

# Enthalpies of formation and isomerization of aromatic hydrocarbons and ethers by G3(MP2)//B3LYP calculations

Esko Taskinen<sup>a\*</sup>

**A computational method for estimation of the gas-phase enthalpies of formation of aromatic hydrocarbons and ethers has been developed. The method is based on high-level G3(MP2)//B3LYP calculations, atomization reactions, and structure-dependent correction terms. By this method, enthalpies of formation  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$  of 86 aromatic compounds were evaluated. The calculated enthalpies of formation raise questions of the reliability of several experimental enthalpies of formation reported in the literature. As an application of the computational enthalpies of formation, reaction enthalpies for several types of isomerization reactions of aromatic compounds were calculated. In cases in which experimental reaction enthalpies were available for comparison, the agreement between the computational and experimental data proved to be excellent. Copyright © 2008 John Wiley & Sons, Ltd.**

**Keywords:** enthalpies of formation; enthalpies of isomerization; G3(MP2)//B3LYP calculations; aromatic ethers; aromatic hydrocarbons

## INTRODUCTION

The main aim of the present work was to develop a computational method, based on G3(MP2)//B3LYP calculations, for estimation of gas-phase enthalpies of formation of aromatic hydrocarbons and ethers. Our previous papers<sup>[1,2]</sup> have shown that the G3(MP2)//B3LYP calculations, without correction terms to account for possible systematic errors, are successful for estimation of the enthalpies of formation of simple saturated and olefinic ethers, as well as those of related hydrocarbons. On the other hand, a recent G3(MP2)//B3LYP work of Blanquart and Pitsch<sup>[3]</sup> has revealed marked systematic deviations between computational and experimental enthalpies of formation of mono- and polycyclic aromatic hydrocarbons from benzene to coronene. The positive deviations,  $\Delta_f H_m^\circ(\text{exp}) - \Delta_f H_m^\circ(\text{comp})$ , abbreviated here as  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$ , were found to increase with increasing number of aromatic rings in the hydrocarbon. Besides the parent compounds (benzene, naphthalene, etc.), ethenyl ( $\text{CH}_2=\text{CH}-$ ) and ethynyl ( $\text{HC}\equiv\text{C}-$ ) derivatives of these hydrocarbons were also investigated.<sup>[3]</sup> From the data gathered, group contributions to the difference between experimental and computational enthalpies of formation could be assigned. Thus, for example, each C—H moiety of benzene was found to have a contribution of  $1.0 \text{ kJ mol}^{-1}$  to the difference in question.

In the present work, enthalpies of formation of selected aromatic compounds were first calculated using the atomization method. The values obtained were then compared with available experimental data, and the correction terms necessary for the computational enthalpies of formation to agree with the experimental ones were evaluated. Specifically, the purpose of the present work was to avoid resorting to isodesmic reactions, because combination of the computational data with the reaction enthalpies of different isodesmic reactions typically results in varying values of the

enthalpy of formation. However, for the sake of comparison, the enthalpies of formation of selected aromatic compounds were also calculated by isodesmic reactions using ethane as a reagent, together with the compound of interest.

Although the present study is mainly concerned with aromatic ethers, it was also considered necessary to extend the study of Blanquart and Pitsch<sup>[3]</sup> to simple aromatic hydrocarbons (benzene, naphthalene) containing saturated hydrocarbon substituents (Me, Et, etc.). In this way, more experimental data could be included in the comparison between experimental and computational data. The aromatic hydrocarbons studied are shown in Scheme 1, and the ethers in Scheme 4. The majority of the experimental enthalpies of formation were taken from the data compilation of Pedley *et al.*<sup>[4]</sup>

Besides the enthalpies of formation, computational enthalpies of isomerization of selected aromatic compounds, some of which have been previously studied by experimental methods, are also treated in the present work.

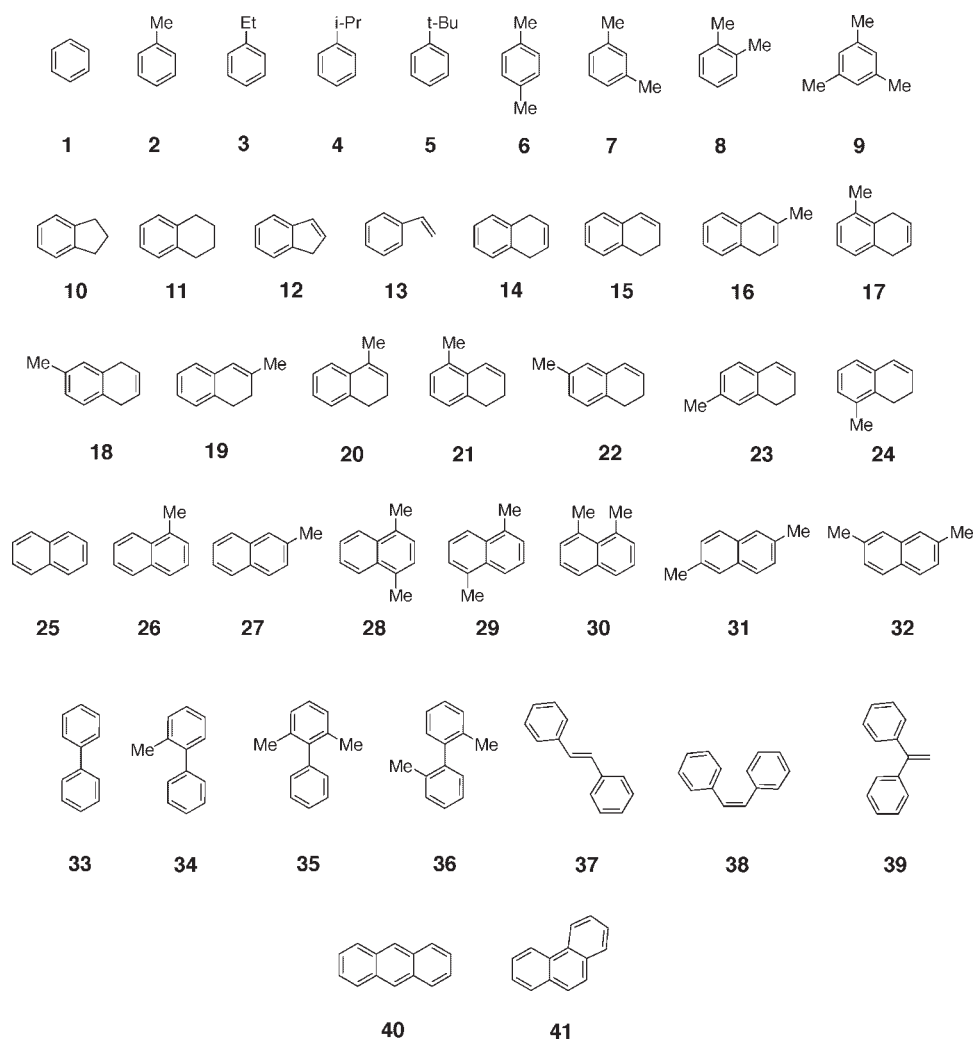
## RESULTS AND DISCUSSION

### Computations

The computations (gas phase, 298.15 K, 1 bar) were carried out using the G3(MP2)//B3LYP method<sup>[5]</sup> and the Gaussian 03 package of software.<sup>[6]</sup> In this method, molecular geometries and vibrational frequencies are obtained at the B3LYP/6-31G\*

\* Correspondence to: E. Taskinen, Department of Chemistry, University of Turku, FI-20014, Turku, Finland.  
E-mail: etaski@utu.fi

a E. Taskinen  
Department of Chemistry, University of Turku, FI-20014, Turku, Finland



**Scheme 1.** The aromatic hydrocarbons studied in this work

level, followed by single-point calculations at the QCISD(T)/6-31G\* and MP2/G3MP2large levels with a frozen core approximation.<sup>[5]</sup> In addition, an empirical “high level correction” (HLC) term is included to account for remaining (basis set) deficiencies.

