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Thermochemical and theoretical studies of 4-methylbiphenyl, 4,4′-dimethylbiphenyl, 4,4′-dimethyl-2,2′-bipyridine

Manuel A.V. Ribeiro da Silva,[a]* M. Agostinha R. Matos,[a] Carolina M. A. do Rio[a] and Victor M. F. Morais[b]

[a] *Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4150 Porto, Portugal.*

[b] *Instituto de Ciências Biomédicas Abel Salazar, University of Porto, P-4050 Porto, Portugal*

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation for 4-methylbiphenyl, 4,4′-dimethylbiphenyl and 4,4′-dimethyl-2,2′-bipyridine were derived from the standard molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, measured by static-bomb combustion calorimetry. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were measured by Calvet microcalorimetry. Theoretical calculations at the *ab initio* restricted Hartree–Fock (RHF) level with second-order Møller–Plesset (MP2) perturbation theory correlation corrections and density functional theory (DFT) have been carried out for all these molecules in order to access their stabilitites relative to the non-substituted ones. The theoretical results are in general good agreement with the experimental results.

Introduction

Following on in the sequence of previous thermochemical and theoretical work on non-substituted bipyridines[1] we decided to study the effect of methyl substitution into 2,2′-bipyridine, and for comparison we carried out a similar study on methyl-substituted biphenyls.

In this paper we report the standard molar enthalpies of combustion for 4-methylbiphenyl, 4,4′-dimethylbiphenyl and 4,4′-dimethyl-2,2′-bipyridine as well as their standard molar enthalpies of sublimation to derive the respective standard molar enthalpies of formation in the gaseous phase.

In addition, *ab initio* calculations were performed to clarify the order of the relative stabilities.

Experimental

The 4-methylbiphenyl, 4,4′-dimethylbiphenyl and 4,4′-dimethyl-2,2′-bipyridine, obtained from Aldrich Chemical Co., were purified by repeated vacuum sublimation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The 4-methylbiphenyl was recrystallized twice from ethanol–water before sublimation. Purity was confirmed by elemental microanalysis. The average ratio, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were: 4-methylbiphenyl, 0.9998 ± 0.0003; 4,4′-dimethylbiphenyl, 0.9996 ± 0.0004; 4,4′-dimethyl-2,2′-bipyridine, 0.9993 ± 0.0003.

Combustion calorimetry

The combustion experiments were performed with a static-bomb calorimeter; the apparatus and technique were as described previously.[2,3] The energy equivalent of the calorimeter ε(calor) was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190 p), having a massic energy of combustion, ($\Delta_c u$) under certificate bomb conditions, of $-(26431.8 \pm 3.7)$ J g^{-1}. The calibration results were corrected to give the energy equivalent ε(calor) corresponding to the average mass of water added to the calorimeter (3119.6 g). From nine calibration experiments, $\varepsilon(\text{calor}) = (15\,911.2 \pm 1.5)$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

Combustion experiments were made in oxygen at 3.04 MPa, with 1 cm^3 of water added to the bomb. In the experiments with 4,4′-dimethyl-2,2′-bipyridine, *n*-hexadecane (Gold Label, Aldrich) was used to moderate the combustions. The massic energy of combustion of this *n*-hexadecane sample was determined in separate measurements to be $\Delta_c u^\circ = -(47\,076.7 \pm 3.3)$ J g^{-1}.[4] For all experiments, ignition was made at (298.150 ± 0.001) K. The electrical energy for 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 $CH_{1.686}O_{0.843}$, the massic energy of combustion $\Delta_c u^\circ = -16\,250$ J g^{-1}.[5] This value was previously confirmed in our laboratory. Corrections for nitric acid formation were based on -59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).[6] Corrections for carbon formation were based on massic energy of combustion of carbon $\Delta_c u^\circ = -33$ kJ g^{-1}.[5] The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton-thread fuse and from the *n*-hexadecane, and that lost due to carbon formation. The relative densities[7] are 4-methylbiphenyl, 1.01 g cm^{-3}; 4,4′-dimethylbiphenyl, 0.917 g cm^{-3}; 4,4′-dimethyl-2,2′-bipyridine, 1.14 g cm^{-3}. An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2$ J g^{-1} MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds, was assumed. The massic energies of combustion, $\Delta_c u^\circ$, for the three compounds were calculated by the procedure given by Hubbard *et al.*[5] The relative atomic masses used were those recomended by the IUPAC Commission in 1993.[8]

