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Ab initio studies on the structures and thermodynamic functions of phenanthrene and anthracene

Xue-Dong Gong and He-Ming Xiao*

Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT: The molecular geometries and electronic structures of phenanthrene and anthracene in the gas phase were studied by using an *ab initio* molecular orbital method at the HF and MP2 levels with the 6–31G* basis set. Normal-mode vibrational analyses were performed at the HF/6–31G* level. The standard thermodynamic functions were calculated using the frequencies scaled by a factor 0.899, and were in good agreement with the experimental results. The equilibrium mole fractions of the title compounds in an equilibrium mixture were derived from the thermodynamic functions. It is shown that, compared with those of anthracene, the molecular total energy of phenanthrene is lower, the conjugation effect in phenanthrene is stronger and the equilibrium mole fraction of phenanthrene is larger, all showing that phenanthrene is more stable than anthracene. The mole fraction of phenanthrene calculated at room temperature is 0.686, and it decreases slightly as the temperature rises. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: Phenanthrene; anthracene; *ab initio* method; geometry; thermodynamic function

INTRODUCTION

Polycyclic aromatic compounds (PACs), the largest class of chemical carcinogens known today, occurring mainly in air as pollutants, are formed and released mainly by the incomplete combustion of organic materials. The known health hazards associated with the increasing emission of PACs into the environment dictate the need for further structural identification and more accurate measurement of these substances.

Phenanthrene and anthracene are the simplest tricyclic aromatic hydrocarbons. Their structures and spectra, etc, have already been studied experimentally.[1–5] However, no complete experimental spectra and structural parameters in the gas phase are available so far. Therefore, numerous theoretical studies[6–8] have been performed by using *ab initio* molecular orbital (MO) methods. However, these calculations were performed at the Hartree–Fock (HF) level[9] for the restriction of molecular size. As already known, the electron correlation effect plays an important role in compounds with π-conjugation such as phenanthrene and anthracene, and calculations performed at the HF level cannot lead to reliable results.[10,11] To obtain the accurate geometry and properties of these compounds, electron correlation must be included in MO calculations and basis sets involving polarization effects for at least heavy atoms should be used.[11]

**Correspondence to:* H.-M. Xiao, Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China.

In this work, we carried out *ab initio* MO calculations using the second-order Møller–Plesset (MP2) perturbation theory[12] and the 6–31G*[13] basis set. The fully optimized geometries and other related properties such as molecular total energies were obtained. The standard thermodynamic functions were computed based on vibrational analyses. The equilibrium mole fractions of phenanthrene and anthracene were derived.

COMPUTATIONAL DETAILS

The geometries of phenanthrene and anthracene obtained in a previous molecular mechanical study[14] were used as the initial inputs, and were subsequently fully optimized under the constrained C_{2v} and D_{2h} symmetries, respectively. Geometry optimizations were carried out at the HF and MP2 levels with the 6–31G* basis set using the Berny gradient optimization method[15] employing the Gaussian 92/DFT program package.[16] All default thresholds given in the program were used throughout.

The IR frequencies were computed on the basis of geometry optimizations at the HF/6–31G* level. The frequencies obtained were subsequently scaled by a factor 0.899[11] to reduce the systematic overestimation of HF calculation and were then used to calculate the standard thermodynamic functions (enthalpy $H°$, entropy $S°$ and heat capacity $C_p°$) based on the statistical mechanical method of Herzberg[17] employing a self-compiled program. The changes in the standard thermo-

