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Accurate and Efficient Method for Predicting Thermochemistry of Furans and *ortho*-Arynes: Expansion of the Bond-Centered Group Additivity Method[†]

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The bond-centered group additivity method (BCGA) method for the estimation of the thermochemical properties of polycyclic aromatic molecules is expanded to aromatic molecules containing furan ring(s) and *ortho*-arynes. The method is based on enthalpies of formation (ΔH_f°), entropies (S_{298}°), and heat capacities (C_p°) obtained from B3LYP/6-31G(d) calculations. The enthalpies of formation were obtained using a set of homodesmic reactions that include only aromatic molecules as the reference. Two new atom-centered groups are defined for the description of furan ring(s) and *ortho*-arynes, leading to the addition of 17 new bond-centered groups to the BCGA method. The ΔH_f°, S_{298}°, and C_p° contributions of these bond-centered groups is derived.

Introduction

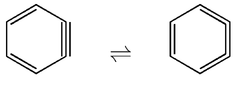
To advance the understanding of combustion systems, a way is needed to rapidly estimate thermochemical properties of all molecules involved. In the 1970s, Benson, Golden, and others developed group-based methods for estimating the thermochemistry of polycyclic aromatics and oxygenated aromatics.[1] However, at that time only very limited data were available for use when regressing the group values, so only a small number of rather generic groups could be used. Now, quantum chemistry can be used to extend the data set, so much more specific groups can be defined, and their group values determined. In this paper, we expand the Bond-Centered Group Additivity (BCGA) method[2] to include aromatic molecules containing furan rings and *ortho*-arynes.

According to the simple Hückel ($4N + 2$) rule, furan should be considered an aromatic ring. This rule states that (planar) cyclic systems with ($4N + 2$) π-electrons are more stable than their open chain analogues. Other measures of aromaticity also confirm that furan is aromatic. For example, its NICS (nucleus-independent chemical shift) index is −12.3, compared to benzene's −9.7 value.[3] The NICSs are based on absolute magnetic shieldings computed at ring centers, negative values denote aromaticity, while positive NICSs denote anti-aromaticity.[3]

The kinetics of formation and consumption of PAHs containing furan rings (especially dibenzofuran) during combustion has attracted considerable attention,[4] because the polychlorinated form of these species are very carcinogenic. Polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) are a major problem in waste incineration (e.g., ref 5). On another note, heterocyclic PAHs have attracted attention due to the possibility of tailoring the curvature and rigidity of buckybowls by the introduction of heteroatoms at strategic positions.[6]

A few estimation methods for PAHs containing a furan ring have been previously proposed.[1,8−12] These works were all based on ring corrections for the entire furan ring. The works from Dorofeeva et al.[11] and Zhu and Bozzelli[12] focus on the derivation of a group additivity method for the estimation of the thermochemical properties of chlorinated dioxins and furans. The proposed ring corrections were derived from the experimental thermochemical properties of furan only or of furan and dibenzofuran. There are no guarantees of how the ring correction estimate will perform for larger PAHs or for furan rings in other environments.

Ortho-arynes are formed through didehydrogenation of the parent arene at the ortho position. They can be viewed as a delocalized structure in which the second π-orbital from the triple bond is perpendicular to the first. The electrons in this second π-orbital are not free to move around the aromatic ring. Molecular orbital (MO) results have shown that both resonance structures **1** and **2** contribute to benzyne[10]



1 **2**

Arynes are believed to be important intermediates in the formation of five-membered rings from benzenoid PAHs. One proposed mechanism suggests that after 1,2-didehydrogenation of the parent arene, the resulting aryne will be in equilibration with its carbene isomer. The latter would then be trapped intramolecularly to form a five-membered ring.[14] The proposed mechanism for thermolysis of benzo[*c*]phenanthrene[15] is shown in Figure 1 as an example.

Experimental Values

Experimental heats of formation of molecules containing furan rings are only available for furan, benzo[*b*]furan (**3**), and dibenzofuran (**4**) (see Table 1). Experimental values for entropy and heat capacities for this class of PAHs are only available for furan. The values cited by Stull et al.[16] are listed in Table 5. The $\Delta H_{f,\mathrm{exp}}^\circ$ of benzyne has been measured by many groups using different methods, and the values have ranged from 98

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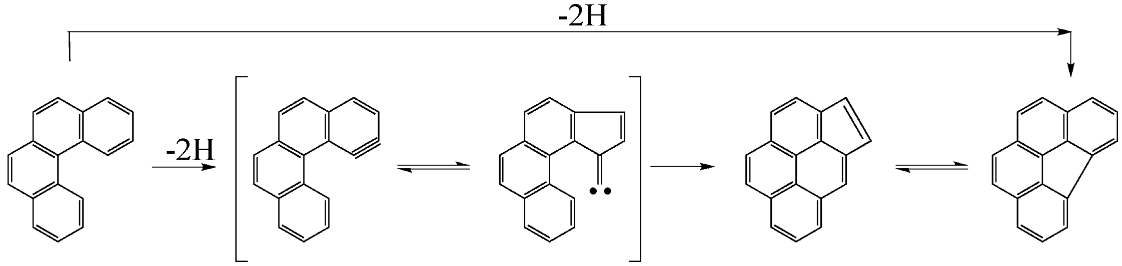


