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Original Scientific Paper

Thermodynamic Functions of Thiazole and *iso*-Thiazole

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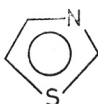
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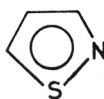
Some thermodynamic functions (the enthalpy and free energy functions, entropy and heat capacity) of thiazole and *iso*-thiazole have been calculated (300–1000° K), using the harmonic-oscillator, rigid-rotor approximation. The reported assignments for the two molecules were used, as were the published values for the moments of inertia of thiazole. Approximate values for the moments of inertia of *iso*-thiazole have been calculated, assuming bond lengths and angles similar to those of thiophene and 1,2,5-thiadiazole. The calculated thermodynamic functions are compared with the results obtained previously for thiadiazoles and thiophene.

INTRODUCTION

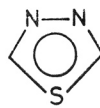
We have recently reported¹ the calculation of some thermodynamic functions (enthalpy and free energy functions, entropy and heat capacity) of thiadiazoles. Using the same harmonic-oscillator, rigid-rotor approximation^{2,3}, we now report the same thermodynamic functions for thiazole (I) and *iso*-thiazole (II), two molecules which are closely related to 1,3,4-thiadiazole (III) and 1,2,5-thiadiazole (IV), to which the previous paper¹ has been devoted.



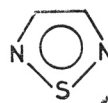
I



II



III



IV

Internal rotation in all these molecules is excluded and so the limiting factor in the calculation of the thermodynamic functions is the accuracy of the molecular and spectroscopic data².

MOLECULAR AND SPECTROSCOPIC DATA

Moments of Inertia

Both thiazole and *iso*-thiazole are asymmetric top molecules, *i. e.* their three principal moments of inertia are different. The values of the moments of inertia for thiazole have been calculated by Bak *et al.*⁴ from the microwave spectrum of this molecule.

The only values for the moments of inertia of *iso*-thiazole we were able to find were those reported by Califano *et al.*⁵, calculated, as stated, assuming

average bond lengths and angles then known in the literature. These values, however, seem to be much too low, much lower, in fact, than those for all other related five-atomic heterocyclic molecules containing sulfur (Table I).

TABLE I
Moments of Inertia of Some Five-Atomic Heterocyclic Molecules Containing Sulfur
(g. cm.² · 10^{-40*}).

	Thiazole ⁴	iso-Thiazole ⁵	iso-Thiazole (this work)	Thio- phene ⁶	1,2,5-Thia- diazole ⁷	1,3,4-Thia- diazole ⁸
I _a	98.40	60.7	98.2	104.37	98.30	94.23
I _b	152.45	84.7	155.3	154.91	132.53	150.71
I _c	250.97	145.4	253.5	259.39	230.97	245.08

* The conversion factor from amu · Å² = 1.6603 · 10⁻⁴⁰

We, nevertheless, attempted to calculate the thermodynamic functions of *iso*-thiazole using the values of Califano *et al.*⁵, but the discrepancies were obvious: whereas the enthalpy function and the heat capacity (which do not depend on the moments of inertia) were very close for thiazole and *iso*-thiazole, the free energy functions differed by 1.5—2 cal. mole⁻¹ deg⁻¹. We, therefore, decided to recalculate the moments of inertia of *iso*-thiazole. The method of Hirschfelder⁹ was used and the structural parameters needed in the calculation were taken from the related thiophene⁶ and 1,2,5-thiadiazole⁷, averaged and slightly rounded. These parameters are listed in Table II. The values of the moments of inertia thus calculated are very close to the ones of other related molecules and were used in the calculation of the thermodynamic functions. The moments of inertia of *iso*-thiazole calculated by us are given in Table I.

TABLE II
Assumed Distances and Angles Used in the Calculation of the Moments of Inertia
of *iso*-Thiazole

Distances (in Å)		Angles	
S—C(2)	1.71	SC(2)C(3)	111.5°
C(2)—C(3)	1.37	C(2)C(3)C(4)	112.5°
C(3)—C(4)	1.42	C(3)C(4)N	111.5°
C(4)—N	1.33	SC(2)H(2)	120°
S—N	1.63	C(2)C(3)H(3)	122.5°
C—H	1.08	NC(4)H(4)	121°

Spectroscopic Data

Thiazole and *iso*-thiazole belong to the C_s point group and all of their eighteen normal vibrational modes should be both infrared and Raman active. Nevertheless, one of the ring modes (ν₁₃ for thiazole and *iso*-thiazole, ν₈ for 1,2,5-thiadiazole, ν₈ for thiophene) gives rise to a very weak infrared band and is easily observable only in the Raman spectrum.