Enthalpies of sublimation

The enthalpies of sublimation of 4-methylbiphenyl, 4,4′-dimethylbiphenyl and 4,4′-dimethyl-2,2′-bipyridine were measured using the 'vacuum sublimation' drop microcalorimetric method.[9] Samples, *ca.* 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 $T = 376$ K for

Table 1 Typical combustion experiments[a] at $T = 298.15$ K

	4-MeBPh[b]	4,4′-diMeBPh[c]	4,4′-diMeBPy[d]
$m(\mathrm{CO_2}, \mathrm{total})/\mathrm{g}$	1.934 46	2.265 18	2.182 62
$m'(\mathrm{cpd})/\mathrm{g}$	0.567 01	0.668 24	0.486 57
$m''(\mathrm{fuse})/\mathrm{g}$	0.003 84	0.003 85	0.003 78
$m'''(n\text{-hexadecane})/\mathrm{g}$			0.251 40
$\Delta T_{\mathrm{ad}}/\mathrm{K}$	1.462 21	1.735 61	1.835 05
$\varepsilon_{\mathrm{f}}/\mathrm{J\ K^{-1}}$	15.74	16.53	16.94
$\Delta m(\mathrm{H_2O})/\mathrm{g}$	0.0	0.0	0.0
$-\Delta U(\mathrm{IBP})/\mathrm{J}$	23 287.35	27 643.16	29 227.76
$\Delta U(\mathrm{HNO_3})/\mathrm{J}$	17.07	13.19	40.24
$\Delta U(\mathrm{ign})/\mathrm{J}$	1.18	1.17	1.17
$\Delta U_{\Sigma}/\mathrm{J}$	12.14	14.20	13.92
$\Delta U(\mathrm{carbon})/\mathrm{J}$	0.00	0.00	0.00
$\Delta U(n\text{-hexadecane})/\mathrm{J}$			11 835.15
$-\Delta U(\mathrm{fuse})/\mathrm{J}$	62.36	62.52	61.39
$-\Delta_{\mathrm{c}}u^{\circ}/\mathrm{J\ g^{-1}}$	40 908.94	41 232.56	35 507.86

[a] For definitions of quantities please see text. [b] 4-MeBPh = 4-methylbiphenyl. [c] 4,4′-diMeBPh = 4,4′-dimethylbiphenyl. [d] 4,4′-diMeBPy = 4,4′-dimethyl-2,2′-bipyridine.

4-methylbiphenyl, at $T = 382$ K for 4,4′-dimethylbiphenyl and at $T = 413$ K for 4,4′-dimethyl-2,2′-bipyridine, and then removed from the hot zone by vacuum sublimation. The observed enthalpies of sublimation were corrected to 298.15 K, using $\Delta^{T}_{298.15\,\mathrm{K}}H^{\circ}_{\mathrm{m}}/\mathrm{kJ\ mol^{-1}} = 16.91$, 20.35 and 27.03 kJ mol^{-1}, respectively, for 4-methylbiphenyl, 4,4′-dimethylbiphenyl and 4,4′-dimethyl-2,2′-bipyridine. These $\Delta^{T}_{298.15\,\mathrm{K}}H^{\circ}_{\mathrm{m}}$ values were estimated by a group method based on the values of Stull *et al.*[10] The microcalorimeter was calibrated *in situ* for these measurements using the reported enthalpy of sublimation for naphthalene.[10]

Results

Results for a typical combustion experiment are given in Table 1, where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, ΔU_{Σ} is the correction to the standard state and the remaining quantities are as previously defined.[5] Samples were ignited at $T = 298.15$ K so that the energy for the isothermic bomb process $\Delta U(\mathrm{IPB})$ can be given by the relation

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O, l}) + \varepsilon_f\}\ \Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}}$$

where $C_{\mathrm{p}}(\mathrm{H_2O, l})$ is the heat capacity of liquid water, ε_{f} is the heat content for the products of the combustion reaction, ΔT_{ad} is the adiabatic temperature rise for the bomb process and ΔU_{ign} is the energy of ignition.