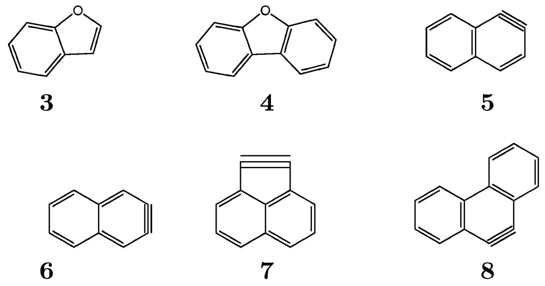
Figure 1. Arynes have been proposed to be intermediates in the formation of five-membered rings, as shown here in the thermolysis of benzo[*c*]phenanthrene.[15]

TABLE 1: Comparison between $\Delta H^\circ_{f,\mathrm{exp}}$ Values and ΔH°_f Calculated from the Proposed Homodesmic Reaction Scheme for PAHs Containing Furan Structures

		$\Delta H^\circ_{f,\mathrm{exp}}$ (kcal mol^{-1})	$\Delta H^\circ_{f,\mathrm{atom}}$ (kcal mol^{-1})[a]	$\Delta H^\circ_{f,\mathrm{homo}}$ (kcal mol^{-1})[a]
furan	C_4H_4O	-8.3 ± 0.2^b	-6.5 ± 0.4	[c]
benzo[*b*]furan (**3**)	C_8H_6O	3.3 ± 0.2^d	5.1 ± 0.9	4.1 ± 3
dibenzofuran (**4**)	$C_{12}H_8O$	11.3 ± 1.1^e, 13.2 ± 0.1^f	13.2 ± 1.3	13.1 ± 4

[a] As a reference, the $\Delta H^\circ_{f,\mathrm{atom}}$ values calculated from atomization reactions are also given. B3LYP/6-31G(d) energies were used for the calculation of $\Delta H^\circ_{f,\mathrm{homo}}$ and $\Delta H^\circ_{f,\mathrm{atom}}$, as described in section 3.1. [b] Reference 17. [c] Furan is used as a reference molecule for the homodesmic reaction scheme. The adopted $\Delta H^\circ_{f,\mathrm{homo}}$ for furan is 8.3 ± 2. [d] Reference 18, as cited in ref 19. [e] Reference 20, as cited in ref 19. [f] Reference 21.

SCHEME 1



to 113 kcal mol^{-1}.[22] More recent values have clustered around 105 kcal mol^{-1} (see Table 2). The ΔH°_f of 1,2- and 2,3-didehydronaphthalenes (**5** and **6**) have been estimated through the study of bromine elimination reactions with bromonaphthalenes.[23] Broadus and Kass determined the $\Delta H^\circ_{f,\mathrm{exp}}$ of 1,2-didehydroacenaphthylene (**7**) by studying the reactivity of the 1,2-didehydroacenaphthylene radical anion.[24] The $\Delta H^\circ_{f,\mathrm{exp}}$ of 9,10-didehydrophenanthrene (**8**) has been estimated through the study of the thermal decomposition of 9,10-disubstituted derivatives of phenanthrene.[25] A list of these scarce experimental ΔH°_f values is found in Table 2.

To the best of our knowledge, no experimental values for the entropy and the heat capacities of *ortho*-aryne compounds have been published.

Computational Methods

3.1. Quantum Chemical Calculations. All optimized geometries and vibrational frequencies were calculated at the B3LYP/6-31G(d) level using the Gaussian 98 suite of programs.[29] A frequency scaling factor of 0.9613 was employed for the vibrational partition function, the zero-point energy, entropy, and heat capacities. Calculations were done for 29 PAHs containing a furan structure (see Table S1 in the Supporting Information), 10 arynes (Table S3), and 2 PAHs containing both furan rings and triple bonds (Table S2).

El-Azhary and Suter[30] compared the performance of various methods (HF, MP2, LDA, BVWN, BLYP, and B3LYP) and basis sets (cc-pVDZ, cc-pVTZ, and 6-31G(d,p)) in the calculation of the geometry and vibrational frequencies of furan. In Table 3, the experimental geometry of this molecule is compared with the geometry obtained at different levels of computation. El-Azhary and Suter found that, among the methods that they tested, the geometry from the B3LYP method provides the best agreement with experimental geometry. The effect of the basis set on the calculated bond angles and frequencies was very small. Indeed, the geometry calculated with the B3LYP/6-31G(d) method is in good agreement with the geometry obtained experimentally.

