Thermochimica Acta, 7 (1973) 69–73
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

THERMODYNAMIC FUNCTIONS FOR BIPHENYL AND THE 4,4′-DIHALOGENOBIPHENYLS

H. ALEMAN AND J. LIELMEZS
Chemical Engineering Department, The University of British Columbia, Vancouver 8 (Canada)
(Received 6 March 1973)

ABSTRACT

Thermodynamic functions, C_p°, S°, $(H^\circ-H_0^\circ)/T$, $-(F^\circ-H_0^\circ)/T$, have been calculated for biphenyl and three 4,4′-dihalogenobiphenyls (4,4′-difluoro-, -dichloro-, and -dibromobiphenyl) in the ideal gas state from 298.15 K to 1000 K at 1 atm pressure. The restricted internal rotational contribution for all these compounds has been treated by the conventional Pitzer–Gwinn method.

The agreement between the calculated and the available experimental values is excellent.

NOMENCLATURE

a, b, c	constants
n_m	number of minima of the rotational barrier function
C_p°	ideal gas heat capacity at constant pressure (cal/mole K)
$-(F^\circ-H_0^\circ)/T$	ideal gas free energy function (cal/mole K)
$(H^\circ-H_p^\circ)/T$	ideal gas enthalpy function (cal/mole K)
I_A, I_B, I_C	principal moments of inertia (g cm^2)
I_m	moment of inertia of rotating top (g cm^2)
I_{red}	reduced moment of inertia (g cm^2)
S°	ideal gas entropy (e.u.)
T	absolute temperature (K)
α_A, α_B, α_C	directional cosines
ν	wave number (cm^{-1})
σ	molecular symmetry number
A	any of the thermodynamic functions (cal/mole K)

Supercripts $^\circ$ refer to the ideal gas state
Subscripts $_p$ refer to pressure.

INTRODUCTION AND DISCUSSION

The recent availability of spectroscopic and structural data for diphenyl and 4,4′-dihalogenobiphenyls[1–3], has made it possible to estimate the thermodynamic

TABLE 1

HEAT CAPACITY, ENTROPY, FREE ENERGY FUNCTION AND ENTHALPY FUNCTION

Temperature (K)	*Biphenyl*	*4,4′-difluorobiphenyl*	*4,4′-dichlorobiphenyl*	*4,4′-dibromobiphenyl*
Heat capacity (C_p°, cal/mole K)				
298.15	39.78	45.43	47.52	48.50
300.00	40.05	45.71	47.79	48.76
400.00	53.86	59.47	61.22	61.92
500.00	65.44	70.74	72.18	72.71
600.00	74.63	79.59	80.77	81.19
700.00	81.95	86.54	87.51	87.85
800.00	87.86	92.09	92.90	93.18
900.00	92.74	96.61	97.28	97.51
1000.00	96.80	100.34	100.90	101.10
Entropy (S°, e.u.)				
298.15	92.86	100.41	105.36	110.18
300.00	93.11	100.70	105.65	110.48
400.00	106.59	115.78	121.29	126.36
500.00	119.87	130.31	136.18	141.38
600.00	132.64	144.02	150.13	155.42
700.00	144.72	156.84	163.11	168.45
800.00	156.06	168.77	175.16	180.54
900.00	166.70	179.88	186.36	191.78
1000.00	176.69	190.26	196.80	202.24
Enthalpy function ($(H^\circ - H_0)/T$ (cal/mole K))				
298.15	21.51	24.70	26.45	27.62
300.00	21.62	24.83	26.57	27.74
400.00	27.94	31.81	33.60	34.69
500.00	34.36	38.52	40.27	41.26
600.00	40.34	44.65	46.33	47.24
700.00	45.77	50.16	51.75	52.57
800.00	50.68	55.07	56.57	57.33
900.00	55.09	59.44	60.86	61.57
1000.00	59.07	63.35	64.69	65.34
Free energy function $-(F^\circ - H_0^\circ)/T$ (cal/mole K)				
298.15	71.35	75.71	78.91	82.56
300.00	71.49	75.87	79.08	82.74
400.00	78.57	83.97	87.69	91.67
500.00	85.51	91.79	95.91	100.12
600.00	92.30	99.37	103.80	108.18
700.00	98.95	106.68	111.36	115.88
800.00	105.38	113.70	118.59	123.21
900.00	111.61	120.44	125.50	130.21
1000.00	117.62	126.91	132.11	136.90

