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Note

The effect of internal rotation on the thermodynamic properties of *ortho-*, *meta-*, and *para-*dinitrobenzenes

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Among the benzene derivatives, the *ortho-*, *meta-*, and *para-*dinitrobenzenes have been extensively investigated by thermochemical and spectroscopic methods[1–3].

However, the internal rotation frequencies of the nitro group and the related barriers are not yet unambiguously established. This scarcity of data is not surprising because internal rotation frequencies are generally very weak and consequently, the observation of the relative absorptions is quite difficult. Green and coworkers[2,3] analyzed the spectra of *ortho-*, *meta-*, and *para-*dinitrobenzenes and suggested for the torsional absorptions of the nitro groups a value of about 200 cm^{-1}.

We have undertaken a systematic investigation of *ortho-*, *meta-*, and *para-*dinitrobenzenes in order to clarify the effects of the internal rotation of the nitro group and in this paper are reported some preliminary results obtained for the evaluation of thermodynamic functions of these molecules.

The calculations were carried out in two steps. First, the usual methods of statistical mechanics were employed[4] leaving out the torsional frequencies contribution to the thermodynamic properties. The values so obtained were subsequently corrected according to the Pitzer and Gwinn tables[5–7] by assuming that the molecules are composed of a rigid frame with attached unsymmetrical tops. A planar configuration was hypothesized[3,8] for all the molecules examined, with a group symmetry D_{2h} for the *para-*dinitrobenzene and C_{2v} for *ortho-*, and *meta-*dinitrobenzenes. The following values for bond lengths and angles were employed: C–C = 1.38 Å, C–H = 1.09 Å, and C–N = 1.47 Å[9], N–O = 1.20 Å, O–O = 2.17 Å and O–N–O = 129° for *ortho-*, and *meta-*dinitrobenzenes; C–N = 1.41 Å, N–O = 1.23 Å, O–O = 2.17 Å[10] and O–N–O = 124°[11] for *para-*dinitrobenzene. The reduced moments of inertia for *ortho-*, *meta-*, and *para-*dinitrobenzenes were found to be 0.56393×10^{-38}, 0.54668×10^{-38}, and 0.44869×10^{-38} g cm^2, respectively. The vibrational frequencies given by Green et al.[2,3] were employed. The height of the torsional barrier was assumed as $V_0 = 21.6$ kcal mol^{-1} for all the molecules[12,13]. Moreover an internal rotation number $\sigma_r = 4$ was assumed in all cases[1], while a symmetry number $\sigma_w = 2$ for *ortho-*, and *meta-*substitutes and $\sigma_w = 4$ for the *para-*substituted molecule were assumed. The calculated values of the thermodynamic properties of *ortho-*, *meta-*, and *para-*dinitrobenzenes are reported in Tables 1, 2 and 3, respectively.

A comparison of the above values with those calculated neglecting the torsional contribution gives the average torsional frequencies for the three molecules. The values obtained are: 359.7, 262.0, 364.5 cm^{-1} for *ortho*-, *meta*-, and *para*-dinitrobenzenes, respectively,

Actually, one should expect that the out-of plane vibrations be larger than the corresponding in-plane vibrations as, in the former case, the repulsion term in the potential energy function is larger than in the latter case. For this reason one could expect a decreasing trend for the out-of-plane torsional modes with the increase of the distance between the nitro groups. However, the average torsional frequencies could hardly account for a possible trend.

TABLE 1

THERMODYNAMIC FUNCTIONS FOR 1,2-$C_6H_4(NO_2)_2$ GASEOUS MOLECULE

$cal_{th} = 4.184$ J.

$T(K)$	$-G°(T)-H°(O)/T$ (cal_{th} K^{-1} mol^{-1})	$H°(T)-H°(O)$ (cal_{th} mol^{-1})	$S°(T)$ (cal_{th} k^{-1} mol^{-1})	C_p (cal_{th} K^{-1} mol^{-1})
100	54.07	971	63.78	13.68
200	62.19	2892	76.65	24.88
298.15	68.94	5877	88.65	35.83
300	69.06	5944	88.87	36.03
400	75.49	10052	100.62	45.87
500	81.65	15054	111.75	53.86
600	87.54	20768	122.15	60.14
700	93.18	27038	131.81	65.06
800	98.58	33746	140.76	68.96
900	103.73	40803	149.07	72.09
1.000	108.66	48144	156.80	74.65

TABLE 2

THERMODYNAMIC FUNCTIONS FOR 1,3-$C_6H_4(NO_2)_2$ GASEOUS MOLECULE

$cal_{th} = 4.184$ J.

$T(K)$	$-G°(T)-H°(O)/T$ (cal_{th} K^{-1} mol^{-1})	$H°(T)-H°(O)$ (cal_{th} mol^{-1})	$S°(T)$ (cal_{th} K^{-1} mol^{-1})	C_p (cal_{th} K^{-1} mol^{-1})
100	54.56	985	64.41	14.27
200	62.88	2975	77.76	25.52
298.15	69.81	6015	89.98	36.33
300	69.93	6083	90.21	36.53
400	76.50	10237	102.09	46.28
500	82.75	15277	113.30	54.20
600	88.72	21021	123.76	60.42
700	94.43	27316	133.45	65.29
800	99.88	34045	142.43	69.15
900	105.07	41120	150.76	72.25
1.000	110.03	48475	158.51	74.78

TABLE 3

THERMODYNAMIC FUNCTIONS FOR 1,4-$C_6H_4(NO_2)_2$ GASEOUS MOLECULE

$cal_{th} = 4.184$ J.

$T(K)$	$-G^\circ(T)-H^\circ(O)/T$ (cal_{th} K^{-1} mol^{-1})	$H^\circ(T)-H^\circ(O)$ (cal_{th} mol^{-1})	$S^\circ(T)$ (cal_{th} K^{-1} mol^{-1})	C_p (cal_{th} K^{-1} mol^{-1})
100	53.22	981	63.03	13.61
200	61.38	2905	75.91	25.07
298.15	68.17	5922	88.03	36.24
300	68.29	5989	88.26	36.44
400	74.78	10145	100.14	46.36
500	80.99	15196	111.38	54.35
600	86.94	20955	121.87	60.58
700	92.63	27266	131.58	65.43
800	98.07	34008	140.58	69.27
900	103.26	41094	148.92	72.35
1.000	108.22	48459	156.68	74.86

It is to be pointed out that, in our case, the absorptions were evaluated in a wave number range higher than the expected one. On the other hand, the absorption frequency of the monosubstituted benzene has been observed[8] at 500 cm^{-1} and this result seems to support our calculations. Experimental work is in progress in order to explain this discrepancy.

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