The individual results, together with the mean values and their standard deviations are given in Table 2. Table 3 lists the derived standard molar energy $[-\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}(\mathrm{cr})]$ and enthalpy $[-\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})]$ of combustion and the standard molar enthalpy of formation $[\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})]$ for the three compounds in the crystalline state (cr), at $T = 298.15$ K. In accordance with normal thermochemical practice, the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean, and includes the uncertainties in calibration and in the values of the auxiliary quantities used.[11] To derive $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$ from $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}$ the standard molar enthalpies of formation of $\mathrm{H_2O(l)}$ and $\mathrm{CO_2(g)}$, at $T = 298.15$ K, respectively, $-(285.830 \pm 0.042)$ kJ mol^{-1},[12] and $-(393.51 \pm 0.13)$ kJ mol^{-1},[12] were used. For each compound at least five independent sublimation determinations were performed, yielding the average standard molar enthalpy of sublimation $\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{0}_{\mathrm{m}}$ values given in Table 3. From the values for the standard molar enthalpies of formation and of sublimation of the crystalline compounds, the values of the standard molar enthalpies of formation in the gaseous state were derived.

Table 2 Values of $-\Delta_{\mathrm{c}}u^{\circ}/\mathrm{J\,g^{-1}}$ at $T = 298.15$ K

4-MeBPh	4,4′-diMeBPh	4,4′-diMeBPy
40 905.81	41 258.49	35 507.86
40 891.34	41 253.56	35 480.07
40 907.83	41 217.80	35 517.60
40 908.30	41 232.56	35 530.31
40 890.88	41 238.54	35 521.64
40 908.94	41 261.78	35 482.79
40 897.73	41 237.00	35 505.17
40 902.45	41 246.08	
	41 256.56	
40 901.7 ± 2.6[a]	41 244.7 ± 4.8[a]	35 506.5 ± 7.2[a]

[a] Values of $- < \Delta_{\mathrm{c}}u^{\circ} > /\mathrm{J\ g^{-1}}$

Theoretical calculations and Discussion

The geometries of all molecules were fully (*i.e.* without any constraint) optimized at the *ab initio* level using the quantum mechanical program GAMESS[13,14] and the split-valence 6-31G*[15,16] atomic basis set. This basis set, which includes polarization (d-type) functions on all heavy (second and further rows) atoms, is known to provide bond lengths and bond angles which are generally in good agreement with experimental findings.

All the stationary points thus obtained were further characterized as true minima through calculation and diagonalization of the corresponding hessian matrices. This procedure also allows the calculation of the harmonic vibrational frequencies and zero point vibrational energies, which are required in order to obtain estimates of reaction energies at temperatures higher than 0 K.

The total RHF/6-31G* energies for the resulting most stable structures of these molecules, in the gaseous state at 0 K, are reported in Table 4.

As is well known, the results of Hartree–Fock calculations suffer from an intrinsic error, called correlation error, which results from a deficient treatment of electron correlation. This error is particularly important for calculations using a single-determinant representation of the electronic wavefunction. In order to get estimates of the electronic energy that can be confidently used in the calculation of reaction energies we must, in some way, go beyond the Hartree–Fock treatment of electronic structure, so that, at least a fraction of the correlation error can be properly taken into account.

Within the framework of Hartree–Fock theory this can be done, *e.g.* through the use of perturbation theory techniques. In this work we have performed post-Hartree–Fock calculations based on Møller–Plesset perturbation theory, using the 3-21G basis set,[17,18] for all isomers studied. Only second-order corrections were calculated using the 3-21G basis set. A more rigorous estimate of the correlation energy, either using the more sophisticated 6-31G* basis set or higher levels of perturbation theory is at present beyond our computational capabilities for molecules of this size.