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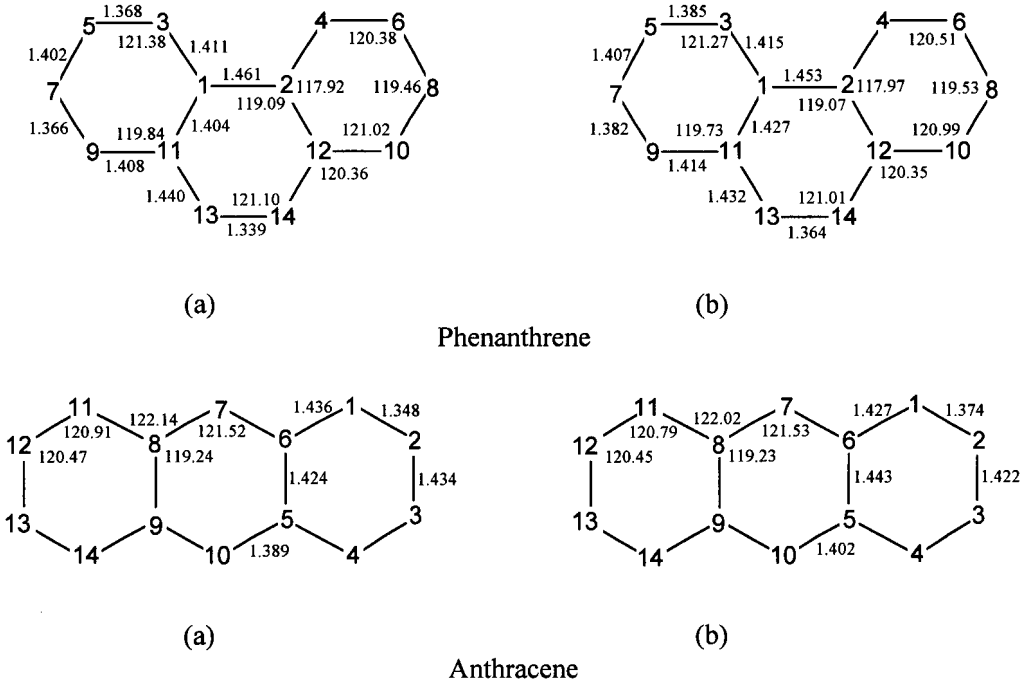

Figure 1. Atomic numbering and optimized geometries of phenanthrene and anthracene (H atoms are omitted; bond lengths are in Å and angles in degrees). (a) HF/6–31G* results; (b) MP2/6–31G* results

dynamic functions ($\Delta S°$, $\Delta H°$ and $\Delta G°$) for the isomerization reaction (1) from anthracene to phenanthrene were also calculated. Here, $\Delta S°$ and $\Delta H°$ were obtained from the differences between the corresponding thermodynamic functions of phenanthrene and anthracene, and $\Delta G°$ was obtained from the basic equation $\Delta G° = \Delta H° - T\Delta S°$.

$$\text{anthracene} \overset{K_p^\circ}{\rightleftharpoons} \text{phenanthrene} \qquad (1)$$

Because the change in the total number of moles in reaction (1) is zero, the equilibrium constant $K_p°$ is thus equal to the mole-fraction equilibrium constant $K_x°$ at constant pressure. Based on the equation $\Delta G° = RT \ln K_p°$, we have $K_x^\circ = K_p^\circ = \exp(-\Delta G^\circ/RT)$. Since $K_x° = \gamma_P/\gamma_A$ and $\gamma_P + \gamma_A = 1$ (where γ_P and γ_A are the equilibrium mole fractions of phenanthrene and anthracene, respectively), therefore

$$\gamma_P = \exp(-\Delta G^\circ/RT)/[1 + \exp(-\Delta G^\circ/RT)] \qquad (2)$$

$$\gamma_A = 1 - \gamma_P = 1/[1 + \exp(-\Delta G^\circ/RT)] \qquad (3)$$

From Eqns (2) and (3), the equilibrium mole fractions of phenanthrene (γ_P) and anthracene (γ_A) can be obtained.

All calculations were performed on a Pentium personal computer in our laboratory.