The gas-phase standard enthalpies of formation at 298.15 K, shown in Table 1 for the hydrocarbons and in Table 2 for the ethers, were calculated from the computational data by atomization reactions.<sup>[7]</sup> Comparison with experimental data, whenever possible, is included in the tables.

### Isodesmic reactions

The isodesmic reactions used in this study are collected in Table 3. The enthalpies of formation  $\Delta_f H_m^\circ$  (g, 298.15 K) of the compounds used in these reactions were taken mainly from Reference<sup>[4]</sup>, but that of ethyl *t*-butyl ether,  $-317.8 \text{ kJ mol}^{-1}$ , from the NIST Chemistry Webbook,<sup>[8]</sup> and that,  $-132.7 \text{ kJ mol}^{-1}$ , of (*E*)-1-methoxypropene from Reference<sup>[2]</sup>. The computational enthalpy values, besides those of the present study, were taken from our previous works.<sup>[1,2]</sup>

### Aromatic hydrocarbons

For benzene and its mono- to trialkylsubstituted derivatives 1–9 the difference between experimental and computational enthalpies

of formation,  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  is remarkably constant,  $7 \pm 3 \text{ kJ mol}^{-1}$ . Indane **10** and tetralin **11**, with a saturated ring fused to benzene, are no exceptions. The same applies to styrene **13**, whereas a higher difference,  $13 \pm 2 \text{ kJ mol}^{-1}$ , is suggested for indene **12** which, like styrene, has an olefinic side-chain attached to the benzene ring. For mono-alkyl-substituted benzenes from toluene to *t*-butylbenzene, the difference in question appears to increase with increasing bulkiness of the alkyl group. At the early stage of this work, experimental gas-phase enthalpies of formation were not available for 1,4- and 1,2-dihydronaphthalenes **14** and **15**, respectively. Thus, they were estimated from the corresponding liquid phase data,  $84.2 \pm 1.5$  and  $71.5 \pm 1.7 \text{ kJ mol}^{-1}$ ,<sup>[4]</sup> respectively, using an equation previously established<sup>[9]</sup> for the relation between the standard enthalpy of vaporization and normal boiling temperature.  $\theta$  of an unsaturated hydrocarbon:

$$\Delta_{\text{vap}} H_m^\circ (298.15 \text{ K}; \text{ kJ mol}^{-1}) \\ = (20.51 \pm 0.25) + (0.161 \pm 0.003)\theta(^{\circ}\text{C})$$

The normal boiling points<sup>[10]</sup> of 211.5 (**14**) and 206.5 °C (**15**) lead to  $\Delta_f H_m^\circ$  (g, 298.15 K) values of 138.8 and 125.3  $\text{kJ mol}^{-1}$  for **14** and **15**, respectively, which seem quite reasonable, because they give rise to  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  values of *ca.* 11  $\text{kJ mol}^{-1}$ , in

**Table 1.** Computational enthalpies  $H^\circ$  and enthalpies of formation<sup>a</sup> of the aromatic hydrocarbons studied in this work

No	Compound	$H^\circ$ (a.u.)		$\Delta_f H_m^\circ$ (g)		Exp. – Atom.	Correction to $\Delta_f H_m^\circ$ (atom.)	$\Delta_f H_m^\circ$ (g) (final)	Source of $\Delta_f H_m^\circ$ (exp)
		Atom.	Exp.	Isod.	Exp. – Atom.				
1	Benzene	–231.835110	82.6 (0.7)	77.0	5.6 (0.7)	7.3	84.3	Reference [4]	
2	Toluene	–271.074372	50.4 (0.6)	44.6	5.8 (0.6)	7.3	51.9	Reference [4]	
3	Ethylbenzene	–310.309539	29.8 (0.3)	22.8	7.0 (0.3)	7.3	30.1	Reference [12]	
4	Isopropylbenzene	–349.546810	4.0 (1.1)	–4.5	8.5 (1.1)	7.3	2.8	Reference [4]	
5	<i>t</i> -Butylbenzene	–388.784412	–22.7 (1.4)	–32.6	9.9 (1.4)	7.3	–25.3	Reference [4]	
6	<i>p</i> -Xylene	–310.313360	17.8 (0.3)	12.8	7.4 (0.3)	7.3	20.1	Reference [12]	
7	<i>m</i> -Xylene	–310.313547	17.2 (0.2)	12.3	4.9 (0.2)	7.3	19.6	Reference [12]	
8	<i>o</i> -Xylene	–310.313903	19.0 (0.2)	11.4	7.6 (0.2)	7.3	18.7	Reference [12]	
9	Mesitylene	–349.552803	–15.9 (1.3)	–20.2	4.3 (1.3)	7.3	–12.9	Reference [4]	
10	Indane	–348.359709	60.7 (1.7)	52.0	8.7 (1.7)	7.3	59.3	Reference [4]	
11	Tetralin	–387.600540	26.0 (2.0)	15.3	10.7 (2.0)	7.3	22.6	Reference [4]	
12	Indene	–347.156618	163.4 (2.1)	150.3	13.1 (2.1)	11.1	161.4	Reference [4]	
13	Styrene	–309.099694	147.9 (1.5)	138.9	9.0 (1.5)	11.1	150.0	Reference [4]	
14	1,4-Dihydronaphthalene	–386.392269	138.8 <sup>b</sup>	127.3	11.5	11.1	138.4	Reference [4]	
15	1,2-Dihydronaphthalene	–386.397001	126.3 (0.6)	114.9	11.4 (0.6)	11.1	126.0	Reference [11]	
16	2-Methyl-1,4-dihydronaphthalene	–425.633398	96.4	89.9	96.4	11.1	101.0		
17	5-Methyl-1,4-dihydronaphthalene	–425.631526	102.9	94.8	102.9	11.1	105.9		
18	6-Methyl-1,4-dihydronaphthalene	–425.631431	103.2	95.1	103.2	11.1	106.2		
19	3-Methyl-1,2-dihydronaphthalene	–425.638621	82.7	76.2	82.7	11.1	87.3		
20	4-Methyl-1,2-dihydronaphthalene	–425.636829	87.4	80.9	87.4	11.1	92.0		
21	5-Methyl-1,2-dihydronaphthalene	–425.635565	92.3	84.2	92.3	11.1	95.3		
22	6-Methyl-1,2-dihydronaphthalene	–425.636000	91.2	83.1	91.2	11.1	94.2		
23	7-Methyl-1,2-dihydronaphthalene	–425.636211	90.6	82.5	90.6	11.1	93.6		
24	8-Methyl-1,2-dihydronaphthalene	–425.635505	92.5	84.4	92.5	11.1	95.5		
25	Naphthalene	–385.223698	150.3 (1.5)	135.1	15.2 (1.5)	15.4	150.5	Reference [4]	
26	1-Methylnaphthalene	–424.463060	116.9 (2.7)	102.3	14.6 (2.7)	15.4	117.7	Reference [14]	
27	2-Methylnaphthalene	–424.463475	116.1 (2.6)	101.2	14.9 (2.6)	15.4	116.6	Reference [14]	
28	1,4-Dimethylnaphthalene	–463.702083	70.4	70.4		15.4	85.8		
29	1,5-Dimethylnaphthalene	–463.702186	70.2	70.2		15.4	85.6		
30	1,8-Dimethylnaphthalene	–463.692663	108.7 (1.5)	95.2	13.5 (1.5)	15.4	110.6	Reference [4]	
31	2,6-Dimethylnaphthalene	–463.703153	67.6	67.6		15.4	83.0		
32	2,7-Dimethylnaphthalene	–463.703153	79.5 (0.6)	67.6	11.9 (0.6)	15.4	83.0	Reference [15]	
33	Biphenyl	–462.501229	181.4 (2.0)	163.0	18.4 (2.0)	15.4	178.4	Reference [4]	
34	2-Methylbiphenyl	–501.738875	152.8 (1.5)	134.7	18.1 (1.5)	15.4	150.1	Reference [16]	
35	2,6-Dimethylbiphenyl	–540.978133	102.2	102.2		15.4	117.6		
36	2,2'-Dimethylbiphenyl	–540.978824	115.1	100.4		15.4	115.8		

<b>37</b>	( <i>E</i> )-Stilbene	-539.765753	225.0	236.1 (1.3)	241.7	11.1 (1.3)	15.4	240.4	Reference [4]
<b>38</b>	( <i>Z</i> )-Stilbene	-539.761575	236.0	252.3 (2.0)	252.7	16.3 (2.0)	15.4	251.4	Reference [4]
<b>39</b>	1,1-Diphenylethene	-539.765512	225.6	245.6 (4.4)	242.3	20.0 (4.4)	15.4	241.0	Reference [4]
<b>40</b>	Anthracene	-538.606421	208.5	226.7 (3.5)		18.2 (3.5)	17.3	225.8	Reference [17]
<b>41</b>	Phenanthrene	-538.615206	185.4	201.7 (2.9)		16.3 (2.9)	17.3	202.7	Reference [3]

<sup>a</sup> In  $\text{kJ mol}^{-1}$ .

