which $p_0 = 101.325$ kPa and A_0, A_1, A_2, and T_0 were adjustable parameters. The evaluated parameters of the Cox equation (eq 5) are summarized in Table 4 along with the normal boiling point. It is documented from Tables 1 and 2 by comparing the mean absolute and standard deviations that the Cox equation is

Table 4. Parameters of the Cox Equation (Eq 5)

	A_0	A_1	A_2	T_0/K	p_0/kPa
perhydroacenaphthylene	2.487 00	$1.741\,07 \times 10^{-4}$	$-7.709\,77 \times 10^{-7}$	514.99	101.325
perhydrophenanthrene	4.546 89	$-8.019\,71 \times 10^{-3}$	$7.508\,66 \times 10^{-6}$	552.47	101.325

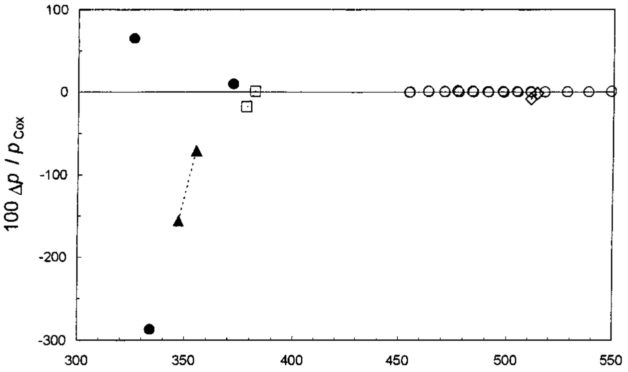

Figure 1. Percent in pressure deviation graph for the vapor pressure of perhydroacenaphthylene with the zero line representing eq 5 with the parameters of Table 4 ($\Delta p = p_{\mathrm{Cox}} - p_{\mathrm{exp}}$): ○, this work; ◇, Grosse et al.;[20] □, Schneider et al.;[21] ▲, Zakharkin et al.;[22] ●, Boldt et al.[7] The dashed line connecting the adjacent points symbolizes the boiling range at a given pressure reported by the author.

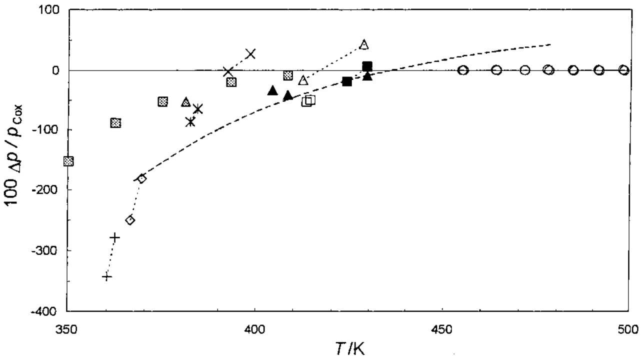

Figure 2. Percent in pressure deviation graph for the vapor pressure of perhydrophenanthrene with the zero line representing eq 5 with the parameters of Table 4 ($\Delta p = p_{\mathrm{Cox}} - p_{\mathrm{exp}}$): ○, this work; ◇, Pinkney et al.;[25] ▲, Durland and Adkins[2]; □, Linstead and Walpole[3]; ∗, Linstead;[23] ■, Grosse et al.;[20] shaded triangle, Boelhouwer et al.;[28] △, Schneider et al.;[21] shaded box, API RP 42;[24] +, Eimasry and Gisvold;[5] ×, Allinger et al.[1]; - - -, TRC Tables.[19] The dashed line connecting the adjacent points symbolizes the boiling range at a given pressure reported by the author.

superior to the Antoine equation in describing the measured vapor pressures over the experimental temperature range.

The Cox equation parameters are used as the zero baseline in Figures 1 and 2, where comparisons of the present vapor pressure data with literature data are given in terms of percentage deviation plots, where $\Delta p = p_{\mathrm{Cox}} - p_{\mathrm{exp}}$. Ebulliometric vapor pressure data determined in this work are included in the deviation plots to show their temperature range.

Some remarks of general validity are summarized below: (i) there are no reliable experimental vapor pressure data for any of the two substances, even though in the *TRC Thermodynamic Tables*[19] parameters of a correlating equation for a mixture of stereoisomers of perhydrophenanthrene are presented in the table k-4700 based on unpublished API data and the data by Durland and Adkins;[2] (ii) most literature data come from measurements of a boiling point when distilling a reaction product at a reduced pressure, which in all cases but one does not exceed 5 kPa; (iii) several authors presented a boiling range rather than a single boiling temperature value at a specified pressure. In Figures 1 and 2 the boiling range is symbolized by connecting the adjacent points with a dashed line.

