Calorimetric and Theoretical Determination of Standard Enthalpies of Formation of Dimethoxy- and Trimethoxybenzene Isomers

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The standard ($p° = 0.1$MPa) molar enthalpies of formation for 1,2-, 1,3-, and 1,4-dimethoxybenzene and 1,2,3- and 1,3,5-trimethoxybenzene in the gaseous phase were derived from the standard molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry and the standard molar enthalpies of evaporation at $T = 298.15$ K, measured by Calvet microcalorimetry: 1,2-dimethoxybenzene, $-(202.4 \pm 3.4)$ kJ·mol^{-1}; 1,3-dimethoxybenzene, $-(221.8 \pm 2.4)$ kJ·mol^{-1}; 1,4-dimethoxybenzene, $-(211.5 \pm 3.0)$ kJ·mol^{-1}; 1,2,3-trimethoxybenzene, $-(339.0 \pm 2.2)$ kJ·mol^{-1}; 1,3,5-trimethoxybenzene, $-(371.4 \pm 3.0)$ kJ·mol^{-1}. Ab initio geometry optimizations for the three dimethoxybenzene and the three trimethoxybenzene isomers were performed using the 3-21G* and the 6-31G* basis sets. Single-point MP2/6-31G* and DFT energy calculations allowed the estimation of the enthalpies of formation of all methoxy-substituted benzenes.

Introduction

In our laboratory we have already studied several substituted benzenes, namely trihydroxybenzenes, methoxynitro- and alkyl-substituted dihydroxybenzenes,[1] and more recently some *tert*-butylphenols.[2] The present work is an additional contribution to the understanding of the energetic effect of substitutions in the benzenic ring. In addition to the experimental thermochemical work, we have done some calculations to obtain a clearer correlation between structure and energy.

This paper reports the standard molar enthalpies of formation of the three dimethoxybenzene isomers, 1,2-dimethoxybenzene (1,2-$(MeO)_2PhH$), 1,3-dimethoxybenzene (1,3-$(MeO)_2PhH$), and 1,4-dimethoxybenzene (1,4-$(MeO)_2PhH$), and two trimethoxybenzene isomers, 1,2,3-trimethoxybenzene (1,2,3-$(MeO)_3PhH$) and 1,3,5-trimethoxybenzene (1,3,5-$(MeO)_3PhH$), in the gaseous state, obtained from measurements of standard molar energies of combustion using a static bomb calorimeter and from the values of the enthalpies of sublimation or vaporization measured by Calvet microcalorimetry. Ab initio calculations were performed in order to obtain the most stable conformations of these molecules and the 1,2,4-trimethoxybenzene isomer. From the theoretical calculations of enthalpies of carefully chosen isodesmic reactions involving the methoxy substituted benzenes it was possible to derive the values for the enthalpies of formation of all the dimethoxy and trimethoxybenzenes. The theoretical calculations are in good agreement with the experimental findings.

Experimental Section

Materials. The di- and trimethoxybenzenes were obtained commercially from Aldrich Chemical Co. and were purified by vacuum distillation (1,2-dimethoxybenzene and 1,3-dimethoxybenzene) or sublimation (1,4-dimethoxybenzene, 1,2,3-trimethoxybenzene, and 1,3,5-trimethoxybenzene) until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were as follows: 1,2-$(MeO)_2PhH$, 0.9989 ± 0.0002; 1,3-$(MeO)_2PhH$, 1.0000 ± 0.0002; 1,4-$(MeO)_2PhH$, 1.0002 ± 0.0001; 1,2,3-$(MeO)_3PhH$, 1.0002 ± 0.0001; 1,3,5-$(MeO)_3PhH$, 1.0000 ± 0.0003. The densities of the samples were as follows: 1,2-$(MeO)_2PhH$, $\rho = 1.084$ g cm^{-3};[3] 1,3-$(MeO)_2PhH$, $\rho = 1.055$ g cm^{-3};[3] 1,4-$(MeO)_2PhH$, $\rho = 1.053$ g cm^{-3};[3] 1,2,3-$(MeO)_3PhH$, $\rho = 1.112$ g cm^{-3};[3] and for 1,3,5-$(MeO)_3PhH$, we estimated the value $\rho = 1.04$ g cm^{-3}.

For all crystalline compounds, purity was checked by differential scanning calorimetry (DSC) while the liquids were analyzed by GLC.