functions—heat capacity, enthalpy, entropy and free energy—for these compounds in the ideal gas state at 1 atm pressure. The functions for each given compound were calculated by statistical-mechanical methods, treating the internal rotational barrier contributions by means of the conventional treatment of Pitzer and Gwinn[4,5]. The results presented in Table 1 are fitted to eqn (1)

$$A = a + bT + cT^2 \qquad (1)$$

where A is the thermodynamic function at temperature T (K). The constants a, b and c (eqn 1) were calculated using least squares curve fitting methods[6] and are found in Table 2. This table also gives the maximum deviation between the values listed in Table 1 and the corresponding values determined through the use of eqn 1. Table 3 presents values of the molecular parameters used in thermodynamic function calculations. The molecular structural data and configurations appeared to be well established[1-3], all the investigators[1-3] suggesting that biphenyl and its various substituted derivatives are non-planar (staggered configuration) in the vapour phase.

TABLE 2

CALCULATED[a] CONSTANTS a, b AND c IN EQUATION (1)

Function	a	$b \times 10^2$	$c \times 10^5$	*Standard[b] deviation (cal/mole K)*
Biphenyl				
C_p°	−8.6319	18.86	−8.380	0.6341
$(H^\circ - H_0^\circ)/T$	−1.2058	8.24	−2.201	0.1525
$-(F^\circ - H_0^\circ)/T$	49.0197	7.75	−0.884	0.0351
S°	47.8139	15.98	−3.085	0.1795
4,4′-Difluorobiphenyl				
C_p°	−2.1746	18.73	−8.570	0.5991
$(H^\circ - H_0^\circ)/T$	−0.0794	9.11	−2.766	0.0634
$-(F^\circ - H_0^\circ)/T$	49.9048	9.06	−1.359	0.0099
S°	49.8254	18.17	−4.125	0.0648
4,4′-Dichlorobiphenyl				
C_p°	1.1736	18.24	−8.364	0.5951
$(H^\circ - H_0^\circ)/T$	1.6596	9.15	−2.848	0.0485
$-(F^\circ - H_0^\circ)/T$	51.4180	9.72	−1.657	0.0179
S°	53.0776	18.87	−4.505	0.0472
4,4′-Dibromobiphenyl				
C_p°	2.9535	17.91	−8.185	0.5703
$(H^\circ - H_0^\circ)/T$	3.1723	9.02	−2.809	0.0463
$-(F^\circ - H_0^\circ)/T$	54.0557	10.13	−1.854	0.0407
S°	57.2280	19.15	−4.663	0.0558

[a] Constants for eqn (1) calculated using input data for temperature range 298.15–1000 K. [b] Standard deviation of residuals, $S = \sum_{i=1}^{n} (Y_{i'} - Y_{i''})^2/(n-m-1)$; where n is the number of observations; m is the number of independent variables; $Y_{i'}$ is the i-th observed value of Y (Table 1) and $Y_{i''}$ is the predicted value of Y (eqn 1).

TABLE 3

MOLECULAR PARAMETERS OF BIPHENYL AND HALOGENATED BIPHENYLS

	Biphenyl	*4,4′-difluoro-biphenyl*	*4,4′-dichloro-biphenyl*	*4,4′-dibromo-biphenyl*
Fundamental frequencies [ν, cm^{-1} (ref. 1)]				
	3073 3073 3072	3073 3073 3072	3072 3072 3072	3072 3072 3072
	3072 3070 3070	3072 3070 3070	3072 3070 3070	3072 3070 3070
	3069 3069 3069	3069 3069 1604	3070 3070 1594	3069 3069 1588
	3069 1613 1595	1600 1586 1555	1593 1593 1556	1587 1584 1538
	1595 1567 1505	1519 1496 1394	1505 1474 1389	1498 1470 1383
	1481 1455 1430	1391 1320 1302	1380 1300 1275	1370 1300 1282
	1337 1317 1282	1284 1283 1267	1275 1271 1242	1263 1245 1224
	1266 1233 1192	1242 1230 1164	1186 1180 1123	1184 1166 1100
	1174 1158 1155	1153 1100 1095	1096 1070 1019	1079 1071 1069
	1094 1072 1042	1018 1017 1008	1013 1004 1000	1016 1010 1000
	1029 1007 1003	966 958 938	957 953 949	970 962 949
	990 979 964	932 847 840	941 843 829	944 941 822
	964 964 917	821 812 812	817 812 768	814 808 757
	902 838 838	806 728 704	722 704 696	718 672 668
	778 740 735	658 638 630	637 627 538	635 624 537
	697 670 626	542 515 515	536 501 423	497 460 412
	615 609 543	454 415 415	406 406 369	408 355 316
	486 405 367	415 389 358	306 306 270	271 237 222
	367 307 265	255 255 178	219 215 157	190 167 145
	112 77	96 72	95 63	89 73
Principal moments of inertia, g cm^2 × 10^{39} (refs. 1 and 2)				
I_A	29.644	29.644	29.644	29.644
I_B	148.386	289.023	464.517	916.478
I_C	178.029	318.668	494.146	946.121
Reduced moment of inertia, g cm^2 × 10^{39} (refs. 1 and 2)				
I_{red}	7.411	7.411	7.411	7.411
Moment of inertia of rotating top, g cm^2 × 10^{39} (refs. 1 and 2)				
I_m	14.822	14.822	14.822	14.822
Used value of the energy (kcal/mole) of internal rotational barrier (refs. 1 and 2)				
	3	3	3	3
Molecular shape factor (refs. 1, 2, 3)				
	4	4	4	4
Number of rotational barrier minima, n_m (ref. 1)				
	2	2	2	2
Physical constants: ref. 12.				