<sup>b</sup> Based on experimental liquid phase data<sup>[4]</sup> and estimated<sup>[9]</sup> enthalpies of vaporization, refer to text.

line with those for the other related compounds **12** and **13**. However, in a very recent paper by Chirico and Steele,<sup>[11]</sup> the experimental gas-phase enthalpy of formation  $\Delta_f H_m^\circ$  (298.15 K) of 1,2-dihydronaphthalene **15** was reported as  $126.3 \pm 0.6 \text{ kJ mol}^{-1}$ , in excellent agreement with the value,  $125.3 \text{ kJ mol}^{-1}$ , given above.

The thermochemistry of the xylenes **6–8** deserves a few comments. Experimentally,<sup>[12]</sup> the enthalpies of formation (at 300 K) of the gaseous xylenes are reported to be  $19.0 \pm 0.2$  (*ortho*),  $17.2 \pm 0.2$  (*meta*) and  $17.8 \pm 0.3 \text{ kJ mol}^{-1}$  (*para*), that is, the *meta* compound has the lowest, the *ortho* form the highest enthalpy of formation. Computationally, however, the order of (thermochemical) stability is different, *cf.* the enthalpies of formation of  $11.4$  (*ortho*),  $12.3$  (*meta*), and  $12.8 \text{ kJ mol}^{-1}$  (*para*). Thus, the relative enthalpies of the *meta* and *para* isomers are the same, computationally and experimentally, but the low computational enthalpy of the *ortho* isomer is unexpected, and in disagreement with experiment. Anyway, the differences between the enthalpies of formation of the xylenes are small.

Compounds **1–11** share the common structural feature of having 0–3 saturated hydrocarbon fragments attached to a benzene ring. For the members of this group of compounds, the difference between experimental and computational enthalpies of formation shows some variation which probably arises mainly from experimental errors. Thus, it is likely that the errors in the experimental enthalpies of formation of these compounds can be reduced by applying the same (mean) value of the term  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  to the computational enthalpies of formation obtained by the atomization reactions. On average, the experimental enthalpies of formation of these compounds are  $7.3 \text{ kJ mol}^{-1}$  more positive than the computational ones. For the hydrocarbons **12–15** containing an olefinic side-chain, the average difference  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  is somewhat higher,  $11.1 \text{ kJ mol}^{-1}$ . Thus, for the aromatic hydrocarbons containing a single phenyl group, correction terms of the magnitudes shown above have been added to the computational B3(MP2)//B3LYP enthalpies of formation. The final enthalpies of formation,  $\Delta_f H_m^\circ(\text{final})$ , of these compounds are shown in Table 1.

The relative enthalpies of formation of the dihydronaphthalenes **14** and **15** appeared interesting enough for surveying the effect of monomethyl substitution on them (compounds **16–24** in Table 1). By analogy with the parent compounds **14** and **15**,  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  terms of  $11.1 \text{ kJ mol}^{-1}$  have been added to the computational  $\Delta_f H_m^\circ(\text{g, atom.})$  values of these methyl derivatives. The relative enthalpies of these isomeric compounds are illustrated by means of isomerization enthalpies in Scheme 2. Expectedly, the enthalpy change for **14**  $\rightarrow$  **15** is not markedly affected by methyl substitution at positions 6 or 7 of the aromatic ring, *cf.* the reaction enthalpies of  $-12.4$ ,  $-12.0$ , and  $-12.6 \text{ kJ mol}^{-1}$  for reactions **14**  $\rightarrow$  **15** (unsubstituted), **18**  $\rightarrow$  **22** (6-Me-substituted), and **18**  $\rightarrow$  **23** (7-Me-substituted), respectively. (Note: compound **18** may be seen either as a 6-Me-substituted or a 7-Me-substituted derivative of **14**). The 7-Me derivative of 1,2-dihydronaphthalene **23** is slightly ( $0.6 \text{ kJ mol}^{-1}$ ) more stable than the 6-Me derivative **22**, apparently because of the favorable effect of the electron releasing Me group in the *para* position relative to the electron accepting olefinic side chain in the former.

On the other hand, methyl substitution at either C4, C5, or C8 has a more tangible (but still small) effect on the isomerization enthalpy of 1,4-dihydronaphthalene to 1,2-dihydronaphthalene. Thus, reactions **17**  $\rightarrow$  **21** and **17**  $\rightarrow$  **24** are exothermic by  $-10.6$  and  $-10.4 \text{ kJ mol}^{-1}$ , respectively, pointing to decreased

Table 2. Computational enthalpies  $H^\circ$  and enthalpies of formation<sup>a</sup> of the aromatic ethers studied in this work