A reliable vibrational assignment for thiazole has appeared quite recently¹⁰. The assignment, published some time ago, for *iso*-thiazole has, as its major weak point, the placing of the lowest in-plane bending mode (ν₁₃) at 755 cm.⁻¹,

instead of in the region between 700 and 600 cm^{-1} where it was subsequently found in all other examined five-atomic heterocyclic molecules containing sulfur¹⁰⁻¹⁴, except in 1,3,4-thiadiazole¹⁵. Fortunately, Dr. Sbrana was kind to communicate to us his revised set of fundamentals for *iso*-thiazole¹¹, which now looks quite convincing and agrees nicely with the assignment of the related 1,2,5-thiadiazole^{12,13}. Of the two bands (at 1071 and 1060 cm^{-1}) which are a typical example of Fermi resonance, the more intense band (that at 1060 cm^{-1}) was taken as a fundamental frequency, although the true value of this fundamental, in the absence of Fermi resonance, would have been somewhat higher. The assignments for thiazole and *iso*-thiazole, used in the present calculation are summarized in Table III.

TABLE III
Vibrational Assignments of Thiazole⁸ and *iso*-Thiazole⁹.

Species	No.	Thiazole	<i>iso</i> -Thiazole	Description
A'	1	3140	3120	CH stretching
	2	3093	3099	CH stretching
	3	3065	3063	CH stretching
	4	1484	1489	Ring
	5	1383	1391	Ring
	6	1325	1295	Ring
	7	1239	1239	CH in-plane bending
	8	1124	1060	CH in-plane bending
	9	1043	1041	CH in-plane bending
	10	888	872	Ring
	11	867	819	Ring breathing
	12	759	756	Ring
	13	612	639	Ring
A''	14	849	910	CH out-of-plane bending
	15	798	859	CH out-of-plane bending
	16	717	726	CH out-of-plane bending
	17	603	590	Ring
	18	467	478	Ring

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The method, described in detail by Colthup *et al.*³ and used in the previous paper¹, was used here too. The results are summarized in Table IV and Table V for thiazole and *iso*-thiazole respectively.

As can be seen from Table VI, the calculated thermodynamic functions of thiazole and *iso*-thiazole are very close. This is not unexpected in view of the close correspondence of the moments of inertia and the fundamental frequencies of the two compounds. The thermodynamic functions of *iso*-thiazole have usually smaller values than those of thiazole, but with the heat capacity at higher temperatures the situation is reversed (although there the differences are minimal).

For purposes of comparison Table VI lists also the calculated thermodynamic functions of the related molecules: 1,3,4-thiadiazole, 1,2,5-thiadiazole and thiophene. The results for the former two compounds are taken from

TABLE IV
 Thermodynamic Functions of Thiazole (cal. mole⁻¹ deg⁻¹).

T (° K)	Contribution	$\frac{H^0 - E_0^0}{T}$	$-\frac{G^0 - E_0^0}{T}$	S ⁰	C _p ⁰
300	Translation	4.9680	34.3008	39.2688	4.9680
	Rotation	2.9808	22.1695	25.1503	2.9808
	Vibration	2.3774	0.7360	3.1134	8.3612
	Total	10.3262	57.2063	67.5325	16.3100
400	Translation	4.9680	35.7300	40.6980	4.9680
	Rotation	2.9808	23.0270	26.0078	2.9808
	Vibration	4.4944	1.7107	6.2051	13.1814
	Total	12.4432	60.4677	72.9109	21.1302
600	Translation	4.9680	37.7443	42.7123	4.9680
	Rotation	2.9808	24.2356	27.2164	2.9808
	Vibration	8.6159	4.3276	12.9435	19.9463
	Total	16.1647	66.3075	82.8722	27.8951
800	Translation	4.9680	39.1735	44.1415	4.9680
	Rotation	2.9808	25.0932	28.0740	2.9808
	Vibration	12.0011	7.2865	19.2876	24.0611
	Total	19.9499	71.5532	91.5031	32.0099
1000	Translation	4.9680	40.2821	45.2501	4.9680
	Rotation	2.9808	25.7583	28.7391	2.9808
	Vibration	14.7006	10.2563	24.9569	26.7899
	Total	22.6494	76.2967	98.9461	34.7387

 TABLE V
 Thermodynamic Functions of iso-Thiazole (cal. mole⁻¹ deg⁻¹).

