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The Experimental and Calculational Thermochemistry of 1,2,4,5-Benzenetetracarboxylic Dianhydride: Is This 10 π Multiring Species Aromatic?

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The standard ($p° = 0.1$ MPa) molar enthalpy of formation of 1,2,4,5-benzenetetracarboxylic dianhydride in the gaseous phase, -826.8 ± 3.1 kJ mol^{-1}, was derived from the standard molar enthalpy of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry and the standard molar enthalpy of sublimation, at $T = 298.15$ K, measured by Calvet microcalorimetry. In addition, density functional theory calculations have been performed with the B3LYP, MPW1B95, and B3PW91 density functionals and the cc-pVTZ basis set for 1,2,4,5-benzenetetracarboxylic dianhydride and 1,2,4,5-benzenetetracarboxylic diimide. Nucleus-independent chemical shifts calculations show that the aromaticity is restricted to the benzenic ring in both compounds even though they are formally 10 π polynuclear species.

Introduction

The cyclic (di)anhydrides and (di)imides of 1,2,4,5-benzenetetracarboxylic acid (trivially known as pyromellitic anhydride and pyromellitic diimide, respectively) are of considerable interest and importance to the polymer and materials science communities as precursors (“monomers”) for diverse plastics, binders, explosives/propellants, films, and coatings. A quick literature search (SciFinder) shows some 5000 references to the former species (and substituted derivatives) in the primary and (a majority to the) patent literature, many of which describe transformation to derivatives of the latter species as well as the ring-opened bis amide/bis carboxylic acid. Reflecting this multiple academic, commercial, and military interest in this species, there are three literature measurements of the enthalpy of formation of the solid cyclic dianhydride[1−3] as well as steps along the polymerization process. However, the results are sorely dissonant, −907.3, −1047, and −953.5 kJ mol^{-1}, respectively, from these sources. No apparent reason can be given to explain these differences, nor is there any seeming way to reconcile the values. Accordingly, we have remeasured this quantity. Our results described below, -949.1 ± 2.0 (solid) and -826.8 ± 3.1 (gas) kJ mol^{-1}, newest and taken as most trustworthy, are additionally employed in answering whether 1,2,4,5-benzenetetracarboxylic dianhydride is a multiring aromatic species as befits its 10 π electrons (i.e., 6 from the central benzene ring, 0 from all four of the carbonyl groups, and 2 apiece from each of the “anhydride” oxygens).

The present work reports the thermochemical study of 1,2,4,5-benzenetetracarboxylic dianhydride (1,2,4,5-btc dianhydride) and 1,2,4,5-benzenetetracarboxylic diimide (1,2,4,5-btc diimide). For 1,2,4,5-benzenetetracarboxylic dianhydride, the standard molar enthalpy of combustion, in oxygen, at $T = 298.15$ K, was determined using static bomb combustion calorimetry, and the standard molar enthalpy of sublimation, at $T = 298.15$ K, was determined using Calvet microcalorimetry. These values allowed the calculation of the standard enthalpy of formation in the gas phase, at $T = 298.15$ K. The experimental study of 1,2,4,5-benzenetetracarboxylic diimide was not performed due to the seeming impossibility to adequately purify this compound for the calorimetric determinations.

In addition to the experimental investigation, we have performed geometry optimizations of 1,2,4,5-benzenetetracarboxylic dianhydride and corresponding diimide with the density functional theory, the B3LYP density functional, and two different basis sets: 6-31G* and 6-311G**. Then single-point energy calculations were also performed using the cc-pVTZ basis set and the B3LYP, MPW1B95, and B3PW91 density functionals. Additionally, we have calculated NICS values for 1,2,4,5-benzenetetracarboxylic dianhydride and 1,2,4,5-benzenetetracarboxylic diimide using B3LYP/6-31G* wave functions and the B3LYP/6-31G* geometries. The results show that the aromaticity is essentially restricted to the benzenic ring even though the dianhydride is nominally a 10 π system, and hence plausibly a heterocyclic polynuclear, not a “merely substituted” mononuclear, aromatic species.

Experimental Section

Materials. 1,2,4,5-Benzenetetracarboxylic dianhydride [CAS 89-32-7] was obtained commercially from Aldrich Co. with the mass fraction of 0.97 and was further purified by sublimation under reduced pressure prior to the experimental measurements. The compound could not be studied by differential scanning calorimetry, as it decomposes upon heating.

Combustion Calorimetry. The combustion experiments were performed with a static bomb calorimeter, with a twin valve bomb, type 1108, Parr Instrument Company. The apparatus and procedure have been described, so only a brief description will be given here.[4,5] Combustion of thermochemical standard benzoic acid, NBS Standard Reference Material 39j, was used

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for calibration of the bomb. Its specific energy of combustion is -26434 ± 3 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. From seven calibration experiments, $\epsilon_{\text{cal}} = 16000.8 \pm 1.4$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. For all experiments, ignition was made at $T = 298.150 \pm 0.001$ K. Hexadecane (Aldrich Gold Label, mass fraction >0.99) was used as an auxiliary combustion measurements, and its standard massic energy of combustion was measured separately to be $-\Delta_c u° = 47141.4 \pm 3.6$ J g^{-1}. Samples in pellet form were ignited at $T = 298.150 \pm 0.001$ K in oxygen, at a pressure $p = 3.04$ MPa, with a volume of 1.00 cm^3 of water added to the bomb. 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 of empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u° = 16240$ J g^{-1}.[6] This value has been confirmed in our laboratory. The amount of compound 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 *n*-hexadecane. The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample: 1.0004 ± 0.0003, where the uncertainty is the standard deviation of the mean.