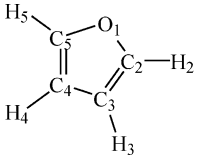
Cioslowski et al.[31] tested many quantum chemical methods for aryne compounds. They found that the B3LYP/6-311G(d,p) method provided a geometry of benzyne comparable to higher level, benchmark calculations such as MP2/6-311G(d,p), QCISD/6-311G(d,p), and CCSD(T)/6-311G(d,p). A comparison between the benzyne geometry from these benchmark calculations and the geometry from B3LYP/6-311G(d,p) and B3LYP/6-31G(d)

TABLE 2: Comparison between the ΔH°_f Calculated from the Proposed Homodesmic Reaction Scheme for *ortho*-Arynes and $\Delta H^\circ_{f,\mathrm{exp}}$ Values

		$\Delta H^\circ_{f,\mathrm{exp}}$ (kcal mol^{-1})	$\Delta H^\circ_{f,\mathrm{atom}}$ (kcal mol^{-1})[a]	$\Delta H^\circ_{f,\mathrm{homo}}$ (kcal mol^{-1})[a]
benzyne	C_6H_4	105 ± 3^b 105^d 106.6 ± 3.0^e	113.9 ± 0.7	[c]
1,2-didehydronaphthalene (**5**)	$C_{10}H_6$	122 ± 6^f	131.9 ± 1.1	121.6 ± 3
2,3-didehydronaphthalene (**6**)	$C_{10}H_6$	122 ± 6^f	134.4 ± 1.1	124.1 ± 3
1,2-didehydroacenaphthylene (**7**)	$C_{12}H_6$	160 ± 4^g	182.5 ± 1.3	173.1 ± 7.5
9,10-didehydrophenanthrene (**8**)	$C_{14}H_8$	143 ± 9^h	141.7 ± 1.6	132.0 ± 4.5

[a] As a reference, the $\Delta H^\circ_{f,\mathrm{atom}}$ values calculated from atomization reactions are also given. B3LYP/6-31G(d) energies were used for the calculation of $\Delta H^\circ_{f,\mathrm{homo}}$ and $\Delta H^\circ_{f,\mathrm{atom}}$, as described in section 3.1. [b] Determined through the bracketing technique for the ion/molecule reaction of an alkoxide with bromobenzene.[26] [c] Benzyne is used as a reference molecule for the homodesmic reaction scheme. The adopted $\Delta H^\circ_{f,\mathrm{homo}}$ for benzyne is 106.6 ± 3. [d] From acidity bracketing.[27] [e] Determined from threshold energies for collision-induced dissociation (CID) measurements.[28] [f] Determined through the bracketing technique for the ion/molecule reaction of an alkoxide with bromonaphthalene.[23] [g] Reference 24. [h] Reference 25.

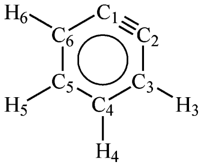
TABLE 3: Comparison between the Experimental Geometry of Furan and the Geometry Calculated at Different Levels



		6-31G(d,p)[b]		6-31G(d)[c]
	exptl[a]	MP2	B3LYP	B3LYP
		Bond Lengths (Å)		
O_1-C_2	1.362	1.364	1.364	1.364
C_2-C_3	1.361	1.365	1.361	1.361
C_3-C_4	1.431	1.426	1.444	1.436
C_2-H_2	1.075	1.074	1.079	1.079
C_3-H_3	1.077	1.075	1.087	1.081
		Bond Angles		
$C_2-O_1-C_5$	106.5	107.2	106.4	106.8
$O_1-C_2-C_3$	110.7	110.8	110.5	110.5
C_2-C_3-C_4	106.0	105.6	106.0	106.1
$O_1-C_2-H_2$	115.9	116.2	115.8	115.6
$C_2-C_3-H_3$	126.1	126.8	126.5	126.6

[a] As cited by ref 30. [b] Reference 30. [c] Calculated in this work.

TABLE 4: Comparison between the Geometry of Benzyne Calculated at Different Levels



		6-311G(d,p)[a]			6-31G(d)[b]
	exptl	QCISD	MP2	B3LYP	B3LYP
		Bond Lengths (Å)			
C_1-C_2	1.24 ± 0.02[c]	1.256	1.268	1.256	1.251
C_2-C_3		1.395	1.393	1.391	1.385
C_3-C_4		1.409	1.410	1.422	1.413
C_4-C_5		1.417	1.414	1.412	1.407
C_3-H_3		1.085	1.085	1.089	1.085
C_4-H_4		1.088	1.088	1.092	1.088
		Bond Angles			
$C_1-C_2-C_3$		126.9	126.8	127.1	126.9
C_1-C_6-C_5		110.5	110.6	110.7	110.3
$C_1-C_6-H_6$		126.7	127.0	127.1	127.2
C_3-C_4-C_5		122.5	122.7	122.4	122.4
$C_3-C_4-H_4$		118.9	118.6	118.5	118.7

[a] Reference 32. [b] Reference 31. [c] Calculated in this work.