RESULTS AND DISCUSSION

Molecular geometry

Figure 1 shows the optimized geometries of the title compounds obtained from the HF/6–31G* (a) and the MP2/6–31G* (b) calculations. One can find easily from Fig. 1 that the bond lengths of the two molecules obtained by the HF/6–31G* and MP2/6–31G* methods differ. The HF/6–31G* results are generally smaller than the MP2/6–31G* results and the differences vary from 0.012 to 0.026 Å, the largest difference being 0.025 Å for phenanthrene and 0.026 Å for anthracene, showing a considerable influence of the electron correlation effect on the calculated bond lengths. According to the MP2/6–31G* calculations, the lengths of C—C bonds range from 1.364 to 1.453 Å in phenanthrene and from 1.374 to 1.443 Å in anthracene. The average lengths of C—C bonds are 1.409 Å for the both compounds. The available experimental results[1,2] are 1.350–1.465 and 1.370–1.440 Å for the C—C bonds in phenanthrene and anthracene, respectively.

As was found previously, the MP2 results are comparable to the experimental data again, and are better than the DFT results obtained at the B3LYP/cc-pvDZ level.[18] Because the complete geometric parameters of phenanthrene and anthracene in the gas phase are not available, the geometries obtained here may be useful, for example, for the optimization of the

Table 1. Selected results obtained from the *ab initio* calculations[a]

Phenanthrene			Anthracene		
Parameter	HF/6–31G*	MP2/6–31G*	Parameter	HF/6–31G*	MP2/6–31G*
E_{tot}	−536.0098	−537.7756	E_{tot}	−535.9988	−537.7656
E_{HOMO}	−7.663	−7.521	E_{HOMO}	−7.011	−6.811
E_{LUMO}	2.730	2.538	E_{LUMO}	1.926	1.678
ΔE	10.393	10.059	ΔE	8.937	8.489
μ	0.018	0.048	μ	0.000	0.000
$q_{C\text{-}1}$	−0.015	0.004	$q_{C\text{-}1}$	−0.181	−0.181
$q_{C\text{-}3}$	−0.194	−0.181	$q_{C\text{-}2}$	−0.215	−0.182
$q_{C\text{-}5}$	−0.211	−0.182	$q_{C\text{-}6}$	−0.000	−0.044
$q_{C\text{-}7}$	−0.203	−0.172	$q_{C\text{-}7}$	−0.234	−0.233
$q_{C\text{-}9}$	−0.211	−0.202	$q_{H\text{-}1}$	0.205	0.174
$q_{C\text{-}11}$	−0.000	0.050	$q_{H\text{-}2}$	0.203	0.174
$q_{C\text{-}13}$	−0.195	−0.190	$q_{H\text{-}7}$	0.210	0.175
$q_{H\text{-}3}$	0.210	0.178			
$q_{H\text{-}5}$	0.203	0.173			
$q_{H\text{-}7}$	0.204	0.174			
$q_{H\text{-}9}$	0.205	0.174			
$q_{H\text{-}13}$	0.208	0.175			

[a] The total energy (E_{tot}) is in hartree; the energies of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) and the energy difference (ΔE) between them are in eV; the dipole moment (μ) is in debye; the net charges on atoms (q) are in e. The atomic numbering of H is the same as that of the attached C.

molecular mechanical force field of conjugated compounds.

The mean absolute deviation of the C—C bond lengths from the average value (1.409 Å for both compounds) is calculated to be 0.019 Å for phenanthrene and 0.021 Å for anthracene. The smaller deviation for phenanthrene implies that the bond lengths of all C—C bonds in this compound are closer to each other or in other words, the degree of equalization of the bond lengths is higher in phenanthrene than in anthracene, implying that the π-conjugation effect in phenanthrene is stronger, and therefore it is more stable and its aromaticity will be stronger.

Examination of the calculated results for bond angles shows that they are little influenced by the electron correlation effect. Bond angles obtained at the HF and MP2 levels are almost identical, with the largest difference being less than 0.2° for both compounds.