The corrections for nitric acid formation were based on -59.7 kJ mol^{-1},[7] for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l).

From the dimensions and the mass of the pellets, the density of the compound was estimated as $d = 1.00$ 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 solid organic compounds, was assumed.[8] For each compound, the corrections to the standard state to calculate the standard massic energy of combustion, $\Delta_c u°$, were made by the procedure given by Hubbard et al.[9] The atomic weights of the elements were those recommended by IUPAC Commission in 1999.[10]

High-Temperature Calvet Microcalorimetry. The standard molar enthalpy of sublimation of 1,2,4,5-benzenetetracarboxylic dianhydride was measured by the "vacuum sublimation" drop microcalorimetric method,[11] using a Calvet High Temperature Microcalorimeter (SETARAM HT 1000), held at $T = 454$ K. Samples about 3 mg contained in a thin glass capillary tube sealed at one end were dropped, at room temperature, into the hot reaction vessel, and then removed from the hot zone by vacuum sublimation. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within $\pm$ 10 μg, into each of the twin calorimeter cells. The observed standard molar enthalpy of sublimation $\Delta_{\text{cr,298.15K}}^{\text{g},T} H_{\text{m}}^{\circ}$ was then corrected to $T = 298.15$ K using the equation

$$\Delta_{298.15\text{K}}^{T} H_{\text{m}}^{\circ}(\text{g}) = \int_{298.15\text{K}}^{T} C_{\text{p,m}}^{\circ}(\text{g})\, \text{d}T \qquad (1)$$

where T is the temperature of the hot reaction vessel and $C_{\text{p,m}}^{\circ}$(g) is the molar heat capacity of gaseous 1,2,4,5-benzenetetracarboxylic dianhydride. The heat capacity and its temperature dependence

$$C_{\text{p,m}}^{\circ}(\text{g})/(\text{J mol}^{-1}\text{ K}^{-1}) = -0.000508(T/\text{K})^2 + 0.817(T/\text{K}) - 13.707 \qquad (2)$$

was derived from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP functional and the 6-31G* basis set.

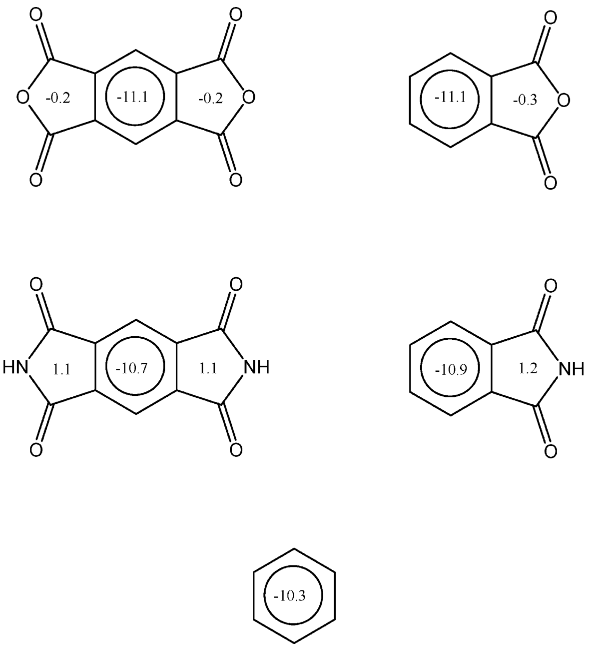


Figure 1. NICS values 0.5 Å above the plane of the ring.

The microcalorimeter was calibrated in situ for these measurements using the reported enthalpy of sublimation of naphthalene.[12] Accuracy tests were performed with benzoic acid.

Computational Details. The geometries of the studied compounds were fully optimized using density functional theory with the Becke 3-parameter hybrid exchange[13] and Lee–Yang–Parr[14] correlation density functional (B3LYP) and two different basis sets: 6-31G*[15,16] and 6-311G**.[17,18] Harmonic vibrational frequencies were calculated through construction and diagonalization of the Hessian matrices at the optimum B3LYP/6-31G* molecular geometries obtained using the same basis set. This procedure allowed characterizing these geometries as true minima and to obtain the corrections needed to derive energies at the temperature of 298.15 K. More accurate energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the triple-ζ correlation consistent basis set, cc-pVTZ,[19–22] and three density functionals: B3LYP, MPW1B95,[23] and B3PW91.[24] All calculations were performed using the UK version of GAMESS,[25,26] except the calculations with the density functionals MPW1B95 and B3PW91 which were performed with the Gaussian 03 series of programs.[27]

The NICS values were calculated using B3LYP/6-31G* wavefunctions at the B3LYP/6-31G* geometries (Figure 1). The methodology used was developed by Schleyer and his coworkers.[28] Two different values were calculated for each ring and each molecule: one at the geometrical center of the ring (i.e., the point whose coordinates are the nonweighted mean of the homologous coordinates of the heavy atoms of the rings) denoted NICS(0) and the other 0.5 Å above the center of the ring, denoted NICS(0.5). The calculation of NICS values has been performed with the Gaussian 03 series of programs.[27]