Combustion Calorimetry. The combustion experiments were performed with a static bomb calorimeter; the apparatus and technique have been described.[1a,4] Benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard, BCS-CRM-190 p) was used for calibration of the bomb. Its massic energy of combustion is $\Delta_c u = -(26\,432.3 \pm 3.8)$ J·g^{-1}, under certificate conditions. The calibration results were corrected to give the energy equivalent ϵ_{cal} corresponding to the average mass of water added to the calorimeter: 3119.6 g; $\epsilon_{cal} = (16\,006.4 \pm 1.4)$ J·K^{-1} was used for all measurements except for the experiments with 1,2-$(MeO)_2PhH$, where we used the calibration constant $\epsilon_{cal} = (16\,007.3 \pm 0.7)$ J·K^{-1}, and 1,3-$(MeO)_2PhH$ where we used the calibration constant $\epsilon_{cal} = (16\,013.8 \pm 1.2)$ J·K^{-1}. The uncertainties quoted are the standard deviations of the mean. For all experiments, ignition was made at 298.150 ± 0.001 K. Combustion experiments were made in oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of water added to the bomb. The electrical energy for ignition ΔU(ign) was determined from the

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TABLE 1: Typical Combustion Experiments at T = 298.15 K

	1,2-$(MeO)_2$PhH	1,3-$(MeO)_2$PhH	1,4-$(MeO)_2$PhH	1,2,3-$(MeO)_3$PhH	1,3,5-$(MeO)_3$PhH
$m(CO_2,\text{total})$/g	1.69114	2.02686	2.01185	1.77568	1.56004
m(cpd)/g	0.62070	0.74478	0.72720	0.69124	0.65970
m(fuse)/g	0.00392	0.00272	0.00422	0.00289	0.00399
m(Melinex)/g	0.04503	0.05440	0.06635	0.06250	-
ΔT_{ad}/K	1.27463	1.52554	1.50446	1.32815	1.17632
$\epsilon_{cal}/(J \cdot K^{-1})$	16007.3 ± 0.7	16013.8 ± 1.2	16006.4 ± 1.4	16006.4 ± 1.4	16006.4 ± 1.4
$\epsilon_f/(J \cdot K^{-1})$	16.46	16.72	16.56	16.75	16.47
$\Delta m(H_2O)$/g	0.2	−0.2	−0.1	0.2	0.0
$-\Delta U$(IBP)/J	20424.35	24452.78	24104.40	21281.40	18847.10
$-\Delta U$(Melinex)/J	1031.21	1245.95	1519.63	1431.45	−
$-\Delta U$(fuse)/J	63.66	44.17	68.53	46.93	64.80
$-\Delta U(HNO_3)$/J	5.31	12.93	2.97	1.23	7.64
$-\Delta U$(carbon)/J	0.00	0.00	0.00	0.00	0.00
ΔU(ign)/J	1.08	1.14	0.87	0.86	0.92
$-\Delta U_{\Sigma}$/J	11.41	14.00	13.91	12.43	10.57
$-\Delta_c u°/(J \cdot g^{-1})$	31114.48	31063.84	30939.82	28628.78	28443.37

TABLE 2: Individual Values of the Massic Energy of Combustion of Di- and Trimethoxybenzenes, at T = 298.15 K

1,2-$(MeO)_2$PhH	1,3-$(MeO)_2$PhH	1,4-$(MeO)_2$PhH	1,2,3-$(MeO)_3$PhH	1,3,5-$(MeO)_3$PhH
		$-\Delta_c u°/(J \cdot g^{-1})$		
31 130.20	31 040.90	30 969.67	28 637.41	28 443.37
31 134.78	31 047.83	30 939.82	28 641.53	28 418.86
31 159.51	31 059.01	30 971.38	28 627.83	28 427.93
31 183.39	31 048.26	30 959.86	28 626.12	28 426.18
31 106.83	31 063.84	30 970.70	28 627.65	28 430.66
31 174.19	31 047.74	30 985.76	28 640.52	28 406.18
31 114.48		30 956.80	28 620.48	
31 148.01		30 957.77	28 642.20	
		30 962.49	28 640.90	
		30 952.64	28 628.78	
		30 951.89		
		$-\langle \Delta_c u° \rangle\ (J \cdot g^{-1})$		
31 143.9 ± 9.7	31 051.3 ± 3.5	30 961.7 ± 3.7	28 633.3 ± 2.5	28 425.5 ± 5.1