An alternative way of obtaining reliable estimates of the electronic energy involves a different methodology, the so

Table 3 Derived standard ($p^{\circ} = 0.1$ MPa) molar values at $T = 298.15$ K

	$-\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}(\mathrm{cr})/\mathrm{kJ\ mol^{-1}}$	$-\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})/\mathrm{kJ\ mol^{-1}}$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})/\mathrm{kJ\ mol^{-1}}$	$\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\circ}_{\mathrm{m}}/\mathrm{kJ\ mol^{-1}}$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{g})/\mathrm{kJ\ mol^{-1}}$
4-MeBPh	6881.2 ± 1.8	6888.6 ± 1.8	58.0 ± 2.5	80.2 ± 1.4	138.2 ± 2.9
4,4′-diMeBPh	7517.4 ± 2.3	7526.1 ± 2.3	16.2 ± 2.9	95.1 ± 2.0	111.3 ± 3.6
4,4′-diMeBPy	6541.7 ± 3.0	6546.7 ± 3.0	109.6 ± 3.4	99.7 ± 2.3	209.3 ± 4.1

Table 4 Calculated total energies[a] in atomic units[b] and zero-point vibrational energies (kJ mol^{-1})

molecule	$-E_{6\text{-}31G*}$	$-E_{DFT/6\text{-}31G*}$	$-E_{MP2/3\text{-}21G*}$	E_{ZP}
biphenyl	460.253 95	463.459 80	458.722 07	515.34
4-methylbiphenyl	499.291 08	502.789 77	497.636 72	591.66
4,4′-dimethylbiphenyl	538.328 16	542.119 81	536.551 38	668.14
2,2′-bipyridine	492.248 48	495.558 06	490.559 21	451.04
4-methyl-2,2′-bipyridine	531.286 06	534.888 96	529.474 80	527.39
4,4′-dimethyl-2,2′-bipyridine	570.323 60	574.219 75	568.390 36	604.38
phenyl radical	230.050 91	231.264 00	229.264 80	—
4-methylphenyl radical	269.087 46	270.969 54	268.178 85	—
2-piridyl radical	246.048 17	247.694 38	245.184 79	—
5-methyl-2-piridyl radical	285.085 26	287.024 79	284.099 91	—

[a] MP2 = second order Møller–Plesset perturbation theory correlation corrections. [b] Atomic unit of energy: $E_h = 2\,625.501\,84$ kJ mol^{-1}.

called density functional theory (DFT), a technique in which the effects of electron correlation are automatically taken into account, through the use of conveniently chosen functional representations of the exchange-correlation energy. We also performed single-point DFT calculations of the energy of all molecules at their most stable 6-31* geometries, using a modified version of the DeMon[19] package. We choose a non-local spin density approximation (NLSDA), to represent the exchange-correlation energy, which uses the non-local exchange-functional of Becke[20] and the non-local correlation functional of Perdew.[21] The molecular orbitals were represented as linear combinations of Gaussian-type atomic orbitals of types double-ζ plus polarization and triple-ζ plus polarization placed on hydrogen and on heavy atoms, respectively. Auxiliary orbital basis sets consisting of s-, p- and d-type functions constrained to the same exponent were used to fit the charge density and the exchange-correlation energy density. The correlated energies resulting from DFT and MP2 calculations are also shown in Table 4.

The importance of the stabilization of a molecule by conjugation and resonance of the extended system of formal single and multiple bonds, when compared with the corresponding isolated linkages, can be characterized by the energy of the bond separation reactions involving it.[22] Bond separation reactions in which the numbers of bonds of each formal type are conserved and only the relationships among the bonds are altered are called isodesmic and, for the present case they can be chosen as

$$\text{biphenyl} + 14CH_4 \rightarrow 7C_2H_6 + 6C_2H_4$$

$$\text{methylbiphenyl} + 15CH_4 \rightarrow 8C_2H_6 + 6C_2H_4$$

$$\text{dimethylbiphenyl} + 16CH_4 \rightarrow 9C_2H_6 + 6C_2H_4$$

$$\text{bipyridine} + 12CH_4 + 2NH_3 \rightarrow 5C_2H_6 + 4C_2H_4 + 2CH_3NH_2 + 2CH_2NH$$

$$\text{methylbipyridine} + 13CH_4 + 2NH_3 \rightarrow 6C_2H_6 + 4C_2H_4 + 2CH_3NH_2 + 2CH_2NH$$