For perhydroacenaphthylene we found in the literature four sources of data. Except for the data by Grosse et al.,[20] who reported a boiling temperature range at atmospheric pressure determined when studying catalytic dehydrogenation of polycyclic naphthenes, all remaining reported boiling point pressures lie below the lower limit of the vapor pressure data determined in this work. As found in ref 18, the Cox equation was suitable for extrapolation toward the fusion temperature. Therefore, the comparison of literature data with those calculated from the Cox equation is considered to be qualitatively correct when extrapolating about 50 K below the lower limit of the present data. The data by Grosse et al.[20] as well as the data by Schneider et al.,[21] who determined a boiling temperature range of a mixture of four isomers at a single pressure during distillation of products of hydrogenation of acenaphthene, agree within less than 20% with the present vapor pressures even though the data by Schneider et al. lie about 40 K below the lower limit of the present data. The data by Zakharkin et al.[22] deviate substantially from the data obtained by a long-range extrapolation of the Cox equation going to the pressure of 1 kPa. Boldt et al.[7] synthesized three of the six possible stereoisomers of perhydroacenaphthylene and reported their boiling points at a reduced pressure around 1 kPa obtained from temperature and pressure readings during distillation of a reaction product. The boiling point for the cis,cis,cis isomer differs significantly from the present data; boiling points for the cis,cis,trans and trans,trans,trans isomers exhibit smaller deviations from the present data.

For perhydrophenanthrene, in addition to the “TRC equation”, we found in the literature 10 more sources of data. With the exception of the “TRC equation”, all reported boiling point pressures lie below the lower limit of the vapor pressure data determined in this work. The data calculated from the “TRC equation” deviate substantially from those calculated from the Cox equation at their lower limit. Durland and Adkins[2] presented boiling points at three pressures obtained by reading temperatures during distillation of pure substances in the fractionating column. Linstead and Walpole[3] reported two boiling points at slightly different pressures in a study of stereoisomerism of perhydrophenanthrenes. Grosse et al.[20] reported a boiling temperature range in a pressure range determined in a study of catalytic dehydrogenation of polycyclic naphthalenes that included perhydroacenaphthylene. Schneider et al.[21] determined a boiling temperature range of a mixture of four isomers at a single pressure during distillation of products of hydrogenation of phenanthrene. Allinger et al.[1] in a conformational analysis study of perhydrophenanthrenes reported a boiling temperature range in a vacuum distillation of a mixture of two isomers consisting of 60% of the cis,syn,cis isomer and 40% of the trans,syn,cis isomer. All the above-mentioned data deviate from the present experimental vapor pressures by less than about 55%. Linstead et al.[23] synthesized cis,syn,cis perhydrophenanthrene by catalytic hydrogenation of

Table 5. Liquid Heat Capacities of Perhydroacenaphthylene and Perhydrophenanthrene

T/K	$C_{p,\mathrm{m}}/R$	$\delta_{\mathrm{r}}{}^{a}$/%	T/K	$C_{p,\mathrm{m}}/R$	$\delta_{\mathrm{r}}{}^{a}$/%
Perhydroacenaphthylene			Perhydrophenanthrene		
307.9	34.5	−0.1	305.4	37.7	0.1
307.9	34.6	0.1	305.4	37.6	−0.1
308.0	34.6	0.1	305.5	37.5	−0.3
315.4	35.1	0.0	310.4	38.1	0.0
317.8	35.3	−0.2	315.3	38.6	−0.1
317.9	35.3	0.0	315.3	38.7	0.2
320.3	35.5	0.1	315.4	38.6	0.1
325.3	36.0	0.2	320.3	39.1	0.1
327.8	36.1	−0.1	320.3	39.2	0.2
			325.2	39.6	−0.1
			325.3	39.6	0.0
			330.2	40.1	0.0
			330.2	40.0	−0.1
			335.2	40.6	0.1
			335.2	40.5	−0.1

[a] $\delta_{\mathrm{r}} = 100\{C_{p,\mathrm{m}}/R - C_{p,\mathrm{m}}/R(\mathrm{calc})\}/(C_{p,\mathrm{m}}/R)$.

9-phenantrol and reported its boiling range, differing from the present data by an average of 80%. API data coming from the API Research Project 42[24] deviate from our data substantially at their low-temperature end. However, the origin of the data is unclear; the data may be estimated. Pinkney et al.[25] reported a boiling temperature range for three fractions of perhydrophenanthrene prepared in a study of its synthesis from dienynes. Only one range is shown in Figure 2, as the remaining ranges overlap the range of boiling points reported by Eimasry and Gisvold.[5] Eimasry and Gisvold[5] studied catalytic hydrogenation of 1,2,3,4,5,6,7,8-octahydrophenanthrene, which yielded a crude perhydrophenanthrene distilled between 87 and 89 °C at 266 Pa. This boiling point differs from the data calculated from the Cox equation by several hundred percent.