Experimental Results

Table 1 lists the results of combustion experiments for 1,2,4,5-benzenetetracarboxylic dianhydride which correspond to the combustion reaction:

$$C_{10}H_2O_6\text{ (cr)} + (15/2)O_2\text{ (g)} \rightarrow 10CO_2\text{ (g)} + H_2O\text{ (l)} \qquad (3)$$

TABLE 1: Combustion Experiments of 1,2,4,5-Benzenetetracarboxylic Dianhydride, at $T = 298.15$ K

$m(CO_2, \text{total})$/g	1.54070	1.65354	1.76107	1.70519	1.55001	1.76985
m(cpd)/g	0.42808	0.49951	0.51112	0.54597	0.40258	0.51375
m(n-hexadecane)/g	0.21644	0.20512	0.23338	0.19280	0.23598	0.23453
m(fuse)/g	0.00244	0.00484	0.00252	0.00252	0.00242	0.00245
ΔT_{ad}/K	1.04234	1.07880	1.17067	1.08330	1.07560	1.17620
$\epsilon_f/(\text{J K}^{-1})$	16.04	16.06	16.22	16.06	16.21	16.26
$\Delta m(H_2O)$/g	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U$(IBP)/J	16694.99	17278.99	18750.64	17351.06	17227.90	18839.27
$-\Delta U(HNO_3)$/J	11.35	11.25	11.40	2.29	2.34	2.62
$-\Delta U$(carbon)/J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU(ignition)/J	0.57	1.15	1.12	0.90	0.83	0.91
$-\Delta U_{\Sigma}$/J	11.23	12.68	13.31	13.48	10.94	13.38
$-\Delta U$(n-hexadecane)/J	10203.19	9669.83	11001.81	9088.80	11124.53	11056.09
$-\Delta U$(fuse)/J	39.63	78.60	40.92	40.92	39.30	39.79
$-\Delta_c u°/(\text{J g}^{-1})$	15018.27	15025.69	15029.90	15027.69	15027.97	15039.38
$-\Delta_c u°/(\text{J g}^{-1}) = 15028.2 \pm 2.8$						

TABLE 2: Standard Molar Enthalpies of Formation in the Gas Phase, at $T = 298.15$ K (kJ Mol^{-1}) Taken from the Literature

compound	$\Delta_f H_m^\circ$ (g)
benzene	82.6 ± 0.7[31]
cyclopentene	34.0 ± 1.4[31]
indane	60.3 ± 1.7[31]
maleic anhydride	-398.3 ± 5.1[31]
N-methylphthalimide	-233.9 ± 2.2[32]
N-methylmaleimide	-256.0 ± 1.5[32]
phthalimide	-211.1 ± 2.1[33]
phthalic anhydride	-371.4 ± 1.9[31]
succinic anhydride	-527.9 ± 1.7[34]
succinimide	-375.5 ± 1.5[34]
tetralin	26.0 ± 1.9[31]

The symbols in this table have been previously described.[9] Samples were ignited at $T = 298.15$ K so that the energy for the isothermic bomb process ΔU(IBP) is given by the relation:

$$\Delta U(\text{IBP}) = -\{\epsilon_{cal} + \Delta m(H_2O)\cdot c_p(H_2O,l) + \epsilon_f\}\Delta T_{ad} + \Delta U_{ign} \quad (4)$$

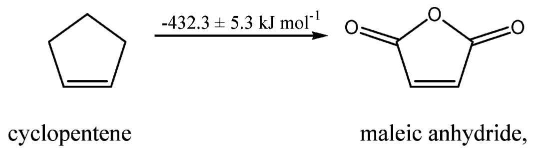
where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the average mass assigned to ϵ_{cal} (the heat capacity of the calorimeter without reagents or products of reaction), $c_p(H_2O,l)$ is the heat capacity of liquid water, ϵ_f is the heat capacity of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature raise, and ΔU_{ign} is the energy of ignition. The individual values of the massic energy of combustion, $\Delta_c u°$, with the mean and its standard deviation are also given in Table 1.

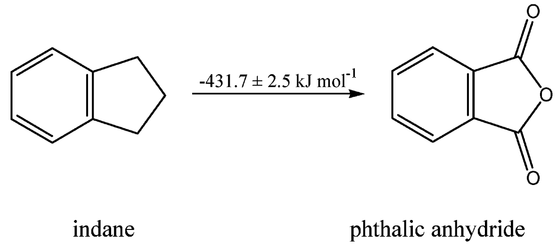
The derived standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation of 1,2,4,5-benzenetetracarboxylic dianhydride, in the crystalline phase are respectively, $\Delta_c H_m^\circ(\text{cr})/(\text{kJ}\cdot\text{mol}^{-1}) = -(3278.0 \pm 1.5)$, $\Delta_c H_m^\circ(\text{cr})/(\text{kJ}\cdot\text{mol}^{-1}) = -(3271.8 \pm 1.5)$, and $\Delta_f H_m^\circ(\text{cr})/(\text{kJ}\cdot\text{mol}^{-1}) = -(949.1 \pm 2.0)$.

In accordance with customary thermochemical practice,[29] 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 value of the combustion energy of the auxiliary compound, n-hexadecane. In order to derive $\Delta_f H_m^\circ(\text{cr})$ from $\Delta_c H_m^\circ(\text{cr})$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$, at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ mol^{-1},[30] and $-(393.51 \pm 0.13)$ kJ mol^{-1},[30] respectively, were used.