TABLE 3: Derived Standard ($p°$= 0.1 MPa) Molar Values at T = 298.15 K

	$-\Delta_c U°_m$(cr,l)/ kJ·mol^{-1}	$-\Delta_c H°_m$(cr,l)/ kJ mol^{-1}	$-\Delta_f H°_m$(cr,l)/ kJ·mol^{-1}
1,2-$(MeO)_2$PhH (l)	4303.0 ± 2.9	4306.7 ± 2.9	270.5 ± 3.1
1,3-$(MeO)_2$PhH (l)	4290.2 ± 1.6	4293.9 ± 1.6	283.3 ± 1.9
1,4-$(MeO)_2$PhH (cr)	4277.9 ± 1.7	4281.6 ± 1.7	295.6 ± 2.0
1,2,3-$(MeO)_3$PhH (cr)	4815.9 ± 1.7	4819.6 ± 1.7	437.0 ± 2.1
1,3,5-$(MeO)_3$PhH (cr)	4780.9 ± 2.0	4784.6 ± 2.0	472.0 ± 2.3

change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u° = -16\,250\ J \cdot g^{-1}$.[5] The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on −59.7 kJ mol^{-1},[6] for the molar energy of formation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). Sealed Melinex bags were used for the combustion of the 1,2- and 1,3-dimethoxybenzene liquids and of the 1,4-dimethoxybenzene and 1,2,3-trimethoxybenzene solid compounds, using the technique described by Skinner and Snelson,[7] who determined the specific energy of combustion of dry Melinex as $\Delta_c u° = -(22\,902 \pm 5)\ J \cdot g^{-1}$. That value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032).[7] The amount of substance m(cpd) used in each experiment was determined from the total mass of carbon dioxide $m(CO_2,\text{total})$ produced after allowance for that formed from the cotton thread fuse and Melinex. An estimated pressure coefficient of specific energy $(\partial u/\partial p)_T = -0.2\ J \cdot g^{-1}.\ MPa^{-1}$ at 298.15 K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard et al.[5] The molar masses used for the elements were those recommended by the IUPAC comission.[8]

Enthalpies of Sublimation and Vaporization. The enthalpies of sublimation and of vaporization were measured by using the "vacuum sublimation" drop microcalorimetric method,[9] which, in the case of vaporization, was previously tested in the Porto laboratory.[10] Samples, about 3−5 mg of each solid compound and 7−9 mg of the 1,3-dimethoxybenzene liquid, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high-temperature Calvet microcalorimeter held at a convenient temperature T, and then removed from the hot zone by vacuum evaporation. The observed enthalpies of evaporation were corrected to 298.15 K by using the value of $\Delta_{298.15K}^{T} H°_m(g)$ estimated by a group method with values from Stull et al.[11] The microcalorimeter was calibrated in situ for these measurements by using the reported enthalpies of sublimation of naphthalene[11] and of vaporization of undecane.[12]

Experimental Results. Results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, and ΔU_{Σ} is the correction to the standard state. The remaining quantities are as previously defined.[5] As samples were ignited at 298.15 K

$$\Delta U(\text{IBP}) = -\{\epsilon_{\text{cal}} + \Delta m(H_2O)c_p(H_2O,l) + \epsilon_f\}\Delta T_{\text{ad}} + \Delta U_{\text{ign}}$$

where ΔU(IBP) is the energy associated to the isothermal bomb process, ϵ_f is the energy of the bomb contents after ignition, and ΔT_{ad} is the adiabatic temperature raise. The individual results of all combustion experiments, together with the mean values and its standard deviations, are given for each compound in Table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U°_m$(cr,l) and $\Delta_c H°_m$(cr,l), and