No	Compound	$H^\circ$ (a.u.)		$\Delta_f H_m^\circ$ (g)			Correction to $\Delta_f H_m^\circ$ (atom.)	$\Delta_f H_m^\circ$ (g) (final)	Source of $\Delta_f H_m^\circ$ (exp)
		Atom.	Exp.	Isod.	Exp. – Atom.	Exp. – Atom.			
42	Anisole	-346.205199	-77.3	-67.9 (0.9)	-69.4	9.4 (0.9)	10.8	-66.5	Reference [4]
43	Phenetole	-385.445440	-112.4	-101.6 (0.6)	-106.0	10.8 (0.6)	10.8	-101.6	Reference [4]
44	Isopropyl phenyl ether	-424.685384	-146.7		-139.9		10.8	-135.9	
45	<i>t</i> -Butyl phenyl ether	-463.923477	-176.1		-168.3		10.8	-165.3	
46	Phenyl vinyl ether, <i>s</i> -trans	-384.233129	10.2	22.7 (1.6)	19.1	12.5 (1.6)	10.8	21.0	Reference [4]
	Phenyl vinyl ether, <i>s</i> -cis	-384.232755	11.2				10.8	22.0	
47	Benzo-2,3-dihydrofuran	-384.259603	-59.3	-46.5 (0.8)	-55.5	12.8 (0.8)	10.8	-48.5	Reference [19]
48	Phthalan (benzo-2,5-dihydrofuran)	-384.252117	-39.6	-30.1 (1.0)	-35.9	9.5 (1.0)	10.8	-28.8	Reference [20]
49	Chroman (benzo-3,4-dihydro-2H-pyran)	-423.501156	-97.8	-82.4 (1.1)	-92.3	15.4 (1.1)	10.8	-87.0	Reference [21]
50	Isochroman (benzo-5,6-dihydro-2H-pyran)	-423.494674	-80.8	-63.1 (1.0)	-75.3	17.7 (1.0)	10.8	-70.0	Reference [21]
51	1,2-Dimethoxybenzene, conf. 1 <sup>b</sup>	-460.570379	-218.8	-202.4 (3.4)	-208.5	16.4 (3.4)	14.0	-204.8	Reference [23]
	1,2-Dimethoxybenzene, conf. 2 <sup>c</sup>	-460.568819	-214.7				14.0	-202.7	
	1,2-Dimethoxybenzene, conf. 3 <sup>d</sup>	-460.567624	-211.5				14.0	-199.5	
52	1,3-Dimethoxybenzene, conf. 1 <sup>e</sup>	-460.575910	-233.3	-221.8 (2.4)	-223.0	11.5 (2.4)	14.0	-221.3	Reference [23]
	1,3-Dimethoxybenzene, conf. 2 <sup>e</sup>	-460.574802	-230.4				14.0	-218.4	
	1,3-Dimethoxybenzene, conf. 3 <sup>e</sup>	-460.575216	-231.5				14.0	-219.5	
53	1,4-Dimethoxybenzene, conf. 1 <sup>e</sup>	-460.572969	-225.6	-211.5 (3.0)	-215.3	14.1 (3.3)	14.0	-213.6	Reference [23]
	1,4-Dimethoxybenzene, conf. 2 <sup>e</sup>	-460.572646	-224.7				14.0	-212.7	
54	Benzo-1,3-dioxole	-420.158542	-168.0	-142.7 (3.0)	-163.5	25.3 (3.0)	14.0	-156.0	Reference [4]
55	Benzo-1,3-diox-4-ene	-459.401073	-209.1		-204.5		14.0	-197.1	
56	Benzo-1,4-dioxene	-459.397905	-200.2	-204.1 (2.8)	-193.1	-3.9 (2.8)	14.0	-188.2	Reference [4]
57	Benzofuran	-383.069933	3.9	13.6 (0.7)	11.5	9.7 (0.7)	10.8	14.7	Reference [19]
58	Benzo-4H-pyran	-422.295570	7.1		16.4		10.8	17.9	
59	5,6-Benzo-2H-pyran	-422.293685	12.1		21.4		10.8	22.9	
60	3,4-Benzo-2H-pyran	-422.294952	8.8		18.1		10.8	19.6	
61	Benzodioxin	-458.186352	-80.2		-68.7		14.0	-68.2	
62	Dibenzofuran	-536.468211	36.4	47.3 (4.6)	46.5	10.9 (4.8)	18.0	54.4	Reference [24]
63	Dibenzo-4H-pyran	-575.697824	29.3	48.4 (4.4)	41.0	19.1 (4.4)	18.0	47.3	Reference [4]
64	Dibenzodioxin	-611.593186	-70.1	-50.1 (2.2)	-56.1	20.0 (2.2)	18.0	-52.1	Reference [25]
65	Diphenyl ether	-537.633554	37.2	52.0 (1.5)	53.1	14.8 (1.5)	18.0	55.2	Reference [4]
66	2-Methoxy-1,4-dihydronaphthalene	-500.766609	-38.2		-26.6		14.0	-24.2	
67	3-Methoxy-1,2-dihydronaphthalene	-500.772868	-54.6		-43.0		14.0	-40.6	
68	4-Methoxy-1,2-dihydronaphthalene	-500.769137	-44.8		-33.2		14.0	-30.8	
69	5-Methoxy-1,2-dihydronaphthalene	-500.766818	-38.7		-27.1		14.0	-24.7	
70	7-Methoxy-1,2-dihydronaphthalene	-500.767085	-39.4		-27.8		14.0	-25.4	
71	6-Methoxy-1,4-dihydronaphthalene	-500.761764	-25.5		-13.8		14.0	-11.5	
72	2-Methoxy-1-methyl-1,4-dihydronaphthalene	-540.004609	-67.4		-55.4		14.0	-53.4	
73	2-Methoxy-1-methyl-3,4-dihydronaphthalene	-540.004776	-67.8		-55.8		14.0	-53.8	
74	$\alpha$ -Phenyl-MVE <sup>f</sup>	-423.473237	-24.5		-13.2		14.0	-10.5	
75	$\beta$ -Phenyl-MVE, <i>E</i> form	-423.470060	-16.2		-4.8		14.0	-2.2	
76	$\beta$ -Phenyl-MVE, <i>Z</i> form	-423.468608	-12.3		-0.9		14.0	1.7	

77	<i>p</i> -Methoxystyrene	-423.469693	-15.2	-3.9	14.0	-1.2
78	$\alpha$ -Methyl- $\beta$ -phenyl-MVE, <i>E</i> form	-462.710795	-52.5	-44.2	14.0	-38.5
79	$\alpha$ -Methyl- $\beta$ -phenyl-MVE, <i>Z</i> form	-462.707256	-43.2	-34.9	14.0	-29.2
80	<i>p</i> -MeO-1-propenylbenzene, <i>Z</i> form	-462.705652	-39.0	-30.7	14.0	-25.0
81	$\alpha$ -Phenyl- $\beta$ -methyl-MVE, <i>E</i> form	-462.706930	-42.4	-34.0	14.0	-28.4
82	$\alpha$ -Phenyl- $\beta$ -methyl-MVE, <i>Z</i> form	-462.706796	-42.0	-33.7	14.0	-28.0
83	$\alpha, \beta$ -Diphenyl-MVE, <i>E</i> form	-654.134836	73.3	95.5	18.0	91.3
84	$\alpha, \beta$ -Diphenyl-MVE, <i>Z</i> form	-654.133972	75.5	97.7	18.0	93.5
85	$\alpha$ -Isopropyl phenyl vinyl ether	-501.949144	-82.6	-70.8	14.0	-68.6
86	$\alpha, \beta, \beta$ -Trimethyl phenyl vinyl ether	-501.951415	-88.6	-76.8	14.0	-74.6

<sup>a</sup> In kJ mol<sup>-1</sup>.

<sup>b</sup> Planar (torsion angle  $\tau(\text{C6-C1-O-C}) = \tau(\text{C3-C2-O-C}) = 0$ ).

<sup>c</sup>  $\tau(\text{C6-C1-O-C}) = 2^\circ$ ,  $\tau(\text{C3-C2-O-C}) = 113^\circ$ .

<sup>d</sup>  $\tau(\text{C6-C1-O-C}) = 112^\circ$ ,  $\tau(\text{C3-C2-O-C}) = 112^\circ$ .

<sup>e</sup> Planar.

<sup>f</sup> MVE = methyl vinyl ether.

**Table 3.** The isodesmic reactions studied in this work

10 + ethane → benzene + cyclopentane
11 + ethane → benzene + cyclohexane
12 + ethane → benzene + cyclopentene
13 + ethane → toluene + propene
14 + ethane → benzene + cyclohexene
15 + ethane → benzene + cyclohexene
16 + ethane → benzene + 1-methylcyclohexene
17 + ethane → toluene + cyclohexene
18 + ethane → toluene + cyclohexene
19 + ethane → benzene + 1-methylcyclohexene
20 + ethane → benzene + 1-methylcyclohexene
21 + ethane → toluene + cyclohexene
22 + ethane → toluene + cyclohexene
23 + ethane → toluene + cyclohexene
24 + ethane → toluene + cyclohexene
33 + ethane → 2 toluene
34 + ethane → toluene + ethylbenzene
35 + ethane → toluene + ethylbenzene
36 + ethane → toluene + ethylbenzene
37 + ethane → styrene + ethylbenzene
38 + ethane → styrene + ethylbenzene
39 + ethane → styrene + ethylbenzene
42 + ethane → benzene + MeOEt
43 + ethane → benzene + EtOEt
44 + ethane → benzene + <i>i</i> -PrOEt
45 + ethane → benzene + <i>t</i> -BuOEt
46 + ethane → benzene + CH <sub>2</sub> =CHOEt
47 + ethane → benzene + tetrahydrofuran
48 + ethane → benzene + tetrahydrofuran
49 + ethane → benzene + tetrahydropyran
50 + ethane → benzene + tetrahydropyran
51 + 2 ethane → benzene + 2 MeOEt
52 + 2 ethane → benzene + 2 MeOEt
53 + 2 ethane → benzene + 2 MeOEt
54 + ethane → benzene + 1,3-dioxolane
55 + ethane → benzene + 1,3-dioxane
56 + ethane → benzene + 1,4-dioxane
57 + 2 ethane → benzene + tetrahydrofuran + ethene
58 + ethane → benzene + 3,4-dihydro-2H-pyran
59 + ethane → benzene + 3,4-dihydro-2H-pyran
60 + ethane → benzene + 3,4-dihydro-2H-pyran
61 + 2 ethane → benzene + 1,4-dioxane + ethene
62 + 2 ethane → 2 benzene + tetrahydrofuran
63 + 2 ethane → 2 benzene + tetrahydropyran
64 + 2 ethane → 2 benzene + 1,4-dioxane
65 + ethane → toluene + anisole
66 + ethane → cyclohexene + anisole
67 + ethane → cyclohexene + anisole
68 + ethane → cyclohexene + anisole
69 + ethane → cyclohexene + anisole
70 + ethane → cyclohexene + anisole
71 + ethane → cyclohexene + anisole
72 + ethane → tetralin + ( <i>E</i> )-1-methoxypropene
73 + ethane → tetralin + ( <i>E</i> )-1-methoxypropene
74 + ethane → styrene + EtOMe
75 + ethane → styrene + EtOMe
76 + ethane → styrene + EtOMe
77 + ethane → styrene + EtOMe