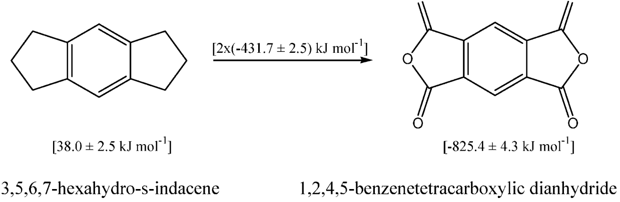
The standard molar enthalpy of sublimation, $\Delta_{cr}^{g} H_m^\circ(298.15\ \text{K})$ (kJ mol^{-1}) $= 122.3 \pm 2.4$, was determined from six independent experiments (the uncertainty of twice the standard deviation of the mean). To obtain the standard molar enthalpy of sublimation, at $T = 298.15$ K, the observed enthalpy in each experiment, at $T = 454$ K, was corrected using eqs 1 and 2. Combining the values of the standard molar enthalpy of sublimation and the standard enthalpy of formation in the solid phase leads to the value of the standard enthalpy of formation in the gaseous phase, at $T = 298.15$ K, $\Delta_f H_m^\circ(\text{g})$ (kJ mol^{-1}) $= -826.8 \pm 3.1$.

Enthalpic Increments and Correlations. Considering the enthalpies of formation in the gaseous phase for the different compounds taken from the literature and listed in Table 2, we have calculated the following enthalpic increments for the hypothetical processes we present below:

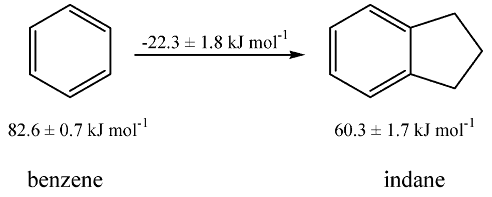


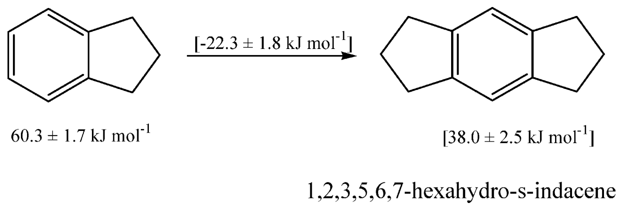


Considering the agreement between the previous calculated values, it is plausible to use twice the value for the enthalpic increment for Indane/phthalic anhydride, for the next process:



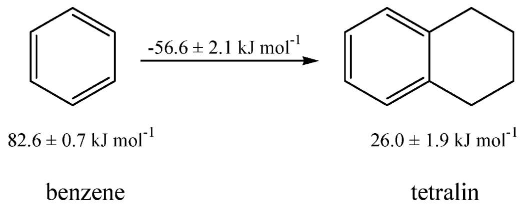
The standard molar enthalpy of formation of 1,2,3,5,6,7-hexahydro-s-indacene, used in the previous estimation, was itself estimated using the following scheme:

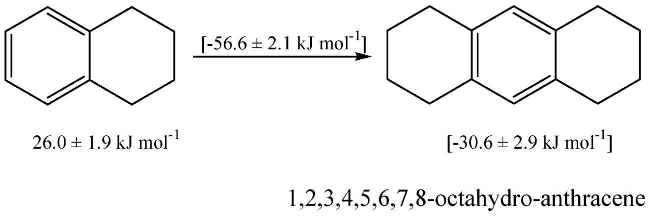




and assuming that in both processes the enthalpic increment is the same.

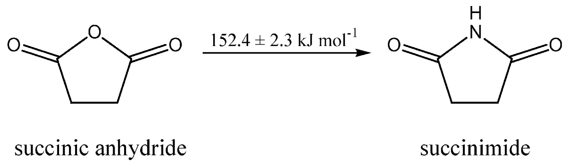
If we use similar reasoning, as presented in the next scheme, we obtain an estimate of −30.6 ± 2.9 kJ mol^{-1} for the standard molar enthalpy of formation of 1,2,3,4,5,6,7,8-octahydro-anthracene, from the benzene/tetralin enthalpic increment, in satisfactory agreement with the literature value −37.2 ± 3.2 kJ mol^{-1}.[31] This additionally supports our previous estimation.

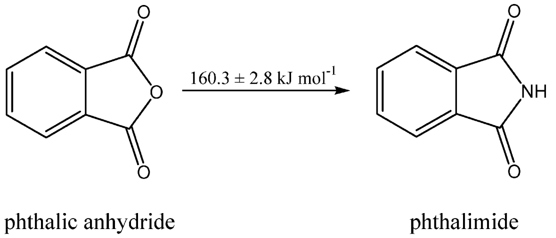


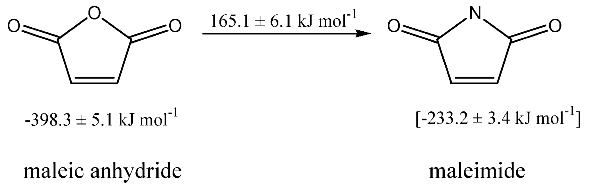


Now that we have a reliable estimate for the enthalpy of formation of 1,2,3,6,7-hexahydro-s-indacene, we return to the estimation of the enthalpy of formation of 1,2,4,5-benzenetetracarboxylic dianhydride. The so-derived numerical value is −825.4 ± 4.3 kJ mol^{-1}. This value is in very good agreement with the experimental one, −826.8 ± 3.1 kJ mol^{-1}, obtained in this work. Equivalently, the net result from the loss of the plausible antiaromaticity-derived weak destabilization of the 8 π phthalic anhydride (cf. the related 4 π maleic anhydride)[32] and gain of stability from the putative aromaticity of the 10 π 1,2,4,5-benzenetetracarboxylic dianhydride is but a negligible change. Equivalently, the net increase of aromaticity of this dianhydride over that of smaller-ring species is negligible.