$$\text{dimethylbipyridine} + 14CH_4 + 2NH_3 \rightarrow 7C_2H_6 + 4C_2H_4 + 2CH_3NH_2 + 2CH_2NH$$

$$\text{phenyl} + 5CH_4 + CH_3 \rightarrow 2C_2H_6 + 2C_2H_4 + CH_3CH_2 + CH_2CH$$

$$\text{2-methylphenyl} + 6CH_4 + CH_3 \rightarrow 3C_2H_6 + 2C_2H_4 + CH_3CH_2 + CH_2CH$$

$$\text{2-pyridyl} + 4CH_4 + CH_3 + NH_3 \rightarrow 3C_2H_6 + 3C_2H_4 + CH_3NH_2 + CH_2NH + CH_3CH_2 + CH_2CH + CH_2NH_2 + CHNH$$

$$\text{5-methyl-2-pyridyl} + 5CH_4 + CH_3 + NH_3 \rightarrow 4C_2H_6 + 3C_2H_4 + CH_3NH_2 + CH_2NH + CH_3CH_2 + CH_2CH + CH_2NH_2 + CHNH$$

This type of reaction, which allows the definition of the isodesmic resonance (or stabilization) energy of a molecule as the negative of the energy of formation of that molecule from the corresponding non-conjugated fragments, is likely to be successfully treated even at the single-determinant level, since the errors inherent in the description of individual reactant and product molecules are expected to become largely cancelled.

In order to calculate the stabilization energies of the molecules calculations at the MP2/RHF/3-21G level and calculations using DFT and the non-local spin density approximation have also been done for all other molecules involved in those reactions, at their most stable 3-21G and 6-31G* geometries, respectively. From these calculations we were able to estimate the bond separation energy for all the molecules, which are shown in Table 5. It must be noted that the reported bond separation energies refer to 0 K and do not include zero point vibrational energy corrections, as we feel that in this way we are comparing purely electronic stabilization effects. The positive bond separation energies for all these molecules is, as stated before, a measure of their stabilization by resonance, relative to the corresponding isolated non-conjugated linkages.

The geometries of biphenyl and the methylbiphenyls are determined by the balance between two phenomena: (i) the stabilization resulting from the extended π-electron conjugation between the two rings, which decreases with increasing inter-ring torsional (twist) angle, and (ii) the steric repulsions between proximate (2- and 2′-) hydrogen atoms in different rings, which favour an orthogonal arrangement of the rings. The effects of this delicate balance are evident in the results of the geometry search, which predict torsion angles about the inter-ring C—C bond of 45.5° (biphenyl), 45.1° (4-methylbiphenyl) and 42.6° (4,4′-dimethylbiphenyl). As a comparison the experimentally determined twist angle of biphenyl in the gas phase is *ca.* 44°.[23]

In the case of subsituted 2,2′-bipyridines the destabilizing repulsion between the proximate hydrogen atoms is not important and the optimum geometry is consequently determined by the requirement of maximal inter-ring electronic delocalization and by the stabilizing interactions between the nitrogen atom on one ring (2- or 2′-) and the neighbouring hydrogen atom at the other ring (6′- or 6-). Their conformation is thus planar with twist angles of 180°.

The amount of inter-ring electronic delocalization can be probed by natural bond orbital (NBO) analysis,[24,25] which aims to provide a description of the bonding structure in terms of highly occupied localized single and double bonds and lone pairs, which are compatible with the electronic density resulting from the Hartree–Fock wavefunction. This