Electronic structure

The *ab initio* calculations also produced the molecular total energies, the energies of HOMO and LUMO, the Mulliken charges on atoms and the dipole moments of the title compounds. The results are collected in Table 1. It is not difficult to find that the total energies obtained at the MP2/6–31G* level are lower than the HF/6–31G* energies by more than 1.7 hartree, implying that electron correlation plays an important role in these compounds and should be accounted for to obtain accurate energies. Furthermore, the total energy of phenanthrene is lower than that of anthracene by 28.85 kJ mol^{-1} (HF/6–31G*) and 26.44 kJ mol^{-1} (MP2/6–31G*), showing again that phenanthrene is comparatively more stable than its isomer anthracene, consistent with the conclusion that the delocalization of π-electrons in phenanthrene is stronger.

The computed energy of HOMO (E_{HOMO}) is lower for phenanthrene than for anthracene, while the energy of LUMO (E_{LUMO}) of the former is higher. Hence the energy difference between the E_{HOMO} and E_{LUMO} (ΔE) of phenanthrene is larger than that of anthracene. From the ΔE the approximate wavelengths λ of the ρ-band for the absorption of UV radiation (arising from the transition of an electron from the π-bonding HOMO to π*-antibonding LUMO) were calculated, and the obtained results are 123.26 and 146.05 nm for phenanthrene and anthracene, respectively. Though the computed values are not very much in line with the experimental values, the order λ(phenanthrene) $<$ λ(anthracene), is consistent with that obtained from the experiment.[3]

Owing to the higher symmetry D_{2h}, the calculated dipole moment (μ) of anthracene is zero and it is a nonpolar compound. Phenanthrene with a comparatively lower C_{2v} symmetry has a very small dipole moment (0.018 and 0.048 D from the HF/6–31G* and the MP2/6–31G* calculations, respectively).

The atomic charges on carbons connected only with other carbons in both compounds are close to zero from both the HF/6–31G* and MP2/6–31G* calculations, but those on carbons connected with both carbon and hydrogen atoms are negative (−0.181 to −0.234e from HF calculations and −0.172 to −0.233e from MP2 calculations). The charges on hydrogens are all positive (0.203 to 0.210e from HF calculations and 0.173 to 0.178e from MP2 calculations).

Table 2. HF/6–31G* frequencies (cm^{-1}) of phenanthrene and anthracene[a]