TABLE 5: Comparison between Experimental and B3LYP/6-31G(d) S°_{298} and C°_p for Furan, in cal K^{-1} mol^{-1}

	Furan	
	expt[a]	calcd
S°_{298}	63.86	64.0
$C^\circ_{p,300}$	15.75	16.1
$C^\circ_{p,400}$	21.20	21.6
$C^\circ_{p,500}$	25.73	26.1
$C^\circ_{p,600}$	29.31	29.6
$C^\circ_{p,800}$	34.41	34.6
$C^\circ_{p,1000}$	37.89	38.0
$C^\circ_{p,1500}$		43.0

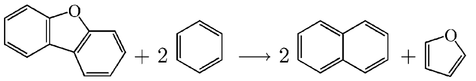
[a] As cited by ref 16.

is given in Table 4. The geometry for benzyne, the prototype aryne compound, calculated with the B3LYP/6-31G(d) method also agrees well with the geometries from the higher level calculations. However, B3LYP/6-31G(d) does not provide good absolute energy for benzyne. While the MP2/6-311G(d,p), QCISD/6-311G(d,p), and B3LYP/6-311G(d,p) methods give heats of 1,2-didehydrogenation of benzene of 86.1, 91.2, and 82.8 kcal mol^{-1} at 0 K, compared with the experimental value of 86.6 ± 3.0 kcal mol^{-1} (at 298 K),[31] the value calculated from B3LYP/6-31G(d) (at 0 K) is ca. 7 kcal mol^{-1} higher, 93.5 kcal mol^{-1}.

Higher level calculations and larger basis sets are still too computationally expensive for the calculation of accurate energies for large molecules such as the ones studied here (see, for example, ref 33). A good alternative for the calculation of ΔH°_f with good agreement with experimental data is working reactions in which reference molecules with known (experimental) heats of formation are used to achieve a cancellation of quantum chemical errors. In the next section, a homodesmic reaction scheme that provides consistent ΔH°_f values (for both furans and *ortho*-arynes) that agree well with the available experimental data is proposed. This reaction scheme allows for the cancellation of the systematic errors that arise in the quantum chemical calculations due to the incomplete description of electron correlation energies.

The entropy and heat capacities values of Furan calculated at the B3LYP/6-31G(d) level show good agreement with experimental values, as shown in Table 5.

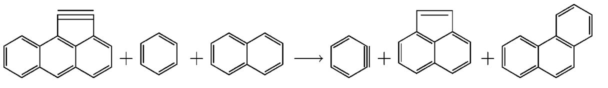
3.2. Homodesmic Reactions. Since this work aims at consistently expanding the Bond-Centered Group Additivity (BCGA) method to describe polycyclic aromatic molecules containing furan rings and *ortho*-arynes, the homodesmic reaction scheme developed for five- and six-membered ring PAHs described in ref 2 is used as a basis for the calculation of accurate ΔH°_f values. This homodesmic reaction scheme uses only aromatic molecules as reference (benzene, naphthalene, acenaphthalene, phenanthrene, and C_{60}), and provides an unequivocal method for calculating the ΔH°_f of any PAH. It was shown to provide ΔH°_f with good agreement to available experimental data of PAHs with five- and six-membered rings. Furan was added as a reference molecule to the homodesmic reaction scheme to account for the furan ring, as exemplified in the calculation of $\Delta H^\circ_{f,\text{homo}}$ of dibenzofuran shown in eq 1.



(1)

The agreement between the ΔH°_f value calculated from this homodesmic reaction scheme ($\Delta H^\circ_{f,\text{homo}}$) with the scarce experimental values is very good, as shown in Table 1. As a comparison, Notario et al., using "bond separation reactions" (a standard set of isodesmic reactions), obtained ΔH°_f values of 6.0 and 16.6 kcal mol^{-1} for 2,3-benzofuran and dibenzofuran, respectively.[34]

To account for the triple bond in aryne compounds, benzyne was added as a reference molecule in the homodesmic reaction scheme. For example, the ΔH°_f of 1,2-didehydroaceanthrylene is calculated through



(2)

As shown in Table 2, the ΔH°_f calculated through the proposed homodesmic reaction scheme in general agrees well with the available $\Delta H^\circ_{f,\text{exp}}$. The $\Delta H^\circ_{f,\text{homo}}$ values for the 1,2- and for 2,3-didehydronaphthalenes agree well with the ΔH°_f values

TABLE 6: Uncertainties Assigned to the $\Delta H^{\circ}_{f,\mathrm{exp}}$ of the Reference Molecules of the Developed Homodesmic Reaction Scheme for the Calculation of ΔH°_{f} from Absolute Energies

reference molecule	$\epsilon_{\mathrm{ref.molecule}}$ (kcal mol^{-1})
benzene	0.5
naphthalene	0.5
acenaphthalene	5.0
phenanthrene	2.0
C_{60}	10.0
furan	2.0
benzyne	3.0

estimated for these molecules by Linnert and Riveros[23] from experimental results of bromine elimination reactions with bromonaphthalenes. On the other hand, the $\Delta H^{\circ}_{f,\mathrm{atom}}$ for benzyne is ca. 7 kcal mol^{-1} higher than its $\Delta H^{\circ}_{f,\mathrm{exp}}$, as was expected, since the heat of 1,2-didehydrogenation of benzene is overestimated by the same amount by the B3LYP/6-31G(d) method.

