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Thermochemical and Theoretical Studies of Some Bipyridines

M. A. V. Ribeiro da Silva,*[,†] V. M. F. Morais,[‡] M. A. R. Matos,[†] and C. M. A. Rio[†]

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, P-4050, Porto, Portugal, and Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, P-4050 Porto, Portugal

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The following standard molar enthalpies of formation in the gaseous state at 298.15 K were determined from the enthalpies of combustion of the crystalline solids and the respective enthalpies of sublimation: 2,2′-bipyridine, 267.9 ± 3.0 kJ mol^{-1}; 2,4′-bipyridine, 284.2 ± 2.7 kJ mol^{-1}; 4,4′-bipyridine, 293.1 ± 3.6 kJ mol^{-1}. *Ab initio* geometry optimizations of these molecules at the 3-21G level suggest that those with at least one ortho nitrogen atom assume near planar conformations preferentially, while the others have nonplanar most stable forms.

Introduction

In our laboratory we have been interested in the thermochemistry of nitrogen heterocycles[1−5] since thermochemical data for this kind of organic compound are still scarce. In this paper we report the standard molar enthalpies of combustion of the crystalline solids 2,2′-bipyridine (2,2′-bpy), 2,4′-bipyridine and 4,4′-bipyridine and their enthalpies of sublimation to derive the standard molar enthalpies of formation in the gaseous state. *Ab initio* calculations on all possible isomers were done in order to clarify the corresponding geometric conformations and the order of the relative stabilities. These calculations also reproduce measured enthalpies of formation with some accuracy and do provide estimates of this property for the isomers not studied experimentally.

Experimental Section

Materials. The bipyridines (Aldrich) were sublimed repeatedly until the recoveries of carbon dioxide from the combustion experiments were satisfactory. The average ratios of the masses of carbon dioxide observed to those calculated from the masses of the samples (the densities of the samples $\varrho = 1.14$ g cm^{-3} was assumed for the three compounds) were as follows: 2,2′-bpy, 1.0006 ± 0.0007; 2,4′-bpy, 0.9997 ± 0.0004; 4,4′-bpy, 1.0001 ± 0.0014. For all the compounds C, H, N microanalysis was used as an additional test of purity.

Combustion Calorimetry. The enthalpies of combustion of 2,2′-bpy, 2,4′-bpy, and 4,4′-bpy were measured using a static-bomb calorimeter.[6,7] The energy equivalent of the calorimeter was determined using the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, CRM190p) for which $-\Delta_c u/\mathrm{J\ g^{-1}} = 26431.8 \pm 3.7$ under certificate conditions. From eight calibrations $\epsilon(\mathrm{calor}) = 16013.9 \pm 1.7$ J K^{-1} for an average mass of water added to the calorimeter of 3116.3 g.

Samples were ignited at 298.15 ± 0.01 K in oxygen at 3.04 MPa with 1 cm^3 of water added to the bomb. The electrical energy of ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^0 = 16250$ J g^{-1}.[8] Corrections for nitric acid formation were based on the value[9] −59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO_3 from N_2, O_2, and $H_2O(l)$. Corrections for carbon formation were based on $-\Delta_c u^0 = -33$ kJ g^{-1}.[8] The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that from the cotton thread fuse and that lost due to carbon formation. For each compound at 298.15 K, $(\delta u/\delta p)_T$ was assumed to be −0.2 J g^{-1} MPa^{-1}, a typical value for most organic solids. For each compound, $-\Delta_c u^0$ was calculated by the procedure given by Hubbard *et al.*[8] The relative atomic masses used were those recommended by the IUPAC Commission.[10]

Enthalpies of Sublimation. The enthalpies of sublimation of 2,2′-bpy, 2,4′-bpy, and 4,4′-bpy were measured using the "vacuum-sublimation" drop microcalorimetric method.[11] Samples, about 3−5 mg, of each compound contained in a thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in a high temperature Calvet microcalorimeter held at 368 K and then removed from the hot zone by vacuum sublimation. The observed enthalpies of sublimation, $[H^0(\mathrm{g},368\ \mathrm{K}) - H^0_\mathrm{m}(\mathrm{cr},298.15\ \mathrm{K})]$ were corrected to 298.15 K using $\Delta_{298.15\ \mathrm{K}}^{368\ \mathrm{K}} H_m^0 = 12.8$ kJ mol^{-1} estimated by a group method based on the values of Stull *et al.*[12] The microcalorimeter was calibrated *in situ* for these measurements using the reported enthalpy of sublimation of naphthalene.[13]