Considering the enthalpies of formation in the gaseous phase taken from the literature and listed in Table 2, a comparison can be made between the following compounds wherein the group −CO−O−CO− is substituted for the −CO−NH−CO− group:

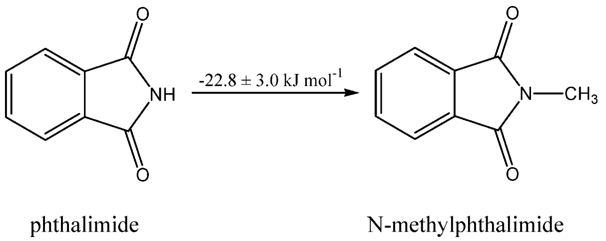


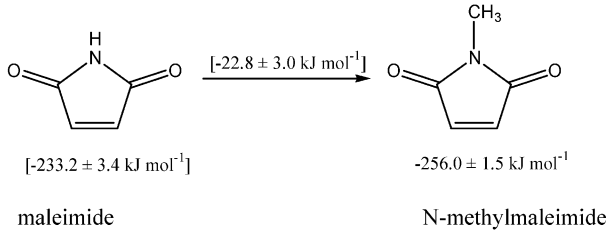




The hypothetical conversions phthalic anhydride/phthalimide and maleic anhydride/maleimide are energetically nearly identical and both significantly different from the analogous succinic anhydride/succinimide transformation. This may be due to the double bond character in one of the C−C bonds in the nonbenzenic ring of the maleic and phthalic species: we recall discussions of the antiaromaticity of maleic anhydride and maleimide.[32]

Notice that in the previous scheme, the value for the standard molar enthalpy of formation of maleimide was estimated, −233.2 ± 3.4 kJ mol^{-1}, using the values in Table 2 and the following reasoning:

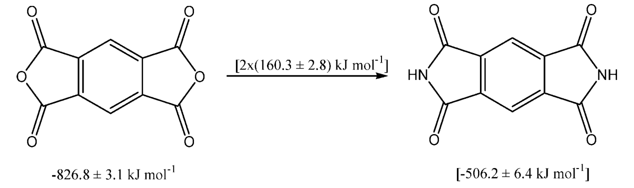




Unfortunately, 1,2,4,5-benzenetetracarboxylic diimide could not be studied experimentally as this compound decomposes upon heating. (We note the photochemical decomposition of the tetracarboxylic dianhydride to form 1,2,4,5-benzdiyne[35] but note no corresponding thermal decomposition to this product.)

Using twice the value of the enthalpic increment for phthalic anhydride/phthalimide (160.3 ± 2.8 kJ mol^{-1}), the following estimation of the standard molar enthalpy of formation for

1,2,4,5-benzenetetracarboxylic diimide, −506.2 ± 6.4 kJ mol^{-1}, seems to be reasonable.



1,2,4,5-benzenetetracarboxylic dianhydride 1,2,4,5-benzenetetracarboxylic diimide

Computational Results and Discussion

The geometries of 1,2,4,5-benzenetetracarboxylic dianhydride and the corresponding diimide have been optimized with the B3LYP density functional and the 6-31G* and 6-311G** basis sets, and we found that both molecules are planar. In the dianhydride the −C(=O)−O−C(=O)− bonds are in the same plane, as well as, the −C(=O)−NH−C(=O)− bonds in the diimide compound.

More accurate energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the B3LYP, the MPW1B95, and the B3PW91 density functionals and the triple-ζ correlation consistent basis set, cc-pVTZ. The results are reported in Table 3 for the two studied compounds and some auxiliary molecules, as well as, B3LYP/6-31G* zero-point vibrational energies and thermal energy corrections.

We have considered the following isodesmic reactions involving the 1,2,4,5-benzenetetracarboxylic dianhydride in order to estimate its enthalpy of formation:

1,2,4,5-benzenetetracarboxylic dianhydride + benzene → 2 phthalic anhydride (I)

1,2,4,5-benzenetetracarboxylic dianhydride + 2 indane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 phthalic anhydride (II)

1,2,4,5-benzenetetracarboxylic dianhydride + 2 cyclopentane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 succinic anhydride (III)

1,2,4,5-benzenetetracarboxylic dianhydride + 2 cyclopentene → 1,2,3,5,6,7-hexahydro-s-indacene + 2 maleic anhydride (IV)

1,2,4,5-benzenetetracarboxylic dianhydride + 2 naphthalene → anthracene + 2 phthalic anhydride (V)

1,2,4,5-benzenetetracarboxylic dianhydride + 2 cyclohexane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 glutaric anhydride (VI)

The following isodesmic reactions were used to estimate the enthalpy of formation of 1,2,3,5,6,7-hexahydro-s-indacene, which was then used in equations II, III, IV, and VI:

1,2,3,5,6,7-hexahydro-s-indacene + benzene → 2 indane (VII)

1,2,3,5,6,7-hexahydro-s-indacene + 2 naphthalene → anthracene + 2 indane (VIII)