The calculation of the errors related to $\Delta H^{\circ}_{f,\mathrm{homo}}$ takes into account the uncertainty in the experimental $\Delta H^{\circ}_{f,\mathrm{exp}}$ of the reference molecules used in the homodesmic reaction scheme and the uncertainty in the quantum chemical calculation of the heat of reaction (ΔH_{rxn}) of the homodesmic reaction, as given by eq 3

$$\epsilon = \epsilon_{\mathrm{expmtl}\Delta H^{\circ}_{f}} + \epsilon_{\mathrm{quantum}\Delta H_{\mathrm{rxn}}} \tag{3}$$

For example, the calculation of $\Delta H^{\circ}_{f,\mathrm{homo}}$ of dibenzofuran requires two benzenes, two naphthalenes, and one furan as reference molecules (as shown in eq 1, thus the $\epsilon_{\mathrm{expmtl}\Delta H^{\circ}_{f}}$ is given by

$$\epsilon_{\mathrm{expmtl}\Delta H^{\circ}_{f}} = 2\epsilon_{\mathrm{benzene}} + 2\epsilon_{\mathrm{naphthalene}} + \epsilon_{\mathrm{furan}} \tag{4}$$

The uncertainties of the $\Delta H^{\circ}_{f,\mathrm{exp}}$ of the reference molecules depend on the accuracy of the available $\Delta H^{\circ}_{f,\mathrm{exp}}$, as described in ref 2, and were assigned as shown in Table 6. The error in the quantum chemical calculation of ΔH_{rxn} is expected to increase with molecular size and was taken to be

$$\epsilon_{\mathrm{quantum}\Delta H_{\mathrm{rxn}}} = (\text{number of C atoms}) \times (0.2\ \mathrm{kcal\ mol^{-1}}) \tag{5}$$

For the molecules that form the base of the homodesmic reaction scheme (i.e., benzene, naphthalene, phenanthrene, acenaphthalene, C_{60}, furan, and benzyne), $\epsilon_{\mathrm{expmtl}\Delta H^{\circ}_{f}}$ is the uncertainty that was assigned to its experimental value and $\epsilon_{\mathrm{quantum}\Delta H_{\mathrm{rxn}}}$ is defined as zero.

Estimation Method

The estimation method proposed here is an expansion of the bond-centered group additivity (BCGA) method presented earlier.[2] In this work, we introduce new bond-centered groups to account for the types of bonds that arise in furan rings and *ortho*-arynes.

In ref 2, we had defined four different carbon-atom-centered groups to describe carbon atoms belonging to aromatic rings. Carbon atoms in aromatic rings belong either to only one ring (C_B) or to two or three fused rings (C_{BF}). The groups previously defined differ according to the neighbors of the central atom: "A" is defined as the $C_B-(H)$ atom-centered group of Benson,[7] and "B" is the $C_{BF}-(C_B)_2(C_{BF})$ atom-centered group. "C" is defined either as a $C_{BF}-(C_B)(C_{BF})_2$ or as a $C_{BF}-(C_{BF})_3$ atom-centered group with a further restriction that it belongs to only two rings, that is, it is on the periphery of the PAH. "D" is defined as a $C_{BF}-(C_{BF})_3$ atom-centered group in which the center C_{BF} atom belongs to three rings. The definition of these atom-centered groups is irrespective of the size of the rings to which these atoms belong. A depiction of these groups for an arbitrary PAH is shown in Figure 2. Possible bond-centered groups between these types of atom-centered groups are: AA, AB, AC, BB, BC, BD, CC, CD, and DD. These groups were then further subdivided according to the size of the ring(s) to which they belong. For a detailed description of these bond groups, see ref 2.

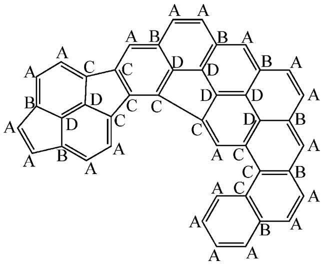


Figure 2. Atom-centered groups used for the definition of the bond-centered groups.[2] These atom-centered groups follow basically the definition established by Benson,[7] with a small difference in the definition of the "C" and "D" groups. "A" corresponds to the [$C_B-(H)$] group, "B" corresponds to the [$C_{BF}-(C_B)_2(C_{BF})$] group, "C" corresponds to a group that is in a bay region, it can be either a [$C_{BF}-(C_B)(C_{BF})_2$] group or a [$C_{BF}-(C_{BF})_3$] group, and "D" corresponds to the [$C_{BF}-(C_{BF})_3$] group that is internal to the PAH.

TABLE 7: Group Values for ΔH°_{f} Obtained for the "AO5", "BO5", and "CO5" Bond Groups

	ΔH°_{f}(kcal mol^{-1})
AO5	-17.65 ± 0.7
BO5	-13.11 ± 0.9
CO5	-18.88 ± 2.0
MAD	3.70
RMS	5.22

In the BCGA method, the thermochemical properties of an aromatic molecule are estimated by classifying each of the bonds in the aromatic ring into a bond group. The contributions of each bond group are then summed up. The resonance energy characteristic of aromaticity is taken into account by adding a ln(K) term to ΔH°_{f}, where K is the Kekulé structure count of the molecule, that is, the number of different ways the double and single bonds can be drawn.[2] Herndon et al. showed that ln(K) correlates very well with the Dewar resonance energy.[35] For example, furan has a Kekulé structure count of 1, dibenzofuran has a Kekulé structure count of 4, and benzyne has a Kekulé structure count of 2. The coefficient of the ln(K) term was derived in ref 2 and is -19.59 ± 1.1 kcal mol^{-1}. The values corresponding to the contributions of the bonds of five- and six-membered rings are given in Table S4 of the Supporting Information, and their derivation is explained in detail in ref 2.