TABLE 4: Microcalorimetric Standard ($p^\circ = 0.1$ MPa) Molar Enthalpies of Vaporization or Sublimation at $T = 298.15$ K

	no. of expts	T/K	$\Delta_{\mathrm{cr,l}}^{\mathrm{g},T}H_\mathrm{m}^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{298.15\mathrm{K}}^{T}H_\mathrm{m}^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_\mathrm{m}^\circ$ $\mathrm{kJ\cdot mol^{-1}}$
1,2-$(MeO)_2PhH$ (l)	6	386	82.7 ± 1.4	14.6	68.1 ± 1.4
1,3-$(MeO)_2PhH$ (l)	6	384	75.8 ± 1.4	14.3	61.5 ± 1.4
1,4-$(MeO)_2PhH$ (cr)	6	368	95.7 ± 2.3	11.6	84.1 ± 2.3
1,2,3-$(MeO)_3PhH$ (cr)	5	375	113.4 ± 0.8	15.4	98.0 ± 0.8
1,3,5-$(MeO)_3PhH$ (cr)	6	375	116.0 ± 1.9	15.4	100.6 ± 1.9

TABLE 5: Derived Standard ($p^\circ = 0.1$ MPa) Molar Values at $T = 298.15$ K

	$-\Delta_\mathrm{f}H_\mathrm{m}^\circ$(cr,l) $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_\mathrm{m}^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$-\Delta_\mathrm{f}H_\mathrm{m}^\circ$(g) $\mathrm{kJ\cdot mol^{-1}}$
1,2-$(MeO)_2PhH$ (l)	270.5 ± 3.1	68.1 ± 1.4	202.4 ± 3.4
1,3-$(MeO)_2PhH$ (l)	283.3 ± 1.9	61.5 ± 1.4	221.8 ± 2.4
1,4-$(MeO)_2PhH$ (cr)	295.6 ± 2.0	84.1 ± 2.3	211.5 ± 3.0
1,2,3-$(MeO)_3PhH$ (cr)	437.0 ± 2.1	98.0 ± 0.8	339.0 ± 2.2
1,3,5-$(MeO)_3PhH$ (cr)	472.0 ± 2.3	100.6 ± 1.9	371.4 ± 3.0

the standard molar enthalpies of formation for the compounds in the condensed phase $\Delta_\mathrm{f}H^\circ_\mathrm{m}$(cr,l) at 298.15 K. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration[13] and in the values of auxiliary quantities. To derive $\Delta_\mathrm{f}H^\circ_\mathrm{m}$(cr,l) from $\Delta_\mathrm{c}H^\circ_\mathrm{m}$(cr,l), the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at 298.15 K, − (285.830 ± 0.042) $\mathrm{kJ\cdot mol^{-1}}$ [14] and −(393.51 ± 0.13) $\mathrm{kJ\cdot mol^{-1}}$,[14] respectively, were used.

Measurements of the enthalpies of sublimation or of vaporization $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H^\circ_\mathrm{m}$ are given in Table 4 with uncertainties of twice the standard deviation of the mean. The derived enthalpies of formation, in both the condensed and gaseous phases, for all the compounds are summarized in Table 5.

Theoretical Calculations

The most stable conformations of the dimethoxybenzene and the trimethoxybenzene isomers have been obtained by fully optimizing their geometries using the single-determinant restricted Hartree−Fock (RHF) theory and two basis sets: 3-21G*[15] and 6-31G*.[16] The 6-31G* basis set is known to provide bond lengths and bond angles in better agreement with experiment than the 3-21G* so we report only the obtained RHF/6-31G* geometries. The optimized bond lengths are presented in Table 6 and the optimized bond angles in Table 7. The numbering of atoms is shown in Figure 1. As can be seen from the dihedral angles defining the orientation of the methoxyl groups, the 1,3-, 1,4-, and 1,3,5- methoxy-substituted benzenes show planar geometries which allow maximal conjugation between the π-electron lone pair of the methoxy oxygen atom and the aromatic ring with the consequent strengthening of the C_b−O bond (the C_b−O bond length is smaller than the H_3C−O bond length). Experimental and theoretical studies of methoxybenzene reported in the literature[17] show that the planar conformation is preferred due to conjugation, although there are steric repulsions between the methyl hydrogen atoms and the ortho hydrogen of the aromatic ring. In the case of 1,2-methoxy-substituted benzenes, steric repulsions between proximate methoxyl groups favor nonplanar conformations with the methoxyl groups taking opposite orientations relative to the aromatic ring. In nonplanar geometries, the conjugation is not so efficient and as a result the C_b−O bond length is longer than in the planar geometries. The steric repulsions between the methyl hydrogen atoms (of the methoxyl group) and the ortho hydrogen atom of the ring in planar conformations increase the angle C_b−C_b−O from about 120°, which is optimum for nonplanar conformations, to about 125°.