Phenanthrene (C_{2v})				Anthracene (D_{2h})			
	ν	ν'	I		ν	ν'	I
a_1	264.4	237.7	0.4	a_g	421.5	379.0	0.0
a_1	437.1	393.0	0.5	a_g	683.7	614.7	0.0
a_1	591.6	531.9	0.5	a_g	823.1	740.1	0.0
a_1	775.4	697.2	0.1	a_g	1085.6	976.1	0.0
a_1	899.0	808.3	0.5	a_g	1290.2	1160.1	0.0
a_1	1108.1	996.4	0.6	a_g	1371.7	1233.4	0.0
a_1	1188.0	1068.2	0.0	a_g	1566.1	1408.2	0.0
a_1	1210.4	1088.3	0.4	a_g	1643.5	1477.8	0.0
a_1	1287.6	1157.8	0.0	a_g	1766.5	1588.4	0.0
a_1	1306.1	1174.4	1.2	a_g	3354.0	3015.9	0.0
a_1	1369.4	1231.3	6.6	a_g	3362.7	3023.7	0.0
a_1	1407.0	1265.1	4.8	a_g	3387.4	3045.9	0.0
a_1	1464.0	1316.4	0.9	a_u	135.1	121.4	0.0
a_1	1587.7	1427.6	4.2	a_u	544.7	489.7	0.0
a_1	1606.7	1444.7	3.5	a_u	822.5	739.5	0.0
a_1	1708.1	1535.9	2.1	a_u	957.1	860.6	0.0
a_1	1808.0	1625.7	5.1	a_u	1120.6	1007.6	0.0
a_1	1840.6	1655.0	0.3	b_{1g}	254.0	228.3	0.0
a_1	3354.0	3015.9	2.1	b_{1g}	531.3	477.7	0.0
a_1	3365.8	3026.5	26.7	b_{1g}	853.8	767.7	0.0
a_1	3376.5	3036.1	48.2	b_{1g}	1094.9	984.5	0.0
a_1	3384.6	3043.4	1.7	b_{1u}	250.4	225.1	1.8
a_1	3418.4	3073.8	29.6	b_{1u}	699.5	628.9	3.4
a_2	104.3	93.7	0.0	b_{1u}	988.3	888.6	4.7
a_2	265.1	238.3	0.0	b_{1u}	1275.3	1146.7	5.4
a_2	437.6	393.4	0.0	b_{1u}	1390.3	1250.1	5.9
a_2	598.3	537.9	0.0	b_{1u}	1453.4	1306.8	3.1
a_2	649.1	583.6	0.0	b_{1u}	1612.0	1449.5	0.4
a_2	850.1	764.4	0.0	b_{1u}	1845.8	1659.7	11.8
a_2	880.8	792.0	0.0	b_{1u}	3351.1	3013.3	1.5
a_2	977.0	878.5	0.0	b_{1u}	3356.9	3018.5	13.4
a_2	1072.7	964.5	0.0	b_{1u}	3374.8	3034.6	96.3
a_2	1105.8	994.3	0.0	b_{2g}	292.3	262.8	0.0
a_2	1119.1	1006.2	0.0	b_{2g}	635.1	571.0	0.0
b_1	109.6	98.5	0.7	b_{2g}	850.7	764.9	0.0
b_1	252.3	226.8	3.5	b_{2g}	937.8	843.2	0.0
b_1	479.8	431.4	6.4	b_{2g}	1022.4	919.3	0.0
b_1	550.8	495.2	4.7	b_{2g}	1121.6	1008.5	0.0
b_1	788.5	709.0	3.2	b_{2u}	651.4	585.7	10.3
b_1	832.5	748.5	80.8	b_{2u}	858.7	772.1	0.2
b_1	918.2	825.6	69.2	b_{2u}	1062.7	955.5	1.7
b_1	982.2	883.1	10.6	b_{2u}	1155.9	1039.3	2.5
b_1	1083.6	974.3	4.2	b_{2u}	1287.2	1157.4	0.5
b_1	1118.4	1005.6	0.0	b_{2u}	1417.7	1274.7	5.6
b_2	474.9	427.0	2.3	b_{2u}	1546.0	1390.1	0.0
b_2	538.7	484.3	0.8	b_{2u}	1613.1	1450.5	1.9
b_2	676.3	608.1	5.8	b_{2u}	1732.6	1557.9	8.4
b_2	772.8	694.9	4.4	b_{2u}	3359.2	3020.5	0.9
b_2	955.6	859.2	2.2	b_{2u}	3386.6	3045.2	94.0
b_2	1088.0	978.3	1.8	b_{3g}	423.7	380.9	0.0
b_2	1141.1	1026.0	2.1	b_{3g}	571.0	513.4	0.0
b_2	1262.5	1135.2	1.9	b_{3g}	994.7	894.4	0.0
b_2	1272.0	1143.7	0.4	b_{3g}	1211.7	1089.5	0.0
b_2	1323.7	1190.2	0.0	b_{3g}	1309.4	1177.4	0.0
b_2	1401.9	1260.5	0.1	b_{3g}	1409.4	1267.3	0.0
b_2	1419.0	1275.9	0.0	b_{3g}	1538.3	1383.2	0.0
b_2	1571.7	1413.2	0.5	b_{3g}	1786.3	1606.2	0.0
b_2	1625.6	1461.7	15.3	b_{3g}	1851.5	1664.8	0.0
b_2	1672.3	1503.7	9.7	b_{3g}	3353.2	3015.1	0.0
b_2	1774.8	1595.9	0.1	b_{3g}	3374.1	3033.9	0.0
b_2	1820.1	1636.6	1.1	b_{3u}	99.6	89.5	1.1
b_2	3351.3	3013.4	0.3	b_{3u}	421.5	379.0	0.3
b_2	3356.0	3017.7	2.0	b_{3u}	525.6	472.6	21.2
b_2	3365.0	3025.8	0.0	b_{3u}	823.7	740.6	89.1
b_2	3381.7	3040.8	79.9	b_{3u}	1008.2	906.5	72.0
b_2	3394.5	3052.3	11.6	b_{3u}	1099.1	988.3	6.0