The enthalpy of formation of 1,2,4,5-benzenetetracarboxylic diimide was estimated from the following isodesmic reactions:

1,2,4,5-benzenetetracarboxylic diimide + benzene → 2 phthalimide (IX)

1,2,4,5-benzenetetracarboxylic diimide + 2 indane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 phthalimide (X)

1,2,4,5-benzenetetracarboxylic diimide + 2 cyclopentane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 succinimide (XI)

1,2,4,5-benzenetetracarboxylic diimide + 2 cyclopentene → 1,2,3,5,6,7-hexahydro-s-indacene + 2 maleimide (XII)

1,2,4,5-benzenetetracarboxylic diimide + 2 naphthalene → anthracene + 2 phthalimide (XIII)

1,2,4,5-benzenetetracarboxylic diimide + 2 cyclohexane → 1,2,3,5,6,7-hexahydro-s-indacene + 2 glutarimide (XIV)

The following isodesmic reaction was used to estimate the enthalpy of formation of maleimide, which was then used in reaction (XII):

maleimide + succinic anhydride f succinimide + maleic anhydride (XV)

Using the B3LYP/cc-pVTZ, MPW1B95/cc-pVTZ and B3PW91/cc-pVTZ energies of the compounds involved in the isodesmic reactions I−VI, we have calculated the reaction enthalpies. With the experimentally measured enthalpies of formation of the auxiliary compounds taken from the literature,[31−34] we have derived the enthalpies of formation, at $T = 298.15$ K, of 1,2,4,5-benzenetetracarboxylic dianhydride. The results are presented in Table 4.

The enthalpy of formation of 1,2,3,5,6,7-hexahydro-s-indacene, at $T = 298.15$ K, which is used in reactions II, III, IV, and VI was estimated using reactions VII and VIII. The theoretical estimates of the enthalpy of formation of 1,2,3,5,6,7-hexahydro-s-indacene are presented in Table 5, and a mean value, 37.5 kJ mol^{-1}, was obtained from the values presented in that table.

The group additivity estimated value for the enthalpy of formation of 1,2,3,5,6,7-hexahydro-s-indacene, 38.0 ± 2.5 kJ mol^{-1}, presented above, is in good agreement with the mean value 37.5 kJ mol^{-1} obtained from the theoretical calculated values.

Our past experience on the calculation of the energetics of organic compounds from different computational techniques corroborates the widely used density functional theoretical (DFT) methods based on the B3LYP density functional as a proper choice for the purpose of describing the energetics of organic compounds with enough accuracy and acceptable computational cost. We also observed persistently that, besides the functional choice, also the quality of the basis sets used is important to ensure the fiability of the computed results. However, what we have unequivocally observed as being of outmost importance whenever we want to describe reaction energetics with necessarily approximate computational methods is the type of reaction we want to properly describe. Thus, the most similar are the reactants and the products, the more likely is that the reaction will be well described energetically, even by approximate computational methods. The reactions we choose to use (I−VI) are all of the isodesmic type (they conserve the number of each formal bond type between reactants and products), and most of them are also homodesmotic (besides being isodesmic they also conserve the number of atoms in each

TABLE 3: Calculated Electronic Energies and Thermal Corrections to $T = 298.15$ K

compound[a]	E_{6-31G*}	$E_{6-311G**}$	$E_{total/6-31G*}$[b]	$E_{B3LYP/cc-pVTZ}$	$E_{MPW1B95/cc-pVTZ}$	$E_{B3PWB91/cc-pVTZ}$
anthracene	−539.53053 4	−539.66228 7	516.66	−539.72175 9	−539.44100 8	−539.49319 5
1,2,4,5-btc dianhydride	−833.64482 3	−833.86989 6	296.92	−833.95812 2	−833.95812 2	−833.61421 3
1,2,4,5-btc acid	−986.50909 8	−986.81122 3	445.42	−986.91401 2	−986.91401 2	−986.50518 8
1,2,4,5-btc diimide	−793.93260 1	−794.15101 9	362.88	−794.23273 0	−794.23273 0	−793.90605 4
benzene	−232.24865 8	−232.31152 3	266.14	−232.33755 3	−232.20297 2	−232.23726 6
cyclohexane	−235.88046 6	−235.94711 5	447.40	−235.96981 2	−235.80752 6	−235.87840 5
cyclopentane	−196.55706 9	−196.61342 2	370.66	−196.63269 7	−196.49751 8	−196.55681 1
cyclopentene	−195.32699 2	−195.38266 5	308.71	−195.40303 8	−195.27758 5	−195.32435 5
glutaric anhydride	−419.83310 5	−419.95403 9	292.66	−419.99782 4	−419.81519 3	−419.82708 8
glutarimide	−399.98235 2	−400.09987 4	326.53	−400.14065 0	−399.95558 3	−399.97850 4
indacene	−465.72726 6	−465.84444 5	604.39	−465.89219 4	−465.63206 6	−465.70795 8
Indane	−348.98812 9	−349.07817 6	435.21	−349.11513 4	−348.91774 0	−348.97286 8
maleic anhydride	−379.28952 5	−379.39817 6	155.02	−379.43919 6	−379.29409 4	−379.28131 7
maleimide	−359.42892 2	−359.53425 7	187.48	−359.57234 6	−359.42470 3	−359.42292 3
naphthalene	−385.89273 9	−385.98997 1	391.54	−386.03274 6	−385.82533 6	−385.86841 0
phthalic anhydride	−532.95204 6	−533.09566 2	282.09	−533.15290 5	−532.93471 0	−532.93074 4
phthalimide	−513.09328 6	−513.23360 7	314.90	−513.28770 2	−513.06732 3	−513.07418 2
succinic anhydride	−380.52306 2	−380.63331 2	216.09	−380.67378 1	−380.51907 1	−380.51916 6
succinimide	−360.66678 1	−360.77374 7	249.28	−360.81105 2	−360.65385 6	−360.66492 1
water	−76.408955	−76.448292	60.87	−76.461250	−76.424115	−76.430668 6