A new atom-centered group "O", corresponding to the oxygen in the furan structure, was introduced to describe the furan ring. The introduction of the "O" atom-centered group leads to three new bond-centered groups: "AO5", "BO5", and "CO5", where the "5" in the notation refers to the size of the furan ring. These three bonds describe the two bonds in the furan ring that are bonded to the oxygen atom. Their difference lies in the environment of the carbon adjacent to the oxygen. For example, in "AO5", the carbon has two benzene bonds and one single bond, and in "CO5", the carbon is in a bay region. The other bonds in the furan ring are treated as normal bonds in a PAH.

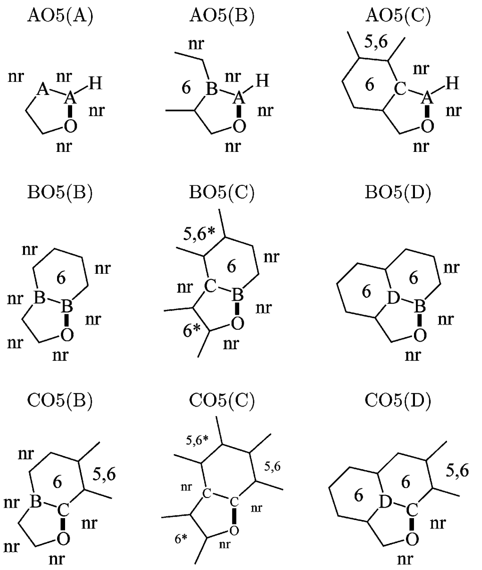


Figure 3. Aromatic bonds defined for PAHs with a furan structure. The rings marked with an * in the "BO5(C)" and "CO5(C)" bond groups do not have to both be present but at least one must be. Positions where no ring is allowed are marked with "nr". Positions that are not marked may or may not have a ring.

TABLE 8: Group Values for the Estimation of ΔH_f° and S_{298}° of PAHs with Furan Rings

	ΔH_f° (kcal mol^{-1})	S_{298}° (cal K^{-1} mol^{-1})
AO5(A)	−19.74 ± 0.5	13.2 ± 0.1
AO5(B)	−15.02 ± 0.7	12.6 ± 0.1
AO5(C)	−14.84 ± 1.3	12.4 ± 0.2
BO5(B)	−12.56 ± 1.2	5.2 ± 0.2
BO5(C)	−14.48 ± 0.6	5.6 ± 0.1
BO5(D)	−9.33 ± 1.0	6.7 ± 0.2
CO5(B)	−17.69 ± 1.7	5.9 ± 0.3
CO5(C)	−19.37 ± 1.8	5.0 ± 0.3
CO5(D)	−17.97 ± 2.0	6.8 ± 0.3
MAD	1.76	0.32
RMS	3.05	0.53

TABLE 9: Group Values for the Estimation of C_p° of PAHs with Furan Rings[a]

	$C_{p,T}$ (cal K^{-1} mol^{-1})						
	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
AO5(A)	2.9	3.9	4.6	5.2	6.1	6.6	7.5
AO5(B)	3.0	3.8	4.6	5.2	5.9	6.7	7.5
AO5(C)	2.8	3.7	4.5	5.1	5.9	6.8	7.3
BO5(B)	2.8	3.4	4.2	4.9	5.3	6.3	6.8
BO5(C)	2.8	3.6	4.3	5.0	5.5	6.4	6.8
BO5(D)	3.0	3.6	4.4	5.0	5.4	6.3	6.8
CO5(B)	2.8	3.3	4.1	4.9	5.1	6.3	6.7
CO5(C)	2.6	3.4	4.3	4.9	5.4	6.4	6.4
CO5(D)	2.9	3.5	4.3	4.9	5.3	6.3	6.5
MAD	0.07	0.06	0.06	0.06	0.09	0.07	0.09
RMS	0.10	0.10	0.09	0.09	0.12	0.12	0.13

[a] The standard error of each C_p° coefficient is smaller than 0.1 cal K^{-1} mol^{-1}.

The contributions from each of these bonds to the ΔH_f° are shown in Table 7. Given the relatively high mean average deviation (MAD) and root-mean-square (RMS) obtained from this method, we conclude that the "AO5", "BO5", and "CO5" bonds are not specific enough to capture the characteristics of PAHs containing the furan structure. Thus, these bonds have been further subdivided depending on the neighbor of the carbon atom. For example, the "AO5" bond has been subdivided into "AO5(A)", "AO5(B)", and "AO5(C)"; see Figure 3. The new group values were obtained through a weighted least-squares regression, where the inverse of the uncertainty of $\Delta H_{f,\mathrm{homo}}^\circ(\epsilon)$ was used as the weight. The bond values are given in Tables 8 and 9. The standard deviations for the C_p° values were 0.1 cal K^{-1} mol^{-1} or smaller.