(Continues)

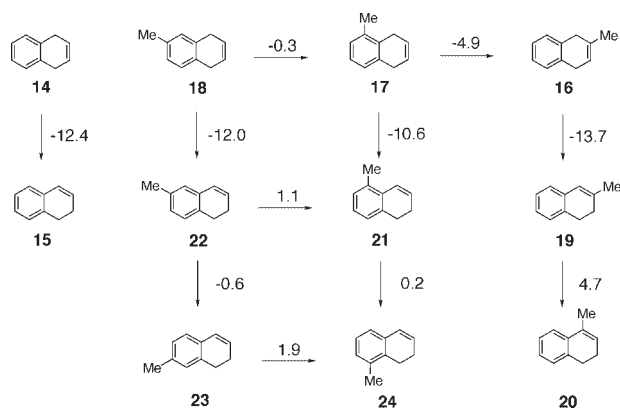


Table 3. Continued

<b>78</b> + ethane → EtPh + ( <i>E</i> )-1-methoxypropene
<b>79</b> + ethane → EtPh + ( <i>E</i> )-1-methoxypropene
<b>80</b> + ethane → EtPh + ( <i>E</i> )-1-methoxypropene
<b>81</b> + ethane → EtPh + ( <i>E</i> )-1-methoxypropene
<b>82</b> + ethane → EtPh + ( <i>E</i> )-1-methoxypropene
<b>83</b> + ethane → styrene + ethene + anisole
<b>84</b> + ethane → styrene + ethene + anisole
<b>85</b> + ethane → <i>i</i> PrPh + EtOCH=CH <sub>2</sub>
<b>86</b> + ethane → <i>i</i> PrPh + EtOCH=CH <sub>2</sub>

exothermic nature of these reactions relative to that between **14** and **15**. This is likely to arise from destabilizing steric interactions between the Me group and the olefinic H atom (on C4) of **21**, and from those between the Me group and the adjacent CH<sub>2</sub> moiety of **24**. Because of the nonplanar nature of the dihydronaphthalene ring of **24** (the tilt between the planes of the aromatic ring and the olefinic system is calculated to be 14°), one of the C—H bonds of the CH<sub>2</sub> group concerned is pseudoequatorial, the other pseudoaxial, and the destabilization in question is likely to originate from the interaction between the Me group and the adjacent pseudoequatorial H atom. That there is some strain of the magnitude indicated above between the aromatic Me group and the neighboring H atom of the dihydronaphthalene ring in both **21** and **24** is also supported by the positive isomerization enthalpies of 1.1 and 1.3 kJ mol<sup>-1</sup> for **22** → **21** and **22** → **24**, respectively.

The difference, -5.2 kJ mol<sup>-1</sup>, between the enthalpies of formation of 2-methyl-1,4-dihydronaphthalene **16** and 6-methyl-1,4-dihydronaphthalene **18** shows that Me substitution at the olefinic carbon of **14** stabilizes this molecule more strongly than Me substitution at the aromatic moiety. This finding agrees with the effects of Me substitution on the enthalpies of formation of cyclohexene and benzene: both the computational (-37.0 kJ mol<sup>-1</sup>) and experimental (-38.3 ± 1.5 kJ mol<sup>-1</sup>) differences between the enthalpies of formation of 1-methylcyclohexene and cyclohexene<sup>[2,4]</sup> are ca. 5 kJ mol<sup>-1</sup> more negative than those between toluene and benzene (Table 1).

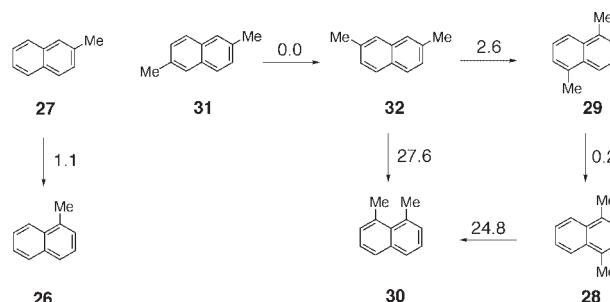


Scheme 2. Computational isomerization enthalpies (in kJ mol<sup>-1</sup>) of 1,4-dihydronaphthalene and 1,2-dihydronaphthalene, and their methyl derivatives

Reaction **16** → **19** is slightly (1.3 kJ mol<sup>-1</sup>) more exothermic than the reference reaction **14** → **15**. This may be ascribed to the favorable electronic effect of the 3-Me group of **19**, pushing electron density from the C=C bond toward the aromatic moiety, and strengthening  $\pi$ - $\pi$  interaction in this compound. On the other hand, the reaction 3-methyl-1,2-dihydronaphthalene (**19**) → 4-methyl-1,2-dihydronaphthalene (**20**) is endothermic by 4.7 kJ mol<sup>-1</sup>. Part of this endothermic reaction enthalpy is likely to arise from a destabilizing steric effect between the Me group and the aromatic hydrogen atom on C5 of **20**, but the remainder probably originates from the electropositive effect of the Me group of **20**, pushing  $\pi$ -electron density toward the other olefinic carbon, instead of toward the aromatic ring like the Me group of **19**.

The next entries **25**–**39** of Table 1 deal with derivatives of aromatic hydrocarbons containing two benzene moieties, fused or unfused, that is, naphthalenes, biphenyls, stilbenes, and 1,1-diphenylethene. On average, the available experimental enthalpies of formation for this group of compounds are 15.4 kJ mol<sup>-1</sup> more positive than the computational ones. This is almost twice as much as the corresponding difference between alkylsubstituted benzenes, and in line with the related results of Blanquart and Pitsch<sup>[3]</sup> for the base compound naphthalene, for which the authors give a group correction term of 14 kJ mol<sup>-1</sup>. Finally, anthracene and phenantrene on average require a correction term of 17.3 kJ mol<sup>-1</sup> to their G3(MP2)//B3LYP enthalpies of formation.

