

# On the enthalpy of formation of cyclohexa-2,4- and -2,5-dienone

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The generally accepted  $\Delta_f H_{298}^\circ$  values for cyclohexa-2,4- and -2,5-dienone **1** and **2** respectively) were critically revised, based on three different approaches: (1) evaluation of available kinetic data; (2) group additivity; (3) density functional theory calculations at the B3LYP/6-31G(d,p) level with isodesmic reactions. The kinetics of the gas-phase Claisen rearrangement of allyl phenyl ether (**3**) sets  $\Delta_f H_{298}^\circ$  for **1** at  $\geq -9$  kcal mol<sup>-1</sup>, at least 8 kcal mol<sup>-1</sup> above the current literature value of  $-17 \pm 3$  kcal mol<sup>-1</sup>. Recent results on the gas-phase recombination of phenoxy radicals also indicate a value for **1** 15 kcal mol<sup>-1</sup> above  $\Delta_f H_{298}^\circ$  of phenol (**40**,  $-23$  kcal mol<sup>-1</sup>). Our DFT calculations led to  $-7.3$  and  $-8.0$  kcal mol<sup>-1</sup> for **1** and **2**, respectively. Simple group additivity approaches yield values higher by *ca.* 6 kcal mol<sup>-1</sup>—likely to be due to underestimating conjugation and specific structural effects. The hitherto accepted difference of 4 kcal mol<sup>-1</sup> between the two isomers also appears to be too large. The literature values for the analogous hydrocarbons, 5-methylenecyclohexa-1,3-diene (**32**) and 3-methylenecyclohexa-1,4-diene (**33**) are critically reviewed as well on the basis of similar approaches; we prefer  $\Delta_f H_{298}^\circ$  (**32**) =  $+43$  kcal mol<sup>-1</sup> rather than the literature value of  $+35$  kcal mol<sup>-1</sup>, and a value for **33** close to 43 kcal mol<sup>-1</sup>.

## Introduction

In the past, enthalpies of formation ( $\Delta_f H_{298}^\circ$ ) for gaseous organic compounds have been obtained by experiment, especially bomb calorimetry.<sup>1-3</sup> Together with data on free radicals, values for bond dissociation enthalpies (BDE) of *e.g.* C–H and C–C became available,<sup>4</sup> and such thermochemical values have become a key instrument to understand, interpret and even predict rates and equilibria of a variety of reactions and processes. When experimental errors have been minimised, reported margins for  $\Delta_f H_{298}^\circ$  of neutral species are often within 0.5 kcal mol<sup>-1</sup>.<sup>2</sup> Radical species have larger uncertainties, but for simple structures these may well be within  $\pm 1$  kcal mol<sup>-1</sup>.<sup>2,5</sup> For decades, a well-accepted approach for inter- and extrapolation of thermochemical quantities has been the group additivity method.<sup>6</sup> More recently, theoretical methods have come into play. With density functional theory (DFT), relatively large structures can be computed even with limited resources, to result in consistent, reliable  $\Delta_f H_{298}^\circ$  and BDE values.

However, in a number of cases, published data deviate beyond reasonable limits—if not contrast. One example is the following. From earlier work in our lab<sup>7</sup> and elsewhere<sup>8</sup> on equilibration of (di)substituted benzenes, it is known that *meta*- and *para*-isomers have almost the same heat of formation, well within tenths of a kcal mol<sup>-1</sup>. *ortho*-Isomers are subject to steric hindrance or can show other effects. So, the equilibrium composition (%) for the fluorobiphenyls (at 140 °C),<sup>8a</sup> is *ortho*–*meta*–*para* = 13 : 58 : 29, showing equal (free) enthalpy values for *meta*- and *para*-isomers, accounting for the statistical factor of two. In this light, the experimental values for the three hydroxybiphenyls reported by Bertholon *et al.*<sup>9</sup> cannot be correct: the *para*-isomer is stated to be 3.5 kcal mol<sup>-1</sup> less stable than *meta* (and 4.5 kcal mol<sup>-1</sup> less stable than *ortho*). Furthermore, the absolute values are well above expectation.<sup>10</sup> A possible reason could be that the calorimetric measurements on the hydroxybiphenyls are in error (too low by some 5 kcal mol<sup>-1</sup>); furthermore the value for the heat of sublimation for the *para*-isomer used by Bertholon *et al.*<sup>9</sup> is at variance with another

reported result.<sup>2</sup> The deviation is even more severe for the benzylphenols.<sup>11</sup>

The present paper focuses on the thermochemistry of phenol itself, and of its two tautomeric keto-forms, cyclohexa-2,4-dienone (**1**) and cyclohexa-2,5-dienone (**2**). Such tautomers play an important role in both the liquid- and gas-phase chemistry of phenols. Note that combination of a phenoxy radical with some other radical—when occurring at an *ortho*- or *para*-position—does give a keto tautomer (which may or may not easily undergo enolisation depending on the applied conditions).<sup>12</sup>

Given the thermodynamic and kinetic instability of cyclohexadienones, their heats of formation cannot be determined by usual techniques. The commonly quoted  $\Delta_f H_{298}^\circ$  values for the title compounds **1** and **2**, resulting from measurements of the gas-phase acidities by bracketing experiments with other acidic compounds applying the flowing afterglow technique, are  $-17 \pm 3$  and  $-13 \pm 3$  kcal mol<sup>-1</sup>, respectively.<sup>13</sup>

These values will be confronted with the results of the kinetics of the gas-phase Claisen rearrangement of allyl phenyl ether (**3**)<sup>14</sup> and of the gas-phase recombination of phenoxy radicals.<sup>12