However, calculations made for planar configuration and staggered configuration (twisted structure[1], possessing a dihedral angle of 45 ± 15°) separately, showed that changes in calculated thermodynamic function values are small (<0.1% increase for biphenyl and even smaller increase for halogen substituted derivatives of biphenyl molecule).

The value of the reduced moment of inertia[4,7], I_{red}, appearing in Table 3, was calculated from eqn (2):

$$I_{red} = I_m \left[\frac{1 - \sum_i \alpha_i^2 I_m}{I_i} \right]_{i=A,B,C} \tag{2}$$

Where I_m is the moment of inertia of the rotating top about the chosen axis of rotation; while I_A, I_B, I_C are the principal moments of inertia and α_A, α_B, α_C are the corresponding directional cosines.

Comparing the calculated thermodynamic function values with the available calorimetric measurements[8], it was found that for biphenyl (using the two-fold internal rotational barrier of 3 kcal/mole as suggested by Barrett and Steele[1]) the spectroscopic entropy at 528.40 K was 0.02 cal/K less than the calorimetric value*. This is in excellent argreement with the measurement and strengthens the certainty in the correctness of the low frequency assignment values[1]. The presented thermodynamic function values (Table 1) also compare satisfactorily with the thermodynamic property values for biphenyl as obtained by Katon and Lippincott[9] who used somewhat different low frequency values.

In this work we have used an internal rotational barrier height (Table 3) of 3.0 kcal/mole for all of the 4 compounds. It should be noted that this is an approximation and neglects the symmetry and substituent halogen atom effects on the internal rotation[10,11] of the rotating tops. However, the uncertainty in the choice of correct internal rotational barrier is apparently much larger[1,9] than the neglected effects[10,11].

ACKNOWLEDGEMENT

The financial assistance of the National Research Council of Canada is gratefully acknowledged.

REFERENCES

1 R. M. Barrett and D. Steele, *J. Mol. Struct.*, 11 (1972) 105.
2 G. Casalane, C. Mariani, J. Mugnoli and M. Simonetta, *Mol. Phys.*, 15 (1968) 339.
3 M. Michelsen, P. Klaeboe, G. Hagen and T. Stroyer-Hansen, *Acta Chem. Scand.*, 26 (1972) 1576.
4 J. Lielmezs and A. A. Bondi, *Rotational Isomers in Thermodynamic Calculations*, Shell Development Company TR-208-58-R, 1958.
5 K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 10 (1942) 428.
6 University of British Columbia Computing Centre, "*TRIP*" *program*, 1971.
7 B. L. Crawford Jr., *J. Chem. Phys.*, 8 (1940) 273.
8 M. Rolla, *Boll. Sci. Fac. Chim. Ind., Bologna*, 2 (1941) 181; *Chem. Abstr.*, 37 (1943) 42962.
9 J. E. Katon and E. R. Lippincott, *Spectrosc. Acta*, 15 (1959) 627.
10 J. Lielmezs and J. P. Morgan, *Nature*, 202 (1964) 1106.
11 J. Lielmezs and B. J. Hagan, *Theor. Chim. Acta*, 15 (1969) 89.
12 E. R. Cohen and J. W. M. Dumond, *Rev. Mod. Phys.*, 37 (1965) 537.

---

* The calculated entropy value at 528.4 K is 123.56 e.u., while the corresponding experimental entropy is 123.58 e.u.