The thermochemistry of isomeric mono- and dimethyl-substituted naphthalenes **26**–**32** is illustrated in Scheme 3. 1-Methylnaphthalene **26** is calculated to have an enthalpy 1.1 kJ mol<sup>-1</sup> higher than that of the 2-Me isomer **27**, in line with the similar enthalpy difference between the structurally related 1,2-dihydronaphthalene derivatives **21** and **22** (Scheme 2). 2,6- and 2,7-dimethylnaphthalenes **31** and **32**, respectively, are calculated to have similar enthalpies, 2.6 kJ mol<sup>-1</sup> lower than that of the 1,5-derivative **29**: this value is about twice of that between **26** and **27**, which sounds reasonable in view of the two Me groups in **29**. The comparable enthalpies of the 1,4- and 1,5-dimethylnaphthalenes **28** and **29**, respectively, are also expected. On the other hand, 1,8-dimethylnaphthalene **30** is markedly strained, ca. 28 kJ mol<sup>-1</sup> above the 'strainfree' 2,7-dimethyl derivative **32**. Steric repulsion between the Me groups leads to a significant distortion of the bond angles of **30**: the angle C2—C1—C(Me) is reduced to 115.9° from 120.1° in **29** and 120.5° in **28**. The relative enthalpies of formation of the isomeric dimethylnaphthalenes have also been recently estimated by B3LYP/6-31G(d,p) calculations by Kassaei *et al.*<sup>[13]</sup> Qualitatively, the results of these calculations agree with those of the present study, but in a quantitative sense marked differences are also found. Thus, for example, the enthalpies of the 2,6- and 2,7-dimethyl isomers were calculated<sup>[13]</sup> to be 34.0–34.2 kJ mol<sup>-1</sup>



Scheme 3. Computational isomerization enthalpies (in kJ mol<sup>-1</sup>) of mono- and dimethyl-derivatives of naphthalene

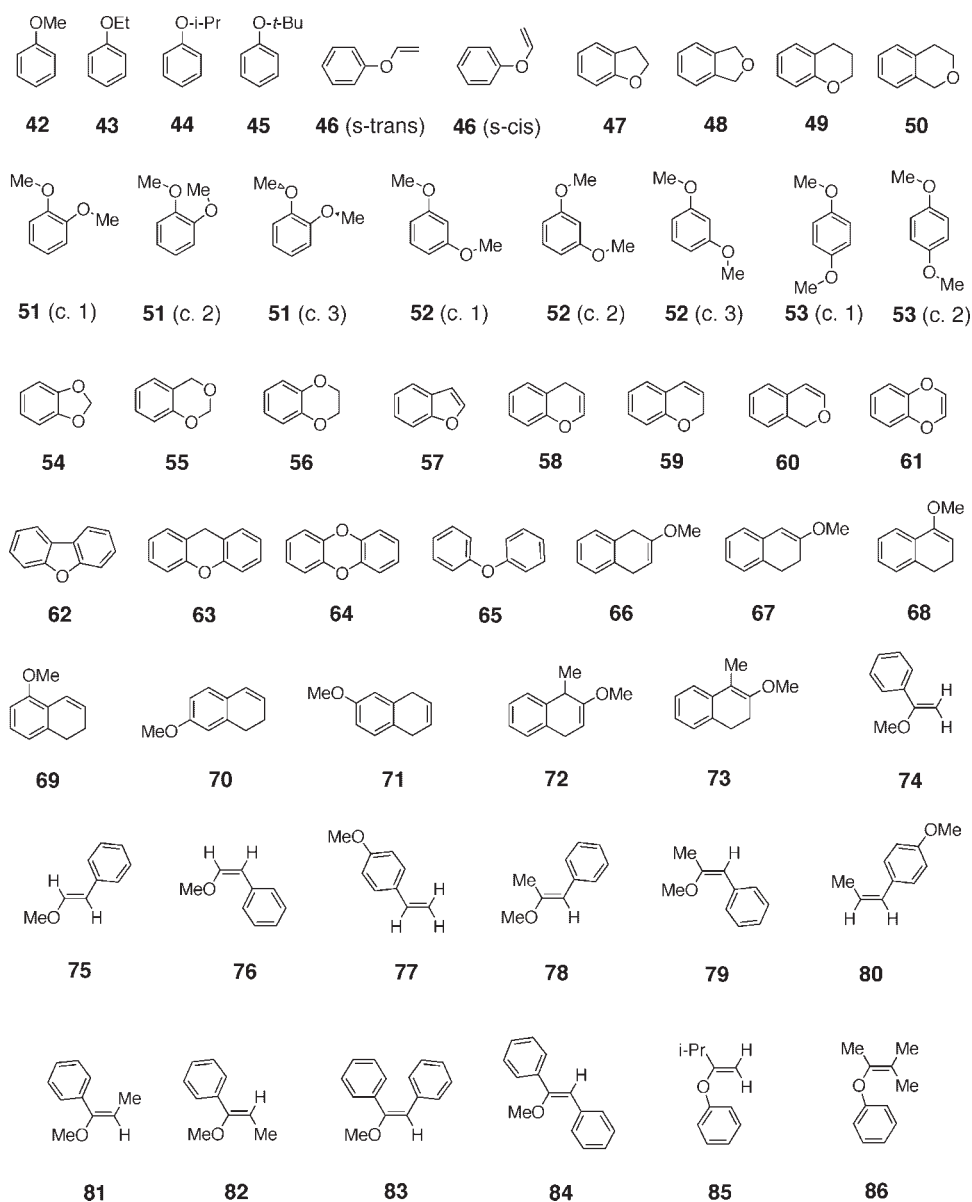
lower than that of the 1,8-isomer; according to the present results the difference in question is only 27.6 kJ mol<sup>-1</sup>.

Summarizing, comparison of the experimental data of Table 1 with those obtained by application of the structure-dependent correction terms to the computational enthalpies of formation shows that high-quality enthalpies of formation,  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ , are accessible for aromatic hydrocarbons by means of the G3(MP2)//B3LYP computations, using the atomization method and structure-characteristic correction terms. On the other hand, the agreement is less good between experimental and isodesmic enthalpies of formation.

### Aromatic ethers

The aromatic ethers studied in this work are shown in Scheme 4, and the respective thermochemical data in Table 2. The ethers **42–65** of Scheme 4 may be divided structurally into two groups of compounds: those with a single benzene moiety (**42–61**), and

those with two benzene moieties (**62–65**) in the molecular structure. The differences between experimental and computational enthalpies of formation for both groups of compounds show marked and unexpected variations, obviously arising mainly from errors in the reported values of the experimental enthalpy of formation. Thus, for both anisole **42** and phenetole **43**, the difference  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$  is ca. 10 kJ mol<sup>-1</sup>, a quite reasonable value in view of that (7.3 kJ mol<sup>-1</sup>) for the alkylbenzenes. On the basis of these values, the respective differences of 15–18 kJ mol<sup>-1</sup> for chroman **49** and isochroman **50** are unexpectedly large: for comparison, the related structural changes from alkylbenzenes to indane **10** and tetralin **11** do not lead to any noteworthy changes in the difference  $\Delta(\Delta_f H_m^\circ)_{\text{exp-comp}}$ . The difference concerned is particularly striking, -3.9 kJ mol<sup>-1</sup>, for benzo-1,4-dioxene **56**, and exceptionally high (25.3 kJ mol<sup>-1</sup>) also for benzo-1,3-dioxole **54**. Thus, the latter two values, together with those for chroman **49** and isochroman **50**, were neglected when the value of the correction term to be added to



Scheme 4. The aromatic ethers studied in this work

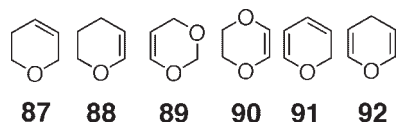


the computational enthalpies of formation of the aromatic ethers **42–61** was evaluated. Moreover, a further subdivision, according to the number of O atoms in the molecule in question seems necessary: the dimethoxybenzenes **51–53** appear to require a higher value of the correction term than monoethers. For the monoethers, the average of the difference  $\Delta(\Delta_f H_m^\circ)_{\text{exp} - \text{comp}}$  was evaluated as  $10.8 \text{ kJ mol}^{-1}$  from the data for compounds **42, 43, 46–48**, and **57**; on the other hand, as  $14.0 \text{ kJ mol}^{-1}$  for the dimethoxybenzenes **51–53**. A higher value of the correction term is expected for ethers containing two aromatic rings, fused or nonfused; thus, the difference  $\Delta(\Delta_f H_m^\circ)_{\text{exp} - \text{comp}}$  of  $10.9 \text{ kJ mol}^{-1}$  for dibenzofuran **62** appears too small, but the mean,  $18.0 \text{ kJ mol}^{-1}$ , of the respective values for **63–65** seems reasonable for the whole group of compounds **62–65**.