The harmonic vibrational frequencies and zero-point vibrational energies (needed to estimate energies at any temperature different from 0 K) were obtained from the RHF/3-21G* geometries through construction and diagonalization of the 3-21G* Hessian matrices. To improve agreement with experiment, the harmonic vibrational frequencies were scaled by the empirical factor 0.9.

In order to account, at least partially, for the correlation error we have also performed single-point energy calculations on the RHF/6-31G* optimum geometries using the Møller−Plesset perturbation theory truncated at the second order of the perturbational expansion with the 6-31G* basis set (MP2/6-31G*) and, the density functional theory (DFT). For the DFT calculations, the local component of the functional for the exchange-correlation energy density and the corresponding potentials were modeled according to the Vosko−Wilk−Nursair[18] local functional while the nonlocal corrections are represented by nonlocal functionals of Becke[19] (for exchange) and Perdew[20] (for correlation) and a double-ζ quality basis set, properly optimized for this type of calculations,[21] was used. In this basis set, which is roughly equivalent to Pople's 6-31G* one, the H atom basis set has a (41) contraction pattern whereas first-row atoms are represented by a (721/51/1*) basis (using Huzinaga's notation).[22] In addition, DFT calculations require auxiliary sets of functions to fit the charge density and the exchange-correlation potential. For hydrogen atoms, the two sets of functions consisted of four uncontracted s-type Gaussians, while for the first-row atoms they consisted of four uncontracted s-type Gaussians and three uncontracted Gaussians.

We have also performed DFT calculations using the B3LYP[23] hybrid exchange-correlation energy functional to represent the exchange and correlation energy potentials.

All ab initio calculations were performed using the American version of GAMESS[24] while the density functional calculations were obtained using an academic version of deMon program[25] and the UK version of GAMESS.[26, 27]

The resulting MP2/6-31G* and DFT electronic energies for all methoxy-substituted benzenes are presented in Table 8, together with the corresponding RHF/3-21G* zero-point energies (ZPE).

Reactions in which the number of any formal type of bond is maintained on going from the reactants to the products, called isodesmic reactions, are often used in theoretical studies of thermochemistry, since correlation errors inherent in the calculation of the energies of reactants and products are expected to largely cancel, thus leading to reliable estimates of the reaction energies.

Bond separation reactions, which are of the isodesmic type, can be devised for the methoxy-substituted benzenes as

$$C_6H_6 + 6CH_4 \rightarrow 3C_2H_4 + 3C_2H_6$$

$$C_7H_8O + 7CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 + CH_3OCH_3$$

$$C_8H_{10}O_2 + 8CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 + 2CH_3OCH_3$$

$$C_9H_{12}O_3 + 9CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 + 3CH_3OCH_3$$

The study of this type of reactions also provides estimates of the stabilization arising from electronic delocalization in the methoxy-substituted benzenes relative to the nondelocalized

TABLE 6: Calculated Bond Lengths (in Å) of the Di- and Trimethoxybenzenes[a]

	1,2-$(CH_3O)_2PH$	1,3-$(CH_3O)_2PH$	1,4-$(CH_3O)_2PH$	1,2,3-$(CH_3O)_3PH$	1,2,4-$(CH_3O)_3PH$	1,3,5-$(CH_3O)_3PH$
1−2	1.392	1.398	1.377	1.384	1.397	1.375
2−3	1.383	1.379	1.399	1.399	1.376	1.401
3−4	1.386	1.399	1.377	1.386	1.393	1.375
4−5	1.384	1.372	1.397	1.389	1.383	1.401
5−6	1.386	1.395	1.371	1.378	1.392	1.375
6−1	1.383	1.381	1.397	1.390	1.376	1.402
1−7	1.361	1.348	1.354	1.358	1.363	1.345
7−8	1.410	1.399	1.396	1.410	1.408	1.400
C_b−9	1.361	1.346	1.354	1.358	1.358	1.345
9−10	1.410	1.399	1.396	1.408	1.410	1.400
C_b−11				1.347	1.350	1.345
11−12				1.399	1.398	1.400

[a] C_b represents a carbon atom of the aromatic ring to which a methoxyl group is attached.