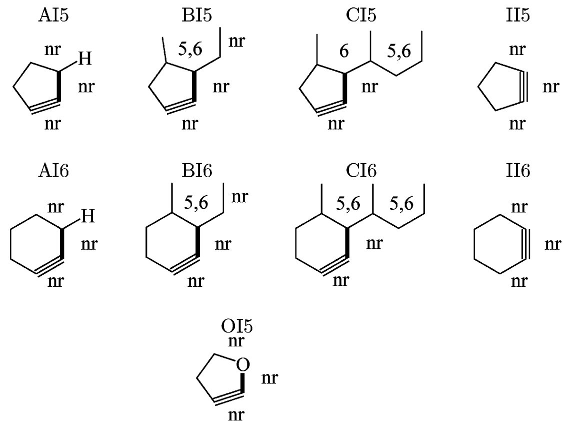


Figure 4. Aromatic bonds defined for PAHs with triple bonds.

TABLE 10: Group Values for ΔH_f° and S_{298}° for Aryne PAHs

	ΔH_f° (kcal mol^{-1})	S_{298}° (cal K^{-1} mol^{-1})
AI5	41.44 ± 2.8	21.3 ± 0.7
BI5	35.02 ± 0.8	13.9 ± 0.2
CI5	29.12 ± 1.9	14.7 ± 0.4
II5	70.00 ± −	0.0 ± −
AI6	26.94 ± 0.2	17.4 ± 0.0
BI6	24.66 ± 0.3	9.5 ± 0.1
CI6	19.57 ± 0.8	9.9 ± 0.2
II6[a]	50.00 ± −	0.0 ± −
MAD	0.423	0.092
RMS	1.038	0.200

[a] This bond-centered group is linearly dependent on the other groups, and thus, its value was arbitrarily assigned.

We introduced one new atom-centered group "I", corresponding to the carbons that belong to a triple bond in benzyne structures. The "I" atom-centered group leads to the following new bond-centered groups: "AI6", "BI6", "CI6", "II6", "AI5", "BI5", "CI5", and "II5", where the "6" and the "5" in the notation refer to the size of the ring to which the bond group belongs. Figure 4 should help in the understanding of these new bonds. Of these eight new bond-centered groups, only six are linearly independent. For example, the number of bonds "II5" and "II6" are related to the number of their remaining bonds through

$$\mathrm{II5} = 0.5 \times \mathrm{AI5} + 0.5 \times \mathrm{BI5} + 0.5 \times \mathrm{CI5} \tag{6}$$

$$\mathrm{II6} = 0.5 \times \mathrm{AI6} + 0.5 \times \mathrm{BI6} + 0.5 \times \mathrm{CI6} \tag{7}$$

The values for these groups were derived from the thermochemical properties of the 10 arynes (shown in Table S3) for which B3LYP/6-31G(d) calculations were performed. The contributions of bonds "II5" and "II6" to the ΔH_f° were assigned to be 70.0 and 50.0 kcal mol^{-1}, respectively. Their contributions to S_{298}° and C_p° were set to zero. The coefficients obtained from a weighted least-squares regression (again, the uncertainties in the $\Delta H_{f,\mathrm{homo}}^\circ$ of each molecule are used as weights) are shown in Tables 10 and 11.

The contribution of the OI5 group was determined separately, from the thermochemical properties of the two smallest PAHs

TABLE 11: Group Values for C_p° for Aryne PAHs

	$C_{p,T}$ (cal K^{-1} mol^{-1})						
	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
AI5	5.6 ± 0.2	6.3 ± 0.4	7.1 ± 0.1	7.6 ± 0.3	8.5 ± 0.4	8.9 ± 1.3	10.2 ± 2.5
BI5	4.9 ± 0.1	5.7 ± 0.1	6.5 ± 0.1	7.1 ± 0.1	7.7 ± 0.1	8.5 ± 0.3	9.1 ± 0.7
CI5	5.0 ± 0.1	5.7 ± 0.3	6.4 ± 0.1	7.2 ± 0.2	7.6 ± 0.3	8.6 ± 0.8	9.0 ± 1.7
II5[a]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AI6	4.7 ± 0.1	5.8 ± 0.1	6.7 ± 0.1	7.3 ± 0.1	8.2 ± 0.1	9.0 ± 0.1	9.7 ± 0.1
BI6	4.7 ± 0.1	5.7 ± 0.1	6.5 ± 0.1	7.2 ± 0.1	7.8 ± 0.1	8.7 ± 0.2	9.2 ± 0.3
CI6	4.7 ± 0.1	5.5 ± 0.1	6.4 ± 0.1	7.2 ± 0.1	7.8 ± 0.1	9.0 ± 0.4	9.6 ± 0.7
II6[a]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MAD	0.019	0.048	0.020	0.035	0.054	0.142	0.281
RMS	0.056	0.112	0.052	0.091	0.122	0.316	0.608

[a] This bond-centered group is linearly dependent on the other groups, and thus, its value was arbitrarily assigned.

TABLE 12: ΔH_f°, S_{298}°, and C_p° Values of the OI5 Group

			$C_{p,T}$[b]						
	ΔH_f°[a]	S_{298}°[b]	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
OI5	27.54	20.8	4.4	5.4	5.9	6.2	6.9	7.0	7.0

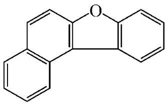
[a] ΔH_f° in kcal mol^{-1}. [b] S_{298}° and C_p° in cal K^{-1} mol^{-1}.

with this group, which are shown in Table S2 of the Supporting Information. The values derived for this group are listed in Table 12.

