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Thermodynamic Functions of Furan and Deuterated Furans

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Using the harmonic oscillator — rigid rotator approximation and available molecular and spectroscopic data, the thermodynamic functions (enthalpy and free energy functions, entropy and heat capacity) were calculated for furan and three deuterated furans at one atmosphere pressure and for the ideal gaseous state in the temperature range 298.16—1000° K.

INTRODUCTION

The thermodynamic properties of furan have been both determined experimentally¹ and calculated.¹⁻⁴ Guthrie *et al.*¹ and, partly, Blinc and Pahor³ have made calculations similar to the one presented here, but their work was based on vibrational assignments^{1,2,5} and moments of inertia⁶ which have recently been subjected to reinvestigation^{4,7,8}. It was exactly this availability of new experimental data, as well as our continuous interest in the thermodynamic properties of five-atomic heterocyclic molecules⁹⁻¹¹ that have led us to calculate anew the thermodynamic functions (enthalpy and free energy functions, entropy and heat capacity) of furan and three deuterated furans, the thermodynamic functions of the latter compounds being evaluated, as far as we know, for the first time. As in our previous papers⁹⁻¹¹, the rigid rotator — harmonic oscillator approximation^{12,13} was used and the values for the thermodynamic functions were calculated for one atmosphere pressure and assuming ideal gaseous behaviour.

MOLECULAR AND SPECTROSCOPIC DATA

Moments of Inertia

The principal moments of inertia of furan and the three deuterated furans have been evaluated by Bak *et al.*⁸ from the analysis of the microwave spectra. The values thus obtained (converted into $g \cdot cm^2$ units) are listed in Table I.

TABLE I
Moments of Inertia* ($g \cdot cm^2 \cdot 10^{-40}$) of Furan and Deuterated Furans⁸

	Furan	Furan-2-d	Furan-3-d	Furan-2,5-d ₂
I _a	88.854	90.451	89.455	92.922
I _b	90.779	97.170	98.866	102.861
I _c	179.709	187.696	183.395	195.853

* Conversion factor from amu. Å² = 1.66043 · 10⁻⁴⁰

The values for the moments of inertia listed in Table I show that all these molecules (as well as oxazole and isoxazole, to which the preceding article of this series¹¹ has been devoted) are slightly asymmetric oblate top molecules. The small value of the inertial defect (approximately 0.04 amu. Å²) indicated that the molecules in question are planar, so that furan and the symmetrically substituted furans (such as furan-2,5-*d*₂) would belong to the C_{2v} symmetry group, whereas the monodeuterated furans would have C_s symmetry.

Vibrational Assignments

Two new assignments of the fundamental vibrational frequencies of furan have appeared recently^{4,7} in addition to the older ones.^{1,2,5} One of the new assignments, that by Rico *et al.*⁴ is based on the extensive investigation of the spectra of furan and several isotopically substituted (deuterated) furans, whereas the work of Loisel and Lorenzelli⁷ makes use mainly of the analysis of the low-temperature spectrum of ordinary furan.

As a check on the applicability of these two assignments in the calculation of the thermodynamic properties (and, therefore, their over-all accuracy) we calculated the heat capacity (thermodynamic property most strongly dependent on the vibrational contribution to it) of furan for several temperatures for which experimental data are available.¹ The assignment proposed by Rico *et al.*⁴ gave very good agreement with the experimentally determined values (a fact

TABLE II
Vibrational Assignments for Furan and Furan-2,5-*d*₂⁴

Species	No.*	Furan**	Furan-2,5- <i>d</i> ₂ **	Approximate description
A ₁	1 (1)	3167	3145	CH stretching
	2 (2)	3140	2364	CH stretching
	3 (5)	1491	1436	Ring stretching
	4 (4)	1384	1357	Ring stretching
	5 (3)	1140	1077	Ring stretching
	6 (6)	1066	1018	CH bending
	7 (7)	995	910	CH bending
	8 (8)	871	781	Ring bending
A ₂	9 (9)	863	849	CH deformation
	10 (10)	728	644	CH deformation
	11 (11)	613	524	Ring deformation
B ₁	12 (12)	3161	3134	CH stretching
	13 (13)	3129	2360	CH stretching
	14 (14)	1556	1553	Ring stretching
	15 (15)	1267	1212	CH bending
	16 (16)	1180	1060	CH bending
	17 (17)	1040	902	Ring stretching + bending
	18 (18)	873	860	Ring bending
B ₂	19 (20)	838	799	CH deformation
	20 (19)	745	679	CH deformation
	21 (21)	603	506	Ring deformation

* Numbering according to Herzberg¹². The numbers in parentheses are the ones originally⁴ used.

** Frequencies in cm⁻¹.

already pointed out by the authors⁴ themselves), whereas the values obtained using the assignment by Loisel and Lorenzelli⁷ were appreciably lower than the experimental ones, whichever of the two proposed possibilities for the ν_{10} mode was used in the calculation. Thus, the value of C_p^0 at 317.25° K was 16.23 or 16.17 cal. deg⁻¹. mole⁻¹ (depending on whether 847 or 885 cm⁻¹ was adopted as the frequency of the ν_{10} mode), as compared with the experimental value of 16.80, or calculated on the basis of the assignment by Rico *et al.*⁴ value of 16.73 cal. deg⁻¹. mole⁻¹. The corresponding values for 487.20° K were 24.57, 24.52, 25.45 and 25.25 cal. deg⁻¹. mole⁻¹, respectively. The values were still too low even when the frequency of 728 cm⁻¹, proposed by Rico *et al.*⁴ was used as the value of the ν_{10} mode.