TABLE 7: Calculated Bond Angles (in deg) of the Di- and Trimethoxybenzenes[a]

	1,2-$(CH_3O)_2PH$	1,3-$(CH_3O)_2PH$	1,4-$(CH_3O)_2PH$	1,2,3-$(CH_3O)_3PH$	1,2,4-$(CH_3O)_3PH$	1,3,5-$(CH_3O)_3PH$
1−2−3	119.7	119.7	120.4	119.7	120.6	118.7
2−3−4	120.4	120.2	120.4	119.8	120.0	121.3
3−4−5	119.9	119.1	119.0	119.7	119.6	118.7
4−5−6	119.9	121.8	120.6	121.0	119.8	121.3
5−6−1	120.4	118.4	120.6	119.3	121.1	118.7
6−1−2	119.7	120.7	119.0	120.6	118.9	121.3
7−1−2	120.5	114.7	125.2	120.0	121.0	124.1
1−7−8	115.5	119.7	119.3	115.8	115.3	119.8
9-$(C_b)_{n-1}$−$(C_b)_n$	119.8	115.7	115.8	120.2	118.5	124.1
C_b−9−10	115.5	119.8	119.3	115.3	118.5	119.8
11-$(C_b)_{n-1}$−$(C_b)_n$				124.6	116.1	124.1
C_b−11−12				119.6	119.7	119.8
2−1−7−8	79.5	−180.0	0.0	78.4	−80.6	−0.0
$(C_b)_n$−$(C_b)_{n-1}$−9−10	−102.2	−180.0	−0.0	−88.8	103.2	−0.0
$(C_b)_n$−$(C_b)_{n-1}$−11−12				2.5	−0.3	−0.0

[a] $(C_b)_{n-1}$−$(C_b)_n$ means that the first carbon atom has lower numeration than the second carbon atom.

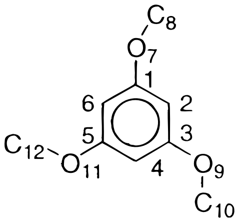

Figure 1. Atom numbering scheme for the methoxybenzenes.

simpler molecules. The energies of all auxiliary simpler molecules were obtained using the same procedures described for the methoxy-substituted benzenes. Theoretical calculations were also performed for benzene and methoxybenzene for a more exhaustive study of the methoxy substitution on the benzene ring. From the calculations performed we were able to estimate the bond separation energies, at $T = 0$ K (BSE), for all dimethoxy- and trimethoxybenzenes which are presented in Table 9. The calculated bond separation energies for all studied methoxybenzenes are positive, indicating the occurrence of aromatic stabilization by electronic delocalization relative to nondelocalized molecules. The 1,2-dimethoxybenzene is the least stabilized isomer of the dimethoxybenzenes and 1,3-dimethoxybenzene the most stabilized one. The introduction of a methoxyl group at the meta position of methoxybenzene provides more stabilization than introduction of a methoxyl group at the para position of methoxybenzene. Since the methoxyl groups in 1,3,5-trimethoxybenzene are all separated from each other and in the plane of the ring, this compound is the most stabilized of the trimethoxybenzenes and in the 1,2,3-trimethoxybenzene isomer the steric repulsions between the three methoxyl groups largely contributes to the destabilization of this compound. For comparison of the theoretical and experimental results, the bond separation enthalpies, at $T = 298$ K (BSH), were calculated from the BSE at $T = 0$ K and are also presented in Table 9, together with the BSH values derived from the experimental standard molar enthalpies of formation of all the compounds. The standard molar enthalpies of formation for all auxiliary molecules were taken from Peddley et al.[12]

In 1958, Cass et al.[28] reported for 1,2-dimethoxybenzene the standard molar enthalpies of combustion and of vaporization: $\Delta_c H^\circ_m = -(4284.0 \pm 2.1)$ kJ·mol^{-1} and $\Delta_l^g H^\circ_m = 66.9$ kJ·mol^{-1}. From these values the derived standard molar enthalpy of formation in the gaseous phase is $\Delta_f H^\circ_m(g) = -(223.4 \pm 2.1)$ kJ·mol^{-1}, which seems too negative when compared with the values obtained in this work for the other two isomers. In the present work, the value redetermined for $\Delta_c H^\circ_m$ is $-(4306.7 \pm 2.9)$ kJ·mol^{-1} (quite different from Cass's value) while the redetermined standard molar enthalpy of vaporization $\Delta_l^g H^\circ_m = (68.1 \pm 1.4)$ kJ·mol^{-1} is in agreement with the one previously measured. These experimental parameters lead to a value of $-(202.4 \pm 3.4)$ kJ·mol^{-1} for $\Delta_f H^\circ_m(g)$, reflecting a destabilization in the 1,2-dimethoxybenzene isomer relative to the other isomers. Actually, from the above theoretical considerations, we have found that the 1,2-isomer shows the largest destabilization of the dimethoxybenzenes. This fact must be ascribed to steric repulsions between the two methoxyl groups which are out of the plane of the ring thus severely restricting stabilization from electronic delocalization.