[a] ν is the frequency calculated at the HF/6–31G* level, ν' is the HF/6–31G* frequency scaled by 0.899 and I is the intensity of the vibrational band.

Table 3. Standard thermodynamic functions calculated with the scaled frequencies[a,b]

	Phenanthrene			Anthracene		
T	$H°$	$S°$	$C_p°$	$H°$	$S°$	$C_p°$
298.15	28.00	396.62	183.27	28.06	390.31	184.23
400	50.08	459.85	248.72	50.23	453.80	249.53
500	77.72	521.31	302.22	77.94	515.42	302.83
600	110.16	580.33	344.93	110.43	574.54	345.39
700	146.42	636.16	379.04	146.74	630.43	379.41
800	185.75	688.64	406.68	186.10	682.96	406.99
900	227.59	737.89	429.41	227.97	732.24	429.69
1000	271.51	784.14	448.33	271.91	778.52	448.59

[a] The units of enthalpy ($H°$), entropy ($S°$) and heat capacity ($C_p°$) are K, kJ mol^{-1} J mol^{-1}K^{-1} and J mol^{-1}K^{-1}, respectively.
[b] The rotational constants (A, B and C) obtained at the HF/6–31G* level and used in calculating the standard thermodynamic functions are 1.6358, 0.5562 and 0.4151 GHz for phenanthrene and 2.1714, 0.4565 and 0.3772 GHz for anthracene, respectively.

Vibrational spectrum and standard thermodynamic functions

Based on the geometry optimizations at the HF/6–31G* level, normal-mode vibrational analyses were performed. The results in Table 2 show that both compounds have 66 fundamental modes, of which 45 are in-plane ($23a_1 + 22b_2$ for phenanthrene and $12a_g + 11b_{1u} + 11b_{2u} + 11b_{3g}$ for anthracene) and the others are out-of-plane($11a_2 + 10b_1$ for phenanthrene and $5a_u + 4b_{1g} + 6b_{2g} + 6b_{3u}$ for anthracene). The a_2 fundamentals of phenanthrene and a_g, a_u, b_{2g} and b_{3g} of anthracene are infrared inactive. According to the computational results, most vibrational bands of the title compounds have weak intensities. Hence it is not easy to make assignments of their IR spectra by experiment. So far, no complete spectra and assignments are available.

Because the frequencies obtained at the HF level are generally systematically larger than the experimental data by about 10–11%,[11,19] a factor of 0.899[11] was used to scale the computed frequencies. The scaled frequencies are also listed in Table 2 (column ν').

Using the scaled frequencies, the standard thermodynamic functions of heat capacity ($C_p°$), entropy ($S°$) and enthalpy ($H°$) were calculated and are collected in Table 3. Comparing the computed results with the corresponding experimental data[20] at 298.15 K (The experimental $S°$ and $C_p°$ at 298.15 K are 394.5 and 186.8 J mol^{-1}K^{-1} for phenanthrene and 392.6 and 185.0 J mol^{-1}K^{-1} for anthracene, respectively), good agreement is observed. The differences between the computed and experimental values of $S°$ are 2.1 and -2.3 J mol^{-1}K^{-1} for phenanthrene and anthracene, respectively, and those of $C_p°$ are -3.5 and -0.8 J mol^{-1}K^{-1}, respectively.