Further work was, therefore, carried out using the assignment by Rico *et al.*⁴ which, together with the assignment for furan-2,5- d_2 due to the same authors, is listed in Table II. The assignments for the two monodeuterated furans⁴ are listed in Table III.

TABLE III
Vibrational Assignments for Furan-2-d and Furan-3-d⁴

Species	No.*	Furan-2-d**	Furan-3-d**	Approximate description
A'	1 (1)	3164	3164	CH stretching
	2 (2)	3145	3159	CH stretching
	3 (12)	3133	3134	CH stretching
	4 (13)	2362	2354	CH stretching
	5 (14)	1552	1546	Ring stretching
	6 (5)	1456	1484	Ring stretching
	7 (4)	1370	1367	Ring stretching
	8 (15)	1228	1240	CH bending
	9 (16)	1169	1171	CH bending
	10 (3)	1036	1121	Ring stretching
	11 (6)	1045	1061	CH bending
	12 (7)	1004	1020	CH bending
	14 (8)	915	886	Ring stretching + bending
	13 (17)	868	864	Ring bending
	15 (18)	811	774	Ring bending
A''	16 (9)	860	849	CH deformation
	17 (20)	814	800	CH deformation
	18 (19)	738	729	CH deformation
	19 (10)	658	646	CH deformation
	20 (11)	601	602	Ring deformation
	21 (21)	516	547	Ring deformation

* Numbering according to Herzberg¹². The numbers in parentheses are the originally⁴ used ones.

** Frequencies in cm⁻¹.

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The method, described in detail in Colthup, Daly and Wiberley's book¹³ and used by us previously⁹⁻¹¹ was employed also in the present calculation. To evaluate the vibrational contribution, tables of the harmonic oscillator functions (calculated by us on an IBM 1130 electronic computer) were used. More details about these tables, as well as other pertinent details about the calculations are given in the preceding article of this series¹¹.

The values for the thermodynamic functions thus obtained were rounded to two decimal places and are compared in Table IV. As seen from that table, the values for all thermodynamic functions of the two monodeuterated furans are extremely close, the differences between them never exceeding the absolute accuracy of the calculated values. For the »reduced enthalpy«, $(H^0 - E_0^0)/T$ and the heat capacity, C_p^0 i. e. for the functions in which the translational and rotational contributions are constant, the values for the monodeuterated furans fall between those of furan (which are lower) and of

TABLE IV
Comparison of the Thermodynamic Functions (cal. deg⁻¹ mole⁻¹)
of Furan and Deuterated Furans

T (°K)	Furan	Furan-2-d	Furan-3-d	Furan-2,5-d ₂
1. Enthalpy function, $(H^0 - E_0^0)/T$				
298.16	9.90	10.20	10.21	10.49
300	9.93	10.24	10.25	10.53
400	12.08	12.51	12.52	12.92
500	14.39	14.88	14.90	15.35
600	16.59	17.13	17.14	17.64
700	18.62	19.19	19.20	19.73
800	20.47	21.05	21.05	21.61
900	22.12	22.72	22.73	23.29
1000	23.63	24.23	24.23	24.81
2. Free energy function, $-(G^0 - E_0^0)/T$				
298.16	53.95	55.62	55.63	54.53
300	54.01	55.69	55.70	54.60
400	57.16	58.94	58.95	57.95
500	60.10	61.99	62.00	61.10
600	62.92	64.90	64.92	64.10
700	65.64	67.70	67.72	66.98
800	68.25	70.39	70.40	69.74
900	70.75	72.96	72.98	72.38
1000	73.16	75.44	75.45	74.92
3. Entropy, S ⁰				
298.16	63.85	65.83	65.84	65.02
300	63.95	65.93	65.94	65.13
400	69.24	71.45	71.47	70.87
500	74.49	76.87	76.90	76.45
600	79.52	82.04	82.06	81.75
700	84.26	86.89	86.91	86.71
800	88.71	91.44	91.46	91.35
900	92.88	95.69	95.71	95.68
1000	96.79	99.67	99.69	99.73
4. Heat capacity, C _p ⁰				
298.16	15.63	16.39	16.43	17.10
300	15.74	16.49	16.53	17.21
400	21.22	22.01	22.04	22.76
500	25.77	26.53	26.54	27.26
600	29.34	30.08	30.08	30.79
700	32.17	32.89	32.88	33.59
800	34.45	35.16	35.14	35.84
900	36.33	37.02	37.01	37.69
1000	37.91	38.57	38.55	39.22

furan-2,5- d_2 (higher). This trend parallels the increasing number of modes shifted, on deuteration, to lower frequencies. On the other hand, the »reduced free energy«, $-(G^0 - E_0^0)/T$ and the entropy, S^0 of the monodeuterated furans are higher than those of both ordinary furan and furan-2,5- d_2 .

It should be noted that the values calculated here for furan are almost identical with those calculated by Guthrie *et al.*¹, the merit of our values being that they are based entirely on experimental data, whereas Guthrie *et al.*¹ chose empirically three frequencies (1300, 1000 and 700 cm^{-1}) in addition to the experimentally determined ones in order to obtain the best possible fit with the experimental values for the thermodynamic properties.

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ИЗВОД

Термодинамички функции на фуран и деутерирани фурани

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За температурното подрачје 298,16—1000° K пресметани се термодинамичките функции (»редуцирана енталпија«, »редуцирана слободна енергија«, ентропија и топлински капацитет) на фуранот и на три деутерирани фурани употребувајќи го моделот за хармоничен осцилатор и крут ротатор, како и објавените молекуларни и спектроскопски податоци.

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
ХЕМИСКИ ИНСТИТУТ
СКОПЈЕ

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