All three methods of calculation systematically overestimate the experimental results for all studied compounds. The DFT results are in much better agreement with the experimental ones, showing errors of about 13−36 kJ·mol^{-1}, which, however, are smaller than the errors associated to the MP2/6-31G* results.

TABLE 8: Calculated Energies (hartrees) and Zero-Point Vibrational Energies (kJ·mol^{-1})

	$E_{MP2/6-31G*}$	$E_{DFT/BP}$	$E_{DFT/B3LYP/6-31G*}$	E_{ZP}
PhH	−231.456 504 46	−232.302 712 57	−232.247 483 86	285.6989
CH_3OPhH	−345.643 201 47	−346.867 892 73	−346.769 228 22	377.7808
1,2-$(CH_3O)_2PhH$	−459.824 095 34	−461.422 333 31	−461.281 344 45	468.6411
1,3-$(CH_3O)_2PhH$	−459.830 222 67	−461.434 195 60	−461.291 436 01	469.7377
1,4-$(CH_3O)_2PhH$	−459.828 110 62	−461.431 354 72	−461.288 708 55	469.2970
1,2,3-$(CH_3O)_3PhH$	−574.006 815 85	−575.984 516 17	−575.798 699 44	559.7192
1,2,4-$(CH_3O)_3PhH$	−574.009 991 70	−575.987 058 35	−575.802 103 87	560.3672
1,3,5-$(CH_3O)_3PhH$	−574.017 510 56	−576.000 232 07	−575.813 762 96	561.8657

TABLE 9: Calculated Bond Separation Energies at $T = 0$ K (BSE) and Bond Separation Enthalpies at $T = 298.15$ K (BSH), and Experimental BSH Results for the Methoxy-Substituted Benzenes (kJ·mol^{-1})

	BSE			BSH			
	MP2/6-31G*	BP	B3LYP/6-31G*	MP2/6-31G*	BP	B3LYP/6-31G*	expt
PhH	300.90	277.80	277.95	314.08	290.97	291.12	269.9 ± 2.8
CH_3OPhH	345.72	316.68	320.28	362.37	333.34	336.94	310.7 ± 3.2
1,2-$(CH_3O)_2PhH$	375.30	327.37	337.34	396.27	348.34	358.31	335.5 ± 4.9
1,3-$(CH_3O)_2PhH$	391.39	358.51	363.84	411.57	378.70	384.02	354.9 ± 4.3
1,4-$(CH_3O)_2PhH$	385.84	351.05	356.68	406.42	371.63	377.26	344.6 ± 4.7
1,2,3-$(CH_3O)_3PhH$	409.68	358.38	368.16	434.30	383.01	392.78	362.4 ± 4.7
1,2,4-$(CH_3O)_3PhH$	418.02	365.06	377.09	442.59	389.64	401.67	
1,3,5-$(CH_3O)_3PhH$	437.76	399.65	407.70	461.24	423.13	431.19	394.8 ± 5.1

TABLE 10: Δ_rE at $T = 0$ K, $\Delta_rH°$ at $T = 298.15$ K, and Experimental $\Delta_rH°$ at $T = 298.15$ K for the Methoxy-Substituted Benzenes (kJ·mol^{-1})

	Δ_rE			$\Delta_rH°$			
	MP2/6-31G*	BP	B3LYP/6-31G*	MP2/6-31G*	BP	B3LYP/6-31G*	expt
CH_3OPhH	44.82	38.88	42.34	48.30	42.36	45.82	40.8 ± 1.2
1,2-$(CH_3O)_2PhH$	74.40	49.57	59.40	82.19	57.36	67.18	65.6 ± 3.7
1,3-$(CH_3O)_2PhH$	90.49	80.72	85.89	97.50	87.73	92.90	85.0 ± 2.8
1,4-$(CH_3O)_2PhH$	84.94	73.26	78.73	92.34	80.66	86.13	74.7 ± 3.3
1,2,3-$(CH_3O)_3PhH$	108.78	80.59	90.21	120.22	92.04	101.66	92.5 ± 3.0
1,2,4-$(CH_3O)_3PhH$	117.12	87.26	99.15	128.52	98.66	110.55	
1,3,5-$(CH_3O)_3PhH$	136.86	121.85	129.76	147.16	132.16	140.06	124.9 ± 3.6