Computationally, phthalan (benzo-2,5-dihydrofuran) **48** has an enthalpy of formation  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$   $19.7 \text{ kJ mol}^{-1}$  higher than that of benzo-2,3-dihydrofuran **47**; experimentally, the corresponding enthalpy difference is  $16.4 \pm 1.9 \text{ kJ mol}^{-1}$ . For comparison, the enthalpy difference between the base compounds 2,5-dihydrofuran and 2,3-dihydrofuran is  $12.4 \text{ kJ mol}^{-1}$  computationally<sup>[2]</sup> and  $12.6 \pm 0.5 \text{ kJ mol}^{-1}$  experimentally<sup>[18]</sup> in DMSO solution. Turning to the 6-membered heterocycles chroman **49** and isochroman **50**, the former, with the O atom conjugated with the benzene ring, is calculated to have an enthalpy of formation  $17.0 \text{ kJ mol}^{-1}$  lower than that of the non-conjugated isomer isochroman. Experimentally, the enthalpy difference between these compounds is  $19.3 \pm 2.1 \text{ kJ mol}^{-1}$ . The computational enthalpy difference between **50** and **49** is almost the same as that,  $17.5 \text{ kJ mol}^{-1}$ , between the computational<sup>[21]</sup> enthalpies of formation<sup>[2]</sup> of the structurally related pair of olefinic compounds, 3,6-dihydro-2H-pyran **87** and 3,4-dihydro-2H-pyran **88** (Scheme 5). Moreover, the experimental gas-phase enthalpy difference,  $19.3 \text{ kJ mol}^{-1}$  (Table 2), between **50** and **49** is similar to that,  $18.9 \pm 1.1 \text{ kJ mol}^{-1}$ , between **87** and **88** in DMSO solution.<sup>[18]</sup>

The enthalpies of formation, calculated for the stable conformers of the dimethoxybenzenes **51–53**, show the most stable form of each dimethoxybenzene to have a planar heavy atom skeleton, in line with other recent evidence.<sup>[22]</sup> Matos *et al.*,<sup>[23]</sup> however, have computationally suggested a nonplanar structure with both MeO groups almost orthogonal (conformer 3 of **51** in Scheme 4) for the most stable form of 1,2-dimethoxybenzene **51**. In addition, the present computational results, like those of Vande Velde *et al.*<sup>[22]</sup> suggest conformer 2 of gaseous 1,4-dimethoxybenzene **53** to have a negligibly higher enthalpy level than conformer 1, contrary to the computational results of Matos *et al.*<sup>[23]</sup>

Our previous computational data<sup>[1]</sup> suggest enthalpies of formation of  $-340.6$  and  $-317.1 \text{ kJ mol}^{-1}$  for 1,3- and 1,4-dioxane, respectively. Thus, on an enthalpy basis, 1,3-dioxane is *ca.*  $23.5 \text{ kJ mol}^{-1}$  more stable than 1,4-dioxane. For the corresponding benzo derivatives **55** and **56**, the respective enthalpy difference is only  $8.9 \text{ kJ mol}^{-1}$ . The origin of the marked leveling of the relative stabilities of the isomeric forms of the dioxanes due to the benzo fusion is obvious: in the 1,3-isomer **55**, there is a single O atom conjugated with the aromatic  $\pi$  system, contrary to



**Scheme 5.** Olefinic ethers structurally related to those of the present aromatic ethers

the 1,4-form **56** with two conjugated O atoms therein. For comparison, for the related pair of olefinic compounds, 1,3-diox-4-ene **89** and 1,4-dioxene **90** (Scheme 5), the G3(MP2)//B3LYP enthalpies of formation, based on atomization reactions, are  $-231.2$  and  $-216.5 \text{ kJ mol}^{-1}$ ,<sup>[2]</sup> respectively, revealing an enthalpy difference of  $14.7 \text{ kJ mol}^{-1}$  in favor of the 1,3-isomer **89**. Accordingly, the relative stability of the 1,4-isomer is enhanced if the two O atoms are conjugated with the aromatic moiety instead of with a C=C bond. This is reasonable because in the benzo derivative **56** the electronic charge, denoted by the O atoms by  $p$ - $\pi$  conjugation, is distributed widely in the aromatic ring, contrary to distribution in the limited space of the single olefinic linkage of 1,4-dioxene **90**.

The computational enthalpy of 5,6-benzo-2H-pyran **59** is  $5.0 \text{ kJ mol}^{-1}$  higher than that of benzo-4H-pyran **58**. For comparison, in the structurally related pair of olefinic compounds, 2H-pyran **91** and 4H-pyran **92** (Scheme 5), the enthalpy of the 2H-isomer has been calculated to be  $8.7 \text{ kJ mol}^{-1}$  higher than that of the 4H-form.<sup>[2]</sup> On the other hand, 3,4-benzo-2H-pyran **60** is calculated to have an enthalpy  $3.3 \text{ kJ mol}^{-1}$  lower than that 5,6-benzo-2H-pyran **59**, possibly because of the longer conjugated system, extending from the O atom to the aromatic moiety, in the former.

Comparison of the experimental enthalpies of formation of the aromatic ethers discussed above with the computational ones shows significant deviations in many cases. In particular, the isodesmic reactions give enthalpies of formation which usually are more negative than those obtained experimentally. The values of  $\Delta_f H_m^\circ(\text{final})$  of necessity show more randomly distributed deviations from the experimental data. The larger the deviation, the higher is the probability that the current experimental value of the enthalpy of formation is in need of redetermination.

### Comparison of the computational reaction enthalpies with experimental data

In our previous experimental studies dealing with the relative stabilities of olefinic ethers, aromatic moieties were occasionally embedded in the compounds investigated. In the following, these experimental thermodynamic data are compared with the present computational enthalpies of isomerization. For the MeO derivatives of 1,4- and 1,2-dihydronaphthalenes **66** and **67** (Scheme 4), the position of chemical equilibrium is highly unfavorable for the former. Experimentally, it could only be inferred that for **66**  $\rightarrow$  **67** the Gibbs energy change  $\Delta_r G_m^\circ \leq -14 \text{ kJ mol}^{-1}$  in cyclohexane solution at 373 K.<sup>[26]</sup> This is in line with the present computational data for the reaction in the gas phase:  $\Delta_r H_m^\circ = -16.4 \text{ kJ mol}^{-1}$  at 298.15 K. The high favor of the 1,2-isomer at equilibrium is reduced by Me substitution on C4 (leading to compound **73**), which prevents a planar *s-cis* conformation, relative to the olefinic linkage, for the MeO moiety of **73**. This conformation is necessary for a maximum strength of  $p$ - $\pi$  conjugation in the  $-\text{O}-\text{C}=\text{C}$  moiety. (The present computational data show that the torsion angle C—O—C=C, while 0 in **67**, is  $132^\circ$  in **73**). As a consequence of this structural change, H  $\rightarrow$  Me on C4, a marked change in the position of chemical equilibrium takes place, and the enthalpy of isomerization could thus be readily determined<sup>[26]</sup> by chemical equilibration with the result  $\Delta_r H_m^\circ = -2.3 \pm 0.8 \text{ kJ mol}^{-1}$  for **72**  $\rightarrow$  **73** in cyclohexane solution at 298.15 K, not far from the present computational gas-phase value of  $-0.4 \text{ kJ mol}^{-1}$ .