[a] All electronic energies are in au ($1E_H = 2625.50184$ kJ mol^{-1}) while the thermal corrections are in kJ mol^{-1}. [b] E_{total} ($T = 298.15$ K) $= E_{trans} + E_{rot} + E_{ZP} + \Delta_{0K}^{298.15K} E_{vib}$.

TABLE 4: Estimated Enthalpies of Formation of 1,2,4,5-Benzenetetracarboxylic Dianhydride in the Gaseous Phase, at $T = 298.15$ K

	$\Delta_f H_m^\circ$/(kJ mol^{-1})		
reaction	B3LYP/ cc-pVTZ	MPW1B95/ cc-pVTZ	B3PW91/ cc-pVTZ
I	−799.9	−800.0	−800.2
II	−801.8	−801.7	−802.1
III	−821.1	−814.3	−815.3
IV	−810.1	−804.0	−806.8
V	−803.0	−804.5	−803.8
VI	−805.0	−802.5	−802.3

TABLE 5: Estimated Enthalpies of Formation of 1,2,3,5,6,7-Hexahydro-s-indacene in the Gaseous Phase, at $T = 298.15$ K

	$\Delta_f H_m^\circ$/(kJ mol^{-1})		
reaction	B3LYP/ cc-pVTZ	MPW1B95/ cc-pVTZ	B3PW91/ cc-pVTZ
VII	39.5	39.3	39.5
VIII	36.3	34.8	35.8

TABLE 6: Estimated Enthalpies of Formation of 1,2,4,5-Benzenetetracarboxylic Diimide in the Gaseous Phase, at $T = 298.15$ K

	$\Delta_f H_m^\circ$/(kJ mol^{-1})		
reaction	B3LYP/ cc-pVTZ	MPW1B95/ cc-pVTZ	B3PW91/ cc-pVTZ
IX	−493.3	−493.0	−493.5
X	−495.2	−494.7	−495.4
XI	−516.9	−511.3	−511.8
XII	−501.9	−497.2	−499.4
XIII	−496.5	−497.5	−497.1
XIV	−500.2	−498.6	−497.7

hybridization state and the number of bonds between atoms in each hybridization state). The only exception is reaction III, which involves bonds of the type Csp^3-Csp^2 only at the products side. Thus we believe that our energy estimations should provide accurate results at the computational level we choose.

The results obtained for the enthalpy of formation show that the dianhydride is consistently described, with reactions III and IV providing the results more close to experiment. The remaining reactions provide estimates with deviations of about 20 kJ mol^{-1}. This represents a moderate agreement, which nevertheless supports our experimental result as compared to the previous experimental data lying well below (by about 80 to 220 kJ mol^{-1}).

In order to ascertain the role that the observed "systematic errors" introduced by "B3LYP and other popular functionals",[36] we decided to confirm our estimates by using a functional (MPW1B95) which has been properly parametrized to describe thermochemical data by Truhlar and co-workers[23] and also an older functional (B3PW91)[24] which has been claimed to perform "best", i.e., better than B3LYP "relative to the highest level coupled cluster {CCSD(T)} energy single point"[37] calculations. In either case we performed only single point energy calculations with the cc-pVTZ basis set at the optimized B3LYP/6-311G** geometries and used the B3LYP/6-31G* thermal corrections. The resulting estimates for the enthalpy of formation of 1,2,4,5-btc-dianhydride are collected in the appropriate columns of Table 4, and agree with our other estimates to within few kilojoules per mole. This supports our earlier argument about the usefulness of the reaction set we use based on their (almost) homodesmotic character. Also the usefulness of this type of reactions can be ascertained by the estimates of −377.5, −373.0, and −371.0 kJ mol^{-1} we obtained for the enthalpy of formation of phthalic anhydride (−371.4 ± 1.9 kJ mol^{-1} from the literature) from reaction similar to III, IV, and VI, respectively, but with 1,2,4,5-benzenetetracarboxylic dianhydride replacing phthalic anhydride and 1,2,3,5,6,7-hexahydro-s-indacene substituted by Indane. In this calculation we used the MPW1B95/cc-pVTZ//B3LYP/6-311G** energies. The quality of the results is apparent and lends further support on the quality of our computational and experimental results for 1,2,4,5-benzenetetracarboxylic dianhydride.

In Table 6 we present the estimated enthalpies of formation, at $T = 298.15$ K, of 1,2,4,5-benzenetetracarboxylic diimide obtained using reactions (IX) to (XIV).