From Table 3 one also sees that the entropies of phenanthrene at various temperatures are systematically larger than those of anthracene by 6.65–5.62 J mol^{-1}K^{-1}, but the heat capacities and enthalpies of the former are slightly smaller than those of the latter (the differences are less than 1 J mol^{-1}K^{-1}). Hence the standard entropy changes for reaction (1) at various temperatures are positive ($\Delta S° > 0$ in Table 4), and the enthalpy changes are negative [$\Delta H° < 0$, i.e. (1) is an exothermic reaction]. The changes in standard Gibbs free energy derived from $\Delta G° = \Delta H° - T\Delta S°$ are also negative at all temperatures considered, which means that reaction (1) is an autoreaction from left to right. The mole fractions of phenanthrene ($\gamma_P \approx 0.68$) obtained from Eqn (2) are systematically larger than those of anthracene ($\gamma_A = 1-\gamma_P \approx 0.32$) in the range of temperatures con-

Table 4. Changes in standard thermodynamic functions for reaction (1) and the equilibrium mole fractions of phenanthrene and anthracene[a]

T(K)	$\Delta S°$	$\Delta H°$	$\Delta G°$	γ_P	γ_A
298.15	6.31	−0.06	−1.94	0.686	0.314
400	6.04	−0.15	−2.56	0.684	0.316
500	5.88	−0.22	−3.16	0.682	0.318
600	5.79	−0.27	−3.74	0.679	0.321
700	5.72	−0.32	−4.32	0.678	0.322
800	5.68	−0.35	−4.89	0.676	0.324
900	5.64	−0.38	−5.46	0.675	0.325
1000	5.61	−0.40	−6.02	0.674	0.326

[a] $\Delta S°$, $\Delta H°$ and $\Delta G°$ are the entropy change (in J mol^{-1}K^{-1}), enthalpy change in (in KJ mol^{-1}) and change in Gibbs free energy (in KJ mol^{-1}) for reaction (1) under standard conditions; γ_P and γ_A are the mole fractions of phenanthrene and anthracene obtained from Eqns (2) and (3), respectively.

sidered (298.15–1000 K), implying that phenanthrene is more stable than anthracene. The result reported here is consistent with that obtained by Albery and Relf[21] using the Benson method.

Furthermore, the equilibrium mole fraction of phenanthrene (γ_P) decreases slightly with increase in temperature. Correspondingly, the mole fraction of anthracene (γ_A) increases. For example, at 298.15 K, γ_P and γ_A are 0.686 and 0.314, whereas at 500 K, they are 0.682 and 0.318, respectively. This can be explained according to the van't hoff equation, $\mathrm{d} \ln K_p^\circ/\mathrm{d}T = \Delta H^\circ/RT^2$. From this equation, we have $\mathrm{d}K_p^\circ/\mathrm{d}T = K_p^\circ \Delta H^\circ/RT^2$. For reaction (1), when the temperature T is increased by $\mathrm{d}T$ at constant pressure, because K_p° and RT^2 are positive and ΔH° is negative, $\mathrm{d}K_p^\circ$ is then negative, i.e. K_p° decreases, and the equilibrium shifts to the left. Hence the mole fraction of phenanthrene γ_P decreases as the temperature rises.

CONCLUSIONS

According to the *ab initio* calculation results, the following conclusions can be drawn. (1) Electron correlation has a strong effect on the bond lengths in phenanthrene and anthracene, but has little influence on the bond angles. The MP2/6–31G* geometries of the title compounds are comparable to the available experimental results. (2) The calculated standard thermodynamic functions of phenanthrene and anthracene at room temperature using the scaled HF/6–31G* frequencies are in good agreement with the corresponding experimental data. (3) The mole fraction of phenanthrene in the equilibrium mixture of phenanthrene and anthracene decreases with increase in temperature. (4) The calculated molecular total energy of phenanthrene is lower than that of anthracene by 26.44kJ mol^{-1} (MP2/6–31G* results), the conjugation effect is stronger and the equilibrium mole fraction is larger for the former than for the latter, all showing that phenanthrene is more stable than anthracene.

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