Computationally, the *E*  $\rightarrow$  *Z* isomerization **75**  $\rightarrow$  **76** of  $\beta$ -phenyl methyl vinyl ether is predicted to be endothermic by  $3.9 \text{ kJ mol}^{-1}$ , while the experimental data<sup>[27]</sup> point to a slightly exothermic

reaction with  $\Delta_r H_m^\circ = -1.50 \pm 0.14 \text{ kJ mol}^{-1}$  for the neat compounds at 298.15 K. The related reaction **78**  $\rightarrow$  **79**, with a Me group introduced at the  $\alpha$  position, is markedly endothermic,  $9.3 \text{ kJ mol}^{-1}$  computationally and  $7.3 \pm 0.5 \text{ kJ mol}^{-1}$  experimentally in the gas phase.<sup>[28]</sup> Changing the relative positions of the Me and Ph groups in the latter compounds leads to an almost thermoneutral  $E \rightarrow Z$  reaction: for **80**  $\rightarrow$  **81**,  $\Delta_r H_m^\circ = 0.4 \text{ kJ mol}^{-1}$  computationally in the gas phase and  $1.8 \pm 0.8 \text{ kJ mol}^{-1}$  experimentally<sup>[29]</sup> in cyclohexane solution at 298.15 K. The  $E \rightarrow Z$  isomerization is slightly more endothermic for  $\alpha, \beta$ -diphenyl-substituted methyl vinyl ether: for **83**  $\rightarrow$  **84** the value of  $\Delta_r H_m^\circ$  is  $2.2 \text{ kJ mol}^{-1}$  computationally in the gas phase and  $3.6 \pm 0.4 \text{ kJ mol}^{-1}$  experimentally<sup>[30]</sup> in cyclohexane solution.

Finally, reaction **85**  $\rightarrow$  **86**, dealing with double bond positional isomerism in alkyl derivatives of phenyl vinyl ether, is clearly exothermic with  $\Delta_r H_m^\circ(\text{g}) = -6.0 \text{ kJ mol}^{-1}$  computationally, in line with the experimental<sup>[31]</sup> value of  $-7.4 \pm 1.1 \text{ kJ mol}^{-1}$  in cyclohexane solution.

### Thermochemistry of the positional isomerism of a Ph group in olefinic ethers

Table 2 shows that the fictitious reaction **74**  $\rightarrow$  **75**, that is, transfer of the Ph group of an  $\alpha$ -phenyl-substituted methyl vinyl ether to the  $\beta$ -( $E$ )-position, is endothermic by  $8.3 \text{ kJ mol}^{-1}$ . On the other hand, changing the relative positions of the Ph and Me groups in **81** (i.e., the process **81**  $\rightarrow$  **78**) is exothermic by  $-10.1 \text{ kJ mol}^{-1}$ . (It is worth noting that this enthalpy change is also close to that,  $-9.8 \text{ kJ mol}^{-1}$ , for the structurally related reaction **68**  $\rightarrow$  **67**.) The markedly different thermochemistries of reactions **74**  $\rightarrow$  **75** and **81**  $\rightarrow$  **78**, in both of which an  $\alpha$ - $\beta$  transfer of a Ph group takes place, are understandable on the basis of the simultaneous inverse ( $\beta \rightarrow \alpha$ ) transfer of a Me group in the latter reaction. Thus, from our previous<sup>[2]</sup> enthalpies of formation for ( $E$ )-MeOCH=CHMe ( $-132.7 \text{ kJ mol}^{-1}$ ) and MeC(OMe)=CH<sub>2</sub> ( $-151.5 \text{ kJ mol}^{-1}$ ) one can see that a  $\beta \rightarrow \alpha$  transfer of the Me group in a Me-substituted methyl vinyl ether is exothermic by  $-18.8 \text{ kJ mol}^{-1}$ . Accordingly, reaction **81**  $\rightarrow$  **78** may be seen as a combination of reactions **74**  $\rightarrow$  **75** and ( $E$ )-MeOCH=CHMe  $\rightarrow$  MeOC(Me)=CH<sub>2</sub>, with an expected enthalpy change of  $(8.3 - 18.8) \text{ kJ mol}^{-1} = -10.5 \text{ kJ mol}^{-1}$ , which agrees with the computational value of  $-10.1 \text{ kJ mol}^{-1}$  for **81**  $\rightarrow$  **78**.

### Thermochemistry of the positional isomerism of a MeO group in the present compounds

3-Methoxy-1,2-dihydronaphthalene **67** is calculated to be  $9.8 \text{ kJ mol}^{-1}$  more stable than the isomeric 4-MeO derivative **68**. Both of these compounds have a MeO group attached to an olefinic carbon. The lower enthalpy level of **67** is likely to be due to the long conjugated system therein, extending from the O atom to the aromatic moiety. On the other hand, if the MeO group of **67** is transferred from the olefinic linkage to the aromatic ring, a marked increase in the enthalpy of formation takes place: the 5-MeO derivative **69** is  $15.9 \text{ kJ mol}^{-1}$  and the 7-MeO derivative **70**  $15.2 \text{ kJ mol}^{-1}$  on a higher enthalpy level than **67**. In addition, the structural change in **78**  $\rightarrow$  **80**, comparable to that in **67**  $\rightarrow$  **70**, is also endothermic by  $13.5 \text{ kJ mol}^{-1}$ , like that in **66**  $\rightarrow$  **71**, with a reaction enthalpy of  $12.7 \text{ kJ mol}^{-1}$ . In each of the compounds **66**–**70**, **78**, and **80**, the MeO group is coplanar with the unsaturated moiety it is bonded to, and thus capable of exerting its full stabilizing power on the

compound in question. Accordingly, one might be tempted to conclude that a MeO group has a markedly weaker stabilizing effect on an aromatic moiety than on an olefinic linkage. This conclusion, however, is in disagreement with the modest enthalpy change of only  $1.0 \text{ kJ mol}^{-1}$  for **75**  $\rightarrow$  **77**, which shows that the MeO groups of **75** and **77** have almost similar effects on molecular stability. The solution to this apparent dilemma becomes from the markedly different stabilizing effects of a Me group (or, more generally, an alkyl group) on the C=C bonds of vinyl ethers and those of ordinary olefins. Thus, a Me substituent introduced to the C=C bond of ethene leads to a decrease of  $-32.1 \text{ kJ mol}^{-1}$  in the computational enthalpy of formation ( $= 51.0 \text{ kJ mol}^{-1}$  for ethene,  $18.9 \text{ kJ mol}^{-1}$  for propene),<sup>[2]</sup> whereas the corresponding structural change in methyl vinyl ether  $\rightarrow$  methyl isopropenyl ether MeC(OMe)=CH<sub>2</sub> causes a decrease of  $-43.6 \text{ kJ mol}^{-1}$  in the enthalpy of formation ( $= -107.9$  and  $-151.5 \text{ kJ mol}^{-1}$  for methyl vinyl ether and methyl isopropenyl ether, respectively).<sup>[2]</sup> Accordingly, a Me group, if attached to the  $\alpha$ -carbon of methyl vinyl ether, has a double-bond stabilizing effect ca.  $11.5 \text{ kJ mol}^{-1}$  stronger than that of the Me group of propene. (Note: the situation is essentially different if the Me group is situated on the  $\beta$ -carbon of methyl vinyl ether: in that case, the double-bond stabilizing effect of the Me group is reduced to only a few  $\text{kJ mol}^{-1}$ , as shown in Reference<sup>[32]</sup>.) Returning to the present compounds, in **75** the  $\alpha$ -position of a Ph derivative of methyl vinyl ether is occupied by a hydrogen atom, in the other formal derivatives of methyl vinyl ether (**66**, **67**, and **78**) by a Me group or a comparable alkyl chain. Thus, almost all (ca.  $11.5 \text{ kJ mol}^{-1}$ ) of the marked enthalpy changes of  $12.7$ ,  $15.2$ , and  $13.5 \text{ kJ mol}^{-1}$  for **66**  $\rightarrow$  **71**, **67**  $\rightarrow$  **70**, and **78**  $\rightarrow$  **80**, respectively, are likely to arise from the strong stabilizing effect of the substituent attached to the  $\alpha$ -carbon of the reactant, an effect absent in **75**.

## SUMMARY

In this work, a method for convenient computational estimation of the gas-phase enthalpies of formation of aromatic hydrocarbons and ethers has been developed. The method is based on high-level G3(MP2)//B3LYP calculations, atomization reactions, and structure-dependent correction terms. The calculated enthalpies of formation raise questions of the reliability of some experimental enthalpies of formation published for aromatic compounds in the literature. As an application of the computational enthalpies of formation, reaction enthalpies for several types of isomerization reactions were calculated. In cases in which comparison with experimental reaction enthalpies is possible, the agreement between the computational and experimental data is excellent.

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