Results. Results for a typical combustion experiment on each compound are given in Table 1; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the average mass assigned to ϵ(calor). Samples were ignited at 298.15 K so that $\Delta U(\mathrm{IPB}) = -\{\epsilon(\mathrm{calor}) + c_p(\mathrm{H_2O,\ l})\Delta m(\mathrm{H_2O} + \epsilon_\mathrm{f}\}\Delta T_\mathrm{ad} + \Delta U(\mathrm{ign})$; ΔU_Σ is the correction to the standard state, and the remaining terms are as previously defined.[8] The individual values of $\Delta_c u^0$ with the mean and its standard deviation are given in Table 2. Table 3 lists the derived standard molar enthalpies of combustion and formation in the crystalline state. In order to derive $\Delta_f H_m^0(cr)$ from $\Delta_c H_m^0$, the values $\Delta_f H_m^0$ $(\mathrm{H_2O}),\ \mathrm{l})/\mathrm{kJ\ mol^{-1}} = -285.83 \pm 0.04$ and $\Delta_f H_m^0(\mathrm{CO_2,\ g})$/kJ

[†] Centro de Investigação em Química, Faculdade de Ciências.

[‡] Instituto de Ciências Biomédicas Abel Salazar.

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Table 1. Typical Combustion Measurements at 298.15 K (p^0 = 0.1 MPa)

	2,2′-bpy	2,4′-bpy	4,4′-bpy
$m(CO_2, \text{total})/g$	2.09214	2.17481	2.11856
$m(\text{cpd})/g$	0.74066	0.76972	0.74980
$m(\text{cotton})/g$	0.00317	0.00366	0.00359
$\Delta T_{ad}/K$	1.56523	1.62980	1.58444
$\epsilon_f/J\ K^{-1}$	15.48	15.54	15.59
$\Delta m(H_2O)/g$	0.0	0.0	0.0
$-\Delta U(\text{IBP})/J$	25088.48	26123.59	25396.57
$-\Delta U(HNO_3)/J$	64.48	65.07	55.88
$-\Delta U(\text{carbon})/J$	0.0	0.0	0.0
$-\Delta U(\text{ignition})/J$	1.19	1.19	1.19
$-\Delta U_\Sigma/J$	17.10	17.87	17.51
$-\Delta U(\text{cotton})/J$	51.48	59.44	58.30
$-\Delta_c u^0(\text{cpd})/J\ g^{-1}$	33693.49	33754.11	33695.50

Table 2. Values of $-\Delta_c u^0$ (J g^{-1}) at 298.15 K

2,2′-bpy	2,4′-bpy	4,4′-bpy
33696.73	33748.53	33695.50
33693.49	33754.11	33678.71
33693.87	33768.54	33691.48
33681.21	33751.35	33696.77
33685.20	33754.01	33706.46
33688.31	33758.38	33698.42
33695.31		
	$-\langle\Delta_c u^0\rangle$ (J g^{-1})	
33690.6 ± 2.2	33755.8 ± 2.9	33694.6 ± 3.8

mol^{-1} = −393.51 ± 0.13 were used.[14] For each compound at least five independent sublimation determinations were performed, yielding the average $\Delta_{cr}^{g}H_m^0$ values given in Table 3. From the values for the standard molar enthalpies of formation and of sublimation of the condensed compounds, the values of the corresponding standard molar enthalpies of formation in the gaseous state were derived. The results are also shown in Table 3. In accordance with normal thermochemical practice, the uncertainties assigned to the derived molar enthalpies are twice the overall standard deviations of the mean and include the uncertainties in calibration. These uncertainties correspond to a Student-t confidence level of 90–95%.

For 2,2′-bpy, Faour and Akasheh[15] have reported the standard specific energy of combustion $\Delta_c u^0 = -33825.2 \pm 30.2$J g^{-1}. This value is quite different from that obtained in this work. It is noteworthy that those investigators did not make CO_2 recoveries, and nothing was said about the purity of the compound. The standard molar enthalpy of sublimation, $\Delta_{cr}^{g}H_m^0 = 81.8 \pm 2.3$ kJ mol^{-1} for 2,2′-bpy is in good accordance with the value determined by Skinner *et al.*,[16] $\Delta_{cr}^{g}H_m^0 = 81.93 \pm 0.33$ kJ mol^{-1} using a similar technique.

Ab Initio Calculations

Full geometry optimizations on all bipyridines were performed using program GAMESS and the 3-21G[17] split-valence basis set. The energies of the most stable structures of these molecules are reported in Table 4 and show good agreement with the order of relative thermochemical stability obtained from the experimental measurements. The optimized bond lengths and bond angles for these structures are given in Table 5 and Table 6, respectively.