The probable usefulness of the above reactions IX−XIV in the estimation of the enthalpy of formation of 1,2,4,5-benzenetetracarboxylic diimide is supported by reasoning similar to the earlier used for reactions I−VI, by invoking the fact that these reactions, excepting XI, are homodesmotic. In this way they should very confidently provide reliable estimates of the

TABLE 7: Estimated Enthalpy of Formation of Maleimide in the Gaseous Phase, at $T = 298.15$ K

	$\Delta_f H_m^\circ$/(kJ mol^{-1})		
reaction	B3LYP/ cc-pVTZ	MPW1B95/ cc-pVTZ	B3PW91/ cc-pVTZ
XV	−235.8	−235.7	−235.7

enthalpy of formation of the diimide. This reasoning is also supported by the excellent agreement of the estimates −220.1, −214.8, and −212.3 kJ mol^{-1} for the enthalpy of formation of phthalimide obtained from reactions similar to XI, XII, and XIV, respectively, and the MPW1B95/cc-pVTZ//B3LYP/6-311G** energies, with the experimentally obtained enthalpy of formation of −211.1 ± 2.1 kJ mol^{-1}. All these observations support our estimates of the enthalpy of formation of 1,2,4,5-benzenetetracarboxylic diimide, which are reported in Table 7.

The enthalpy of formation of maleimide, at $T = 298.15$ K, which was used in reaction (XII) was estimated using reaction XV. The theoretical estimates are presented in Table 7 and a mean value was obtained from the results presented in that table, −235.7 kJ mol^{-1}.

The group additivity estimated value for the enthalpy of formation of maleimide −233.2 ± 3.4 kJ mol^{-1} is in good agreement with the mean value −235.7 kJ mol^{-1} obtained from the theoretical calculated values.

Quantitative characterization of aromaticity can be obtained from a large variety of approaches based mainly on structural, energetic or magnetic criteria. In the present work we choose one of the most widely used method, based on magnetic criteria, as originally proposed in 1996 by Schleyer and his co-workers[28] and successfully refined and improved until now.[38−41] This method originally involved the calculation of the NMR chemical shift as felt by a probe located at the center of the planar ring, referred to as nucleus-independent chemical shift (NICS), as a measure of the magnitude of the ring currents induced by the magnetic field, i.e., a measure of electronic circular delocalization effects. However, later, it was recognized that a better measure of aromaticity would be provided by the NICS at some point above (or below) the center of the ring, in order to account for the effect of the nodal plane of the π molecular orbitals at the ring plane and also to minimize the effect of the sigma electron density on the chemical shielding. The NICS values calculated are traditionally reported as the symmetric of the isotropic component of the calculated chemical shift tensor in order to respect the conventions adopted in NMR work, and thus negative NICS values are assumed to indicate aromaticity whereas positive NICS values are associated with antiaromaticity. In this work we have thus calculated the NICS values using B3LYP/6-31G* wavefunctions at the B3LYP/6-31G* geometries, at two different points for each ring: the geometrical center of the ring (i.e., the point whose Cartesian coordinates are the nonweighted mean of the homologous coordinates of the heavy atoms of the ring), denoted NICS(0) and 0.5 Å above the center of the ring, denoted NICS(0.5). The NICS values, presented in Table 8, show that the benzenic rings of 1,2,4,5-btc-dianhydride and 1,2,4,5-btc-diimide are unequivocally aromatic; we can even observe a small increase of the aromaticity (as measured from the NICS(0.5) values) of these benzenic rings as compared to benzene itself. The pentagonal rings of both molecules, on the other hand, show a clear nonaromatic character as associated to their virtually zero NICS(0.5) values. Thus, even though we can in fact count a total of 10 π electrons for each of these systems, the extra 4 π electrons contributed by the two oxygen atoms at the pentagonal rings are largely maintained out of the delocalized central ring π system. The only way these 4 electrons have to enter the delocalized system involves the two C=O moieties at each ring, but this seems to be a non-effective delocalization mechanism and should only contribute to a very small increase in the aromaticity as measured by the NICS(0.5) values.

TABLE 8: Nucleus Independent Chemical Shifts (ppm)

	6-ring		5-ring	
	NICS(0)	NICS(0.5)	NICS(0)	NICS(0.5)
1,2,4,5-btc dianhydride	−9.5	−11.1	1.8	−0.2
1,2,4,5-btc diimide	−9.0	−10.7	2.9	1.1
phthalic anhydride	−9.3	−11.1	1.5	−0.3
phthalimide	−9.1	−10.9	2.9	1.2
benzene	−9.6	−10.3	−	−

Conclusions

A combined experimental and computational study has been carried out to determine the standard molar enthalpy of formation of gaseous 1,2,4,5-benzenetetracarboxylic dianhydride of −826.8 ± 3.1 kJ mol^{-1}. Our experimental result for the standard molar enthalpy of formation of the crystal, −949.1 ± 2.0 kJ mol^{-1}, is taken as more trustworthy than the previous literature values, 907.3, −1047, and −953.5 kJ mol^{-1}.

Both group additivity and computational calculations allowed the estimation of a reasonable value for the standard molar enthalpy of formation of gaseous 1,2,4,5-benzenetetracarboxylic diimide, a value that could not be measured because of inadequate sample purity and thermal stability.

Well-chosen isodesmic reactions and NICS calculations for both 1,2,4,5-benzenetetracarboxylic dianhydride and diimide lead us to the conclusion that the aromaticity is essentially restricted to the benzenic ring in both species despite the fact that they are 10 π electron species. Accordingly we believe that the same "localization" of the aromaticity can plausibly happen with other similar polycyclic aromatic heterocyclic species. This finding is reminiscent of our earlier study of diphenic anhydride[42] with its 14 π electrons.

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