T (° K)	Contribution	$\frac{H^0 - E_0^0}{T}$	$-\frac{G^0 - E_0^0}{T}$	S ⁰	C _p ⁰
300	Translation	4.9680	34.3008	39.2688	4.9680
	Rotation	2.9808	22.1960	25.1768	2.9808
	Vibration	2.3270	0.7104	3.0374	8.2783
	Total	10.2758	57.2072	67.4830	16.2271
400	Translation	4.9680	35.7300	40.6980	4.9680
	Rotation	2.9808	23.0535	26.0343	2.9808
	Vibration	4.4417	1.6653	6.1069	13.1405
	Total	12.3905	60.4488	72.8392	21.0893
600	Translation	4.9680	37.7443	42.7123	4.9680
	Rotation	2.9808	24.2621	27.2429	2.9808
	Vibration	8.5752	4.2672	12.8424	19.9441
	Total	16.5240	66.2736	82.7976	27.8929
800	Translation	4.9680	39.1735	44.1415	4.9680
	Rotation	2.9808	25.1197	28.1005	2.9808
	Vibration	11.9712	7.2172	19.1884	24.0665
	Total	19.9200	71.5104	91.4304	32.0153
1000	Translation	4.9680	40.2821	45.2501	4.9680
	Rotation	2.9808	25.4707	28.4515	2.9808
	Vibration	14.6809	10.1904	24.8713	26.8020
	Total	22.6297	76.2573	98.8870	34.7508

Ref. 1 and those for thiophene are from the paper by Rico *et al.*¹⁴. The thermodynamic functions for all these compounds at 300° K have been calculated in the present work. It can be seen that the enthalpy function and the heat capacity (where the translational and rotational contributions are constant)

TABLE VI

Comparison of the Thermodynamic Functions of Thiazole and iso-Thiazole with those of 1,3,4-Thiadiazole, 1,2,5-Thiadiazole and Thiophene (cal. mole⁻¹ deg⁻¹).

T (° K)	1,3,4-thia- diazole ¹	1,2,5-thia- diazole ¹	iso-Thiazole	Thiazole	Thio- phene ¹⁴
1. Enthalpy function, (H° — E ₀ ⁰)/T					
300	9.70	10.01	10.28	10.33	10.69
400	11.39	11.83	12.39	12.44	13.10
600	14.81	15.38	16.51	16.56	17.78
800	17.77	18.32	19.92	19.95	21.64
1000	20.12	20.62	22.63	22.65	24.72
2. Free energy function, —(G° — E ₀ ⁰)/T					
300	55.57	55.52	57.21	57.21	56.03
400	58.61	58.65	60.45	60.47	59.40
600	63.90	64.14	66.27	66.31	65.62
800	68.59	68.98	71.51	71.55	71.28
1000	72.89	73.33	76.26	76.30	76.45
3. Entropy, S°					
300	65.27	65.53	67.48	67.53	66.72
400	70.01	70.48	72.84	72.91	72.50
600	78.71	79.52	82.80	82.87	83.40
800	86.36	87.30	91.43	91.50	92.92
1000	93.01	93.95	98.89	98.95	101.18
4. Heat capacity, C _p ⁰					
300	14.35	15.16	16.23	16.31	17.52
400	18.50	19.27	21.09	21.13	22.98
600	24.44	25.14	27.89	27.90	30.65
800	28.22	28.65	32.02	32.01	35.39
1000	30.60	30.89	34.75	34.74	38.61

change in the order: thiadiazoles < thiazoles < thiophene, *i. e.* in the order of the increase of the number of vibrational degrees of freedom. On the other hand, the free energy function of thiophene is smaller than those of thiazole and iso-thiazole, as is the entropy at lower temperatures (at 1000° K the free energy function of thiophene is larger than that of the thiazoles).

It should, however, be borne in mind that the calculated values of the thermodynamic functions are reported to more significant figures than are warranted by their absolute accuracy, that the anharmonicity of the vibrations may be significant at higher temperatures *etc.*, so that making far — reaching

conclusions concerning the order in which the thermodynamic functions change is hardly advisable. Nevertheless we believe that the order of magnitude of the thermodynamic functions is correct and that they can be used for most practical purposes, at least until experimentally determined values become available.

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ИЗВОД

Термодинамички функции на тиазол и изотиазол

B. Шоптрајанов

Пресметани се некои термодинамички функции (функциите на енталпија и слободна енергија, ентропијата и топлинскиот капацитет) на тиазол и *изо*-тиазол во подрачјето меѓу 300 и 1000° K, употребувајќи го моделот на хармоничен осцилатор и крут ротор, објавените податоци за вибрационите асигнации на горните две молекули, како и податоците за моментите на инерција на тиазолот. Моментите на инерција на *изо*-тиазолот се пресметани, претпоставувајќи дека растојанијата и аглиите кај оваа молекула се слични на оние кај тиофенот и 1,2,5-тиадизолот. Пресметнатите термодинамички функции се споредени со резултатите добиени порано за тиадиазолите и тиофенот.

ХЕМИСКИ ИНСТИТУТ

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ

Примено 30. јуни 1967.