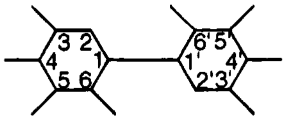

Figure 1. Labeling of atoms in bipyridines. The conformation shown (for 2,2′-bpy) is the trans-planar (Θ = 180°) one.

One important question concerning the conformational behavior of the bipyridines is the problem of the occurrence of electron delocalization between the two rings. As is well known, in order to occur such extended delocalization the molecule must assume a planar or near planar conformation. From the present optimizations we can conclude that all isomers with at least one ortho nitrogen are more stable in planar or near planar trans conformations. In these conformations some stabilization due to electron delocalization across the rings can be expected and the interaction between the ortho hydrogen atom of one ring and the lone electron pair of the nitrogen atom of the other ring is also maximal. On the other hand, the trans planar conformation minimizes the (destabilizing) hydrogen–hydrogen and lone pair–lone pair interactions at ortho positions on both rings. These results agree with the experimental data available for 2,2′-bpy.[18–23] The other isomers have most stable conformations with a torsional angle about the inter-ring C–C bond of Θ ≃ 130°. Electron diffraction[24] and NMR[25] data suggest, respectively, a most probable torsional angle of 37.2° and 30° for 4,4′-bpy in the gaseous phase. It can be argued that this conformation results from an optimum balance between the electron delocalization, which stabilizes the molecule, and the H–H repulsions, destabilizing it. Note the similarity between these isomers without any asymmetries at ortho positions and biphenyl, which has a most stable conformation with Θ = 136°.[26] This similarity can of course be justified by the identical environments of the inter-ring C–C bond. Thus, asymmetries occurring at meta positions must have a minor effect on the conformational behavior of bipyridines.

Single point energy calculations with the same basis set were performed for all molecules with all the geometric parameters frozen at their optimum values, except the torsion angle between the two rings, which was varied by 20° increments through the entire 0–180° interval. The use of rigid (instead of optimized) geometries in the calculation of the torsional energy curves may seem debatable. However, sample test calculations showed us that the torsional curves obtained with optimized geometries at fixed torsion angle differ by no more than 0.5 kJ mol^{-1} from those obtained with rigid geometries. In addition, the geometrical parameters show very little variations with torsion angle. Similar findings were reported also in a study of 2,2′-bipyrimidine.[29] The resulting torsion potential energy curves are shown in Figure 2. We can see from this figure, that 2,2′-bpy has in addition to the absolute minimum, a secondary relative minimum near Θ = 40°. This secondary mini-

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Table 3. Derived Standard Molar Values (kJ mol^{-1}) at 298.15 K

	$-\Delta_c U_m^0$(cr)	$-\Delta_c H_m^0$(cr)	$\Delta_f H_m^0$(cr)	$\Delta_{cr}^{g} H_m^0$(cr)	$\Delta_f H_m^0$(g)
2,2′-bpy	5262.0 ± 1.5	5264.5 ± 1.5	186.1 ± 2.0	81.8 ± 2.3	267.9 ± 3.0
2,4′-bpy	5272.2 ± 1.6	5274.7 ± 1.6	196.3 ± 2.1	87.9 ± 1.7	284.2 ± 2.7
4,4′-bpy	5262.7 ± 1.8	5265.2 ± 1.8	186.8 ± 2.2	106.3 ± 2.8	293.1 ± 3.6

Table 4. Calculated RHF/3-21G//RHF/3-21G Energies

compound	total energy, E_h[a]	relative energy[b]	zero point energy[b]
2,2′-bipyridine	−489.490397	0.0	451.0
2,3′-bipyridine	−489.480617	25.7	450.5
2,4′-bipyridine	−489.479556	28.5	450.5
3,3′-bipyridine	−489.474102	42.8	449.3
3,4′-bipyridine	−489.474074	42.9	449.5
4,4′-bipyridine	−489.473947	43.2	449.8

[a] Atomic unit of energy: E_h = 2625.50184 kJ mol^{-1}. [b] In kJ mol^{-1}.