Table 5 Calculated bond separation energies and bond separation enthalpies (kJ mol^{-1})

molecule	bond separation energy at 0 K MP2/3-21G	 DFT/NLSDA	bond separation enthalpy at 298.15 K MP2/3-21G	 DFT/NLSDA	 exp.
biphenyl	588.41	591.53	616.09	619.22	589.38
4-methylbiphenyl	610.32	607.96	643.96	641.59	623.20
4,4′-dimethylbiphenyl	632.28	624.58	666.93	659.22	640.73
2,2′-bipyridine	657.44	641.64	689.76	673.96	651.66
4,-methyl-2,2′-bipyridine	681.83	660.52	726.16	704.85	—
4,4′-methyl-2,2′-bipyridine	706.13	677.31	745.42	716.60	681.22
phenyl radical	247.86	251.93	—	—	—
4-methylphenyl radical	268.19	267.16	—	—	—
2-pyridyl radical	236.49	250.13	—	—	—
5-methyl-2-piridyl radical	259.63	267.69	—	—	—

description corresponds closely to the classical Lewis picture of chemical bonding. Since in systems showing electronic delocalization, no single localized description can account for all the Hartree–Fock electronic density, a convenient measure of the delocalization is the fraction of the total electronic density not described by the localized structures; this fraction will appear as small populations of the corresponding antibonding orbitals which are formally unoccupied in classical (localized) systems. Thus, the delocalization effects can be depicted as charge-transfer processes from the highly occupied bond orbitals into adjacent unoccupied antibonding orbitals and their occurrence implies that any attempt to describe the bonding structure through localized bonds and lone pairs will fail. Tables 6 and 7 show the contributions to some relevant natural localized molecular orbitals (NLMO) of the studied systems which result from interactions with the p_π atomic orbitals at a different ring (see below for the numbering of the atoms).

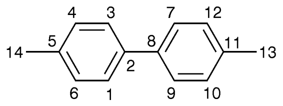

Table 6 6-31G* natural localized molecular orbitals (NLMO) of biphenyls

NLMO	composition	molecule
π_{C1-C2}	0.21% p_{C7}; 0.50% p_{C8}; 0.22% p_{C9}	biphenyl
π_{C1-C2}	0.20% p_{C7}; 0.48% p_{C8}; 0.22% p_{C9}	dimethylbiphenyl
π_{C1-C2}	0.22% p_{C7}; 0.53% p_{C8}; 0.24% p_{C9}; 0.10% p_{C11}	dimethylbiphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	biphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	methylbiphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	dimethylbiphenyl
π_{C5-C6}	0.12% p_{C8}	biphenyl
π_{C5-C6}	0.11% p_{C8}	methylbiphenyl
π_{C5-C6}	0.14% p_{C8}; 0.21% p_{C14}	dimethylbiphenyl
π_{C8-C9}	0.21% p_{C3}; 0.50% p_{C2}; 0.22% p_{C3}	biphenyl
π_{C8-C9}	0.22% p_{C3}; 0.52% p_{C2}; 0.23% p_{C1}	methylbiphenyl
π_{C8-C9}	0.22% p_{C3}; 0.53% p_{C2}; 0.24% p_{C1}; 0.10% p_{C5}	dimethylbiphenyl
$\pi_{C10-C11}$	0.12% p_{C2}	biphenyl
$\pi_{C10-C11}$	0.14% p_{C2}	methylbiphenyl
$\pi_{C10-C11}$	0.14% p_{C2}	dimethylbiphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	biphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	methylbiphenyl
π_{C3-C4}	<0.10% from orbitals at other ring	dimethylbiphenyl

Table 7 6-31G* natural localized molecular orbitals (NLMO) of bipyridines

NLMO	composition	molecule
π_{N1-C2}	0.11% p_{C11}; 0.21% p_{N7}; 0.58% p_{C8}; 0.13% p_{C9}	bipyridine
π_{N1-C2}	0.13% p_{C11}; 0.24% p_{N7}; 0.59% p_{C8}; 0.15% p_{C9}	methylbipyridine
π_{N1-C2}	0.12% p_{C11}; 0.23% p_{N7}; 0.59% p_{C8}; 0.14% p_{C9}	dimethylbipyridine
π_{C3-C4}	0.17% p_{C9}	bipyridine
π_{C3-C4}	0.15% p_{C9}	methylbipyridine
π_{C3-C4}	0.15% p_{C9}	dimethylbipyridine
π_{C5-C6}	0.24% p_{C8}	bipyridine
π_{C5-C6}	0.26% p_{C8}	methylbipyridine
π_{C5-C6}	0.26% p_{C8}	dimethylbipyridine
π_{N7-C8}	0.11% p_{C5}; 0.21% p_{N1}; 0.58% p_{C2}; 0.13% p_{C3}	bipyridine
π_{N7-C8}	0.11% p_{C5}; 0.20% p_{N1}; 0.58% p_{C2}; 0.12% p_{C3}	methylbipyridine
π_{N7-C8}	0.12% p_{C3}; 0.23% p_{N1}; 0.59% p_{C2}; 0.14% p_{C5}	dimethylbipyridine
π_{C9-C10}	0.17% p_{C2}	bipyridine
π_{C9-C10}	0.17% p_{C2}	methylbipyridine
π_{C9-C10}	0.15% p_{C2}	dimethylbipyridine
$\pi_{C11-C12}$	0.10% p_{C2}	bipyridine
$\pi_{C11-C12}$	0.10% p_{C2}	methylbipyridine
$\pi_{C11-C12}$	0.10% p_{C2}	dimethylbipyridine