A general remark may be drawn from Figures 1 and 2. Boiling points measured by different authors agree in a qualitative manner, defined by a ±50% pressure deviation margin from the present data, within the temperature range and about 50 K below the lower limit of the present data. Taking into account the complex nature of both substances studied, each being a mixture of several stereoisomers, the ±50% margin is acceptable.

The measured heat capacities of perhydroacenaphthylene and perhydrophenanthrene are presented in Table 5. Results of repetitive experiments are given only if they differed significantly. In Table 5 relative deviations are also given between the experimental data and the data fitted by the polynomial equation

$$\frac{C_{p,\mathrm{m}}}{R} = \sum_{i=0}^{k} A_{i+1}^{C}\left(\frac{T}{100}\right)^{i} \tag{6}$$

($R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$). The parameters of eq 6 were determined by using the weighted least-squares method. An objective function was used of the form

$$S = \sum_{i=1}^{n} (\Delta C_i/R)^2 (\sigma_{C/R,i})^{-2} \tag{7}$$

where the variance $\sigma_{C/R,i}$ was estimated for each value on the basis of the assumed experimental error of the set of data used in the correlation and n is the number of experimental data points. The input information was the percentage error of the experimental data $\sigma_{\mathrm{r}}C$ given by the author for the whole data set. The variance of the i-th data point was expressed as

$$\sigma_{C/R,i} = 10^{-2}(C/R)_i \sigma_{\mathrm{r}} C \tag{8}$$

The parameters of eq 6 derived from the fit are given in Table 6 along with the relative standard deviation of the fit and an estimate of uncertainty, which reflects both the uncertainty of the experimental data and the possible error due to the fitting procedure.

Only for perhydrophenanthrene are there other experimental data for liquid heat capacities, namely four data points for an unspecified stereoisomer covering the temperature range from 313 K to 483 K published by Gudzinowicz et al.[26] and smoothed data by Nuzzi[27] for three specified stereoisomers, trans,anti,trans, cis,anti,trans, cis,syn,trans, covering the merged temperature range from 283 K to 403 K (depending on the stereoisomer). As our experimental data differ from those of Gudzinowicz et al.[26] by more than 3%, which may be attributed to a different composition of the mixture of stereoisomers, we correlated our data separately. The parameters of eq 6 calculated from the data by Gudzinowicz et al.[26] are given in Table 6. Obviously, the heat capacity data by Nuzzi[27] differ mutually for each stereoisomer as well as from our data with relative deviations from our data ranging from −13% to 12%.

Conclusion

Two tricyclic perhydroaromatics, perhydroacenaphthylene and perhydrophenanthrene, were synthesized by hydrogenation on a nickel catalyst at an elevated temperature and pressure. Their vapor pressure and liquid heat capacity were measured by precision comparative ebulliometry and heat conduction calorimetry, respectively. The Antoine and the Cox equations within experimental uncertainty represented the results of vapor pressure measurements. Comparison of the present data with boiling points reported in the literature showed a qualitative agreement in the temperature range of the measurement and for temperature extrapolations about 50 K below the lower limit of the present data. The experimental heat capacities for a mixture of stereoisomers of perhydrophenanthrene agree with the literature data within 3% whereas the present measurement reports so far unavailable heat capacity data for perhydroacenaphthylene. A conclusive analysis of possible causes of deviations between the present data and most of the literature vapor pressure data is hindered by

Table 6. Parameters of Eq 6

	parameters		temp range			
substance	$A_1{}^C$	$A_2{}^C$	T_{min}/K	T_{max}/K	$s_{\mathrm{r}}{}^{a}$	uncertainty/%
perhydroacenaphthylene	9.961 15	7.979 31	307.9	327.8	0.1	1
perhydrophenanthrene, this work	7.659 13	9.817 04	305.4	335.2	0.1	1
perhydrophenanthrene, Gudzinowicz et al.[26]	9.601 03	9.634 00	313.2	483.2	0.5	3

[a] $s_{\mathrm{r}} = 10^2(\sum_{i=1}^{n}[[\{C_{p,\mathrm{m}} - C_{p,\mathrm{m}}(\mathrm{calc})\}/C_{p,\mathrm{m}}]/(n-m)]_i^2)^{1/2}$, where n is the number of fitted data points and m is the number of independent adjustable parameters.

the lack of a precise analysis of the composition of the substances used by different authors in their measurements. Except for a few cases, the composition of substances reported in terms of the relative amount of stereoisomers is not available. Further, and very likely even more important, is the fact that most of the literature data were obtained by measurement of a boiling temperature at a reduced pressure in studies of reaction pathways. Such measurements provide only a very inaccurate value of vapor pressure.

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