Table 5. Optimized RHF/3-21G Bond Lengths (Å)

bond	2,2′-bpy	2,3′-bpy	2,4′-bpy	3,3′-bpy	3,4′-bpy	4,4′-bpy
1−2	1.33	1.33	1.33	1.39	1.39	1.39
2−3	1.33	1.33	1.33	1.33	1.33	1.38
3−4	1.38	1.38	1.38	1.33	1.33	1.33
4−5	1.39	1.38	1.38	1.38	1.38	1.33
5−6	1.38	1.38	1.38	1.38	1.38	1.38
6−1	1.39	1.39	1.39	1.39	1.39	1.39
1−1′	1.48	1.48	1.49	1.48	1.48	1.49
1′−2′	1.33	1.39	1.39	1.39	1.39	1.39
2′−3′	1.33	1.33	1.38	1.33	1.38	1.38
3′−4′	1.38	1.33	1.33	1.33	1.33	1.33
4′−5′	1.39	1.38	1.33	1.38	1.33	1.33
5′−6′	1.38	1.38	1.38	1.38	1.38	1.38
6′−1′	1.39	1.39	1.39	1.39	1.39	1.39

Table 6. Optimized RHF/3-21G Bond Angles

bonds	2,2′-bpy	2,3′-bpy	2,4′-bpy	3,3′-bpy	3,4′-bpy	4,4′-bpy
1−2−3	120	120	120	123	123	119
2−3−4	122	122	122	119	119	123
3−4−5	118	118	118	122	122	119
4−5−6	119	120	119	119	119	123
5−6−1	119	119	119	120	120	119
6−1−2	122	121	121	117	118	118
2−1−1′	118	116	116	121	121	121
1−1′−2′	118	123	123	121	121	121
1′−2′−3′	120	123	120	123	119	119
2′−3′−4′	122	119	123	119	123	123
3′−4′−5′	118	122	118	122	118	119
4′−5′−6′	119	119	123	119	123	123
5′−6′−1′	119	120	119	120	119	119
6′−1′−2′	122	117	118	117	118	118
2−1−1′−2′	179.92	179.37	177.55	131.48	131.82	130.88

mum occurs at a torsion angle approximately equal to the optimum value of this angle in biphenyl. The energy differences between the two minima and the barrier between them are about 45 kJ mol^{-1} and 7.5 kJ mol^{-1}, respectively. As can also be seen from Figure 2 the torsional curves of 2,3′-bpy and 2,4′-bpy are very flat near planarity, making very slow the convergence of the optimization process, when started from a nonplanar model. This is also a possible source of error in the experimental characterization of the preferred conformations of these molecules, at least in the gas phase where large amplitude torsional motion can thus occur. Previous STO-3G calculations[27−29] predicted optimum torsional angles of 145° and 147° for 2,3′-bpy and 2,4′-bpy, respectively, and secondary minima symmetrically located relative to Θ = 90°. In the present calculations those minima are strongly shifted toward the extremes, Θ = 0° and Θ = 180° and, in the case of 2,4′-bpy, the preferred structure in now perfectly trans planar.

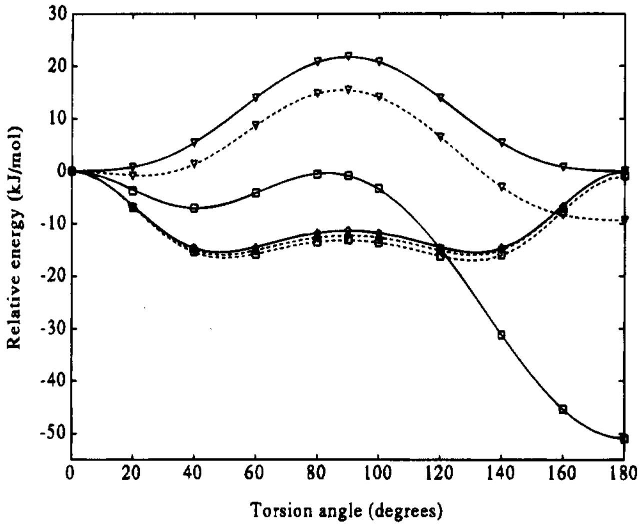

Figure 2. Torsional curves for bipyridines. Solid curves for (a) 2,2′-bpy: □; (b) 2,4′-bpy: ▽; (c) 3,4′-bpy: ◇. Dashed curves for (a) 3,3′-bpy: □; (b) 2,3′-bpy: ▽; (c) 4,4′-bpy: ◇.

Table 7. Calculated Coefficients of the Fourier Expansion of the Energy (eq 1)

coefficient (kJ mol^{-1})	2,2′	2,3′	2,4′	3,3′	3,4′	4,4′
V_1	−39.6	−7.2	−	−1.0	−	−
V_2	25.1	20.8	22.2	−11.1	−9.6	−10.5
V_3	−9.9	−1.7	−	−0.1	−	−
V_4	−3.8	−4.5	−3.6	−10.0	−9.8	−9.8
V_5	−1.4	−0.4	−	−0.1	−	−
V_6	−0.5	−0.7	−0.4	−1.6	−1.8	−1.8

The torsional curves for 3,3′-bpy, 3,4′-bpy, and 4,4′-bpy are almost identical except the slight asymmetry in the curve of 3,3′-bpy.