We can see from the results in these tables that, in both classes of compounds, several non-negligible inter-ring contributions are present. Note, however, that the magnitudes of such contributions are always larger in the bipyridine derivatives. This constitutes further evidence for the enhanced inter-ring delocalization stabilization in this class of molecules, which is favoured with their planar conformations.

The bond separation energies calculated at 0 K from the above isodesmic reactions show an almost constant increase in going from biphenyl to methylbiphenyl and from methylbiphenyl to dimethylbiphenyl of about 22 kJ mol^{-1} and 17 kJ mol^{-1}, at the MP2/3-21G and at the DFT/NLSDA levels, respectively. This seems to indicate that successive substitution of a hydrogen atom by a methyl group has the same stabilizing effect. In the case of the bipyridines, we can also observe a constant effect of about 24 kJ mol^{-1} at the MP2/3-21G, but this effect assumes, in the DFT/NLSDA calculation, a magnitude of 18 kJ mol^{-1} for the first substitution and 17 kJ mol^{-1} for the second one.

Bond-separation energies for the radical fragments phenyl, methylphenyl, pyridyl and methylpyridyl have also been determined at both levels of calculation, and are shown in Table 5.

From the results in the two tables we can observe that, relative to their radical moieties, biphenyl, methylbiphenyl and dimethylbiphenyl are stabilized, respectively, by 93, 94 and 96 kJ mol^{-1}, according to the MP2/3-21G level, and by 88, 89 and 90 kJ mol^{-1}, at the DFT/NLSDA level.

For 2,2′-bipyridine, 4-methyl-2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine the corresponding stabilizations are 184, 186 and 188 kJ mol^{-1}, at the MP2/3-21G level, and 141, 143 and 142 kJ mol^{-1}, at the DFT/NLSDA level. We must note again that nearly constant stabilization results, for each group of molecules, from successive substitutions of hydrogen atoms by methyl groups, and that the magnitude of such stabilization is consistently larger for bipyridines than for biphenyls at both levels of calculation. This difference can, of course, be explained by the larger extended inter-ring electronic delocalization occurring in the former molecules, as their planar conformations suggest.

Note that all these stability comparisons are based on bond separation energies calculated at 0 K and do not include corrections for the zero point vibrational energies of the molecules. In order to compare the experimental results with the theoretical predictions, bond separation enthalpies must then be calculated from bond separation energies by including the zero point vibrational energies and the relevant thermal corrections. The calculated bond separation enthalpies, at 298.15 K, as well as the corresponding experimental values, at 298.15 K, are also shown in Table 5. From the experimental results we can see that the first and second methylations of biphenyl account for stabilizations of 33.82 and 17.53 kJ mol^{-1}, respectively. These findings support the values of 22.37 and 17.63 kJ mol^{-1} found in the DFT/NLSDA calculations, and the values of 27.87 and 22.97 kJ mol^{-1} resulting from the MP2/3-21G calculations. In the case of bipyridines a similar trend is found on theoretical grounds. This trend is in contrast to the relative constancy of the stabilizations found earlier for each group of molecules, on the basis of bond separation energies at 0 K (not including zero point vibrational corrections). It seems therefore, that the observed differences must result from vibrational effects rather than from purely electronic ones.

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