In arynes, the number of Kekulé structures is counted in the same way as the corresponding five- and six-membered ring PAHs. For example, benzyne is considered to have two Kekulé structures like benzene, and the didehydronaphthalenes each have three, like naphthalene.

Results and Discussion

The differentiation of the "AO5", "BO5", and "CO5" according to the neighbor of the carbon atom improves the estimation method. Both the MAD and the RMS decrease by almost 2 kcal mol^{-1}. The predictive capability of this estimation method can be assessed through the "leave one out" procedure. The discrepancy between the ΔH_f° for each observation and its prediction from the regression equation obtained by leaving that observation out was calculated. The MAD and RMS for these residuals are 2.37 and 3.98 kcal mol^{-1}. These values are not significantly larger than the values for the ordinary least-squares regression presented in Table 8, indicating that the method has good predictive capabilities. The maximum residual $y_i - \hat{y}_{i(i)}$, where y_i is $\Delta H_{f,\text{homo}}^\circ$ and $\hat{y}_{i(i)}$ is the predicted ΔH_f° from group values derived without including the *i*th observation in the regression, was -10.99 kcal mol^{-1} for benzo[*b*]naphtho[1,2-*d*]furan



This is the only furan ring in which the "C" carbon of the "BO(5)C" group is bonded to two other "C" carbons. This arrangement leads to steric repulsion between the H atoms in the bay region. If the bond-centered groups are to be refined further, the "BO(5)C" (and probably the "CO(5)C") group should be subdivided according to the atoms that are bonded to the "C" carbon.

The triple bond introduces considerable strain to aryne PAHs, as is attested by the high values of the ΔH_f° coefficients for each of the bonds. Ford and Biehl[36] studied the relative stability of polycyclic arynes using semiempirical (AM1) MO calculations. They concluded that two factors affected the stability of arynes: The first is the relief of steric strain that accompanies the removal of the hydrogen atoms from the parent arene, and the second is the ability of the carbon skeleton to accommodate the shorter dehydro bond. The bond-centered groups proposed here for *ortho*-arynes are directly related to the relief of steric strain provided by the removal of the hydrogens from the parent arene. When a dehydro bond has a "C" atom-centered group as a neighbor, it means that it is adjacent to a bay region and removal of the H atoms reduces steric conflicts. Thus, the ΔH_f° group values for the "CI" bonds are significantly lower (more stable relative to the original PAH) than those for aryne bonds in different local environments. The second factor affecting the stability of *ortho*-arynes is related to the bond order at the position of the dehydro bond in the parent arene. Thus, the triple bond that is formed in a bond that has a high bond order in the parent arene is more stable than a triple bond that is formed in a bond that has a lower bond order in the parent arene. The BCGA method indirectly captures this effect through the ln(*K*) term. The ln(*K*) term is a nonlocal property of the molecule, unlike the bond order, which is a property of each bond.

Only one experimental value of ΔH_f° is available for *ortho*-arynes in which the triple bond is in a five-membered ring (see Table 2). Although the ΔH_f° of 1,2-didehydroacenaphthylene calculated through the proposed homodesmic reaction scheme falls within the uncertainty range of the corresponding experimental ΔH_f°, the agreement between the two values is not excellent. We find however that this poor agreement is not sufficient justification to adjust the homodesmic reaction scheme such that the $\Delta H_{f,\text{homo}}^\circ$ of 1,2-didehydroacenaphthylene is closer to the measured $\Delta H_{f,\text{exp}}^\circ$, since there are no other independent indications to the correctness (or incorrectness) of this single $\Delta H_{f,\text{exp}}^\circ$ of 1,2-didehydroacenaphthylene. Thus, until more experimental ΔH_f° values are available for *ortho*-arynes in which the triple bond is in a five-membered ring, the "XI5" group values might not be very accurate, with uncertainties higher than those reported in Table 10.

Conclusions

The Bond-Centered Group Additivity (BCGA) method for the estimation of thermochemical properties previously presented for PAHs containing five- and six-membered rings is expanded to include aromatic molecules containing furan rings and *ortho*-arynes. The estimation method is based on thermochemical properties calculated at the B3LYP/6-31G(d) level. To correct for effects that are not completely captured by the DFT method, ΔH_f° are calculated through a set of homodesmic reactions that uses only aromatic molecules as reference molecules.

This work shows that the BCGA method can easily be systematically expanded. The major hindrance to the expansion of the method is the lack of experimental thermochemical data for the validation of the method.

Supporting Information Available: A list of the furans and *ortho*-arynes used for the derivation of the bond-centered group values is shown in Tables S1 to S3, along with their structures and Kekulé structure count, their $\Delta H^\circ_{f,\mathrm{homo}}$, and its $\Delta H^\circ_{f,\mathrm{est}}$. Figure S1 shows the bond-centered groups for PAHs with five- and six-membered rings, and Table S4 their contributions to the enthalpy, entropy, and heat capacities. This material is available free of charge via the Internet at http://pubs.acs.org.

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