All the torsional potential energy curves shown in Figure 2 were obtained by fitting the calculated energies to a Fourier cosine series:

$$\Delta E(\Theta) \equiv E(\Theta) - E(0) = {}^1/_2 \sum_{k=1}^{\infty} V_k[1 - \cos(k\Theta)] \quad (1)$$

We have found necessary to maintain the six leading terms in the Fourier expansion, in order to fit accurately (rmsd error less than 1 kJ mol^{-1}) the torsional curves of 2,2′-bpy, 2,3′-bpy, and 3,3′-bpy. For the isomers having at least a nitrogen atom at the 4′-position the torsional potential energy curves are symmetrical about Θ = 90°. As a consequence, for these isomers only even terms in the previous expansion are allowed by symmetry. In this case three term Fourier expansions are found sufficient to give accurate fits (rmsd error less than 1 kJ mol^{-1}). The calculated coefficients are shown in Table 7.

All the stationary points found were further characterized as true minima through calculation and diagonal-

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ization of the hessian matrix. This process also provided the harmonic vibrational frequencies for all the molecules. The calculated zero point vibrational energies are included in Table 4.

The importance of the stabilization of a molecule due to conjugation and resonance of the extended system of formal single and multiple bonds when compared with the corresponding isolated linkages can be well characterized by the energy of bond separation reactions involving it. Bond separation reactions which are isodesmic, that is, in which the numbers of bonds of each formal type are conserved and only the relationships among the bonds are altered, can be written for pyridine and for the bipyridines as:

$$C_5H_5N + 5CH_4 + NH_3 \rightarrow 2C_2H_6 + 2C_2H_4 + CH_3NH_2 + CH_2NH \quad (2)$$

and

$$C_{10}H_8N_2 + 12CH_4 + 2NH_3 \rightarrow 5C_2H_6 + 4C_2H_4 + 2CH_3NH_2 + 2CH_2NH \quad (3)$$

This type of reaction, as is well known, is likely to be successfully treated at the single-determinant level, since the errors inherent in the description of individual reactant and product molecules are expected to become largely canceled. Reaction 3 also allows the definition of the isodesmic resonance energy of a bipyridine as the negative of the energy of formation of that bipyridine from nonconjugated components in that reaction. Calculations at the RHF/3-21G//RHF/3-21G level have also been done for all the auxiliary molecules involved in reactions 2−3. From these calculations we were able to calculate the bond separation energy for pyridine and all the bipyridines. The results are shown in Table 8. The positive bond separation energies for all these molecules is, as stated before, a measure of the stabilization by resonance, relative to the corresponding isolated linkages. As can be seen from that table, the order of stability predicted for bipyridines is in agreement with that found experimentally. In particular, 2,2′-bpy is predicted to be the most stable molecule, 4,4′-bpy being the least stable one, as observed experimentally. Moreover, these results indicate also that all the bipyridines have more than twice the resonance energy of pyridine, an indication of the occurrence of some electron delocalization across the two pyridine rings.

Table 8. Calculated Bond Separation Energies and Enthalpy of Formation (kJ mol^{-1})

molecule	bond separation energy	enthalpy of formation		
		ab initio	PM3	exp
pyridine	268.56	143.5	127.1	140.4 ± 0.7
2,2′-bipyridine	605.88	276.3	261.8	268.2 ± 3.0
2,3′-bipyridine	580.21	301.6		
2,4′-bipyridine	577.42	304.5	261.1	284.4 ± 2.8
3,3′-bipyridine	563.10	317.8		
3,4′-bipyridine	563.02	318.1		
4,4′-bipyridine	562.69	318.6	260.4	293.3 ± 3.6

Finally, on the basis of the last results, we can estimate the enthalpy changes associated with the bond separation reactions. These, used together with the known values of the enthalpy of formation of the species involved in that reaction, provide the estimates of the enthalpy of formation of bipyridines shown in Table 8. As we can see, these estimates are in very good agreement with the experimental findings. Also shown in that table, for comparison purposes, are the estimates of the enthalpies of formation of bipyridines obtained from the semiempirical method PM3.[30] As is well known this semiempirical method has been specially parameterized to reproduce enthalpies of formation and has largely superseded the older MNDO and AM1 parameterizations. We can conclude for the results in Table 8 that PM3 estimates of the enthalpies of formation of bipyridines are generally less reliable than those we have obtained from first principles.

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