TABLE 11: Δ_rE at $T = 0$ K, $\Delta_rH°$ at $T = 298.15$ K, and Experimental $\Delta_rH°$ at $T = 298.15$ K for the Methoxy-Substituted Benzenes (kJ·mol^{-1})

	Δ_rE			$\Delta_rH°$			
	MP2/6-31G*	BP	B3LYP/6-31G*	MP2/6-31G*	BP	B3LYP/6-31G*	expt
1,2-$(CH_3O)_2PhH$	−15.24	−28.20	−25.28	−14.41	−27.37	−24.45	−16.0 ± 3.8
1,3-$(CH_3O)_2PhH$	0.85	2.95	1.22	0.90	3.00	1.27	3.4 ± 3.0
1,4-$(CH_3O)_2PhH$	−4.69	−4.51	−5.94	−4.25	−4.07	−5.50	−6.9 ± 3.5
1,2,3-$(CH_3O)_3PhH$	−25.68	−36.07	−36.80	−24.67	−35.06	−35.79	−29.9 ± 3.5
1,2,4-$(CH_3O)_3PhH$	−17.33	−29.39	−27.86	−16.38	−28.43	−26.90	
1,3,5-$(CH_3O)_3PhH$	2.40	5.20	2.75	2.27	5.06	2.61	2.5 ± 4.1

We have further considered a different type of isodesmic reactions

$$C_7H_8O + CH_4 \rightarrow C_6H_6 + CH_3OCH_3$$

$$C_8H_{10}O_2 + 2CH_4 \rightarrow C_6H_6 + 2CH_3OCH_3$$

$$C_9H_{12}O_3 + 3CH_4 \rightarrow C_6H_6 + 3CH_3OCH_3$$

The energies of these reactions represent in each case the stabilizing effect of the methoxyl group on the benzene ring relative to its effect on the stability of methane. The calculated reaction energies at $T = 0$ K and enthalpies at $T = 298.15$ K together with the experimental values are presented in Table 10. The theoretical results obtained from this type of reaction are in better agreement with the experimental ones than that from the bond separation reactions. The DFT methods are also in better agreement with the experimental results than the MP2/6-31G* the largest error, of 15 kJ·mol^{-1}, being found for 1,3,5-trimethoxybenzene.

We have also derived the energies of the following isodesmic reactions

$$C_6H_6 + C_8H_{10}O_2 \rightarrow 2C_7H_8O$$

$$2C_6H_6 + C_9H_{12}O_3 \rightarrow 3C_7H_8O$$

representing the stabilization or destabilization of the di- and trimethoxybenzenes relative to methoxybenzene, as measured by the interaction energies between the methoxyl substituents. The resulting reaction energies at $T = 0$ K and enthalpies at $T = 298.15$ K together with the corresponding values are presented in Table 11. As can be seen from that table, all methods of calculation predict a large destabilization for the 1,2-, 1,2,3-, and 1,2,4-isomers relative to methoxybenzene, the 1,4- isomer being only marginally destabilized. On the other hand, the isomers with the methoxyl groups at the meta position are stabilized relative to methoxybenzene. All three methods of calculation reproduce the experimental results fairly well with differences not exceeding 11 kJ·mol $^{-1}$. From the results in Table 11 we have estimated the standard enthalpy of formation of the 1,2,4-trimethoxybenzene isomer as being (in kJ·mol^{-1}): −352.5 (MP2/6-31G*), −340.5 (DFT/BP), and −342.0 (DFT/B3LYP/6-31G*). It is reasonable to think that the accuracy of the theoretical results obtained for these reactions is uniform and so our estimate is confident to better than 11 kJ·mol^{-1}.

We may conclude from the results in Tables 9, 10, and 11 that the successful treatment of the reported theoretical calculations depends crucially on the choice of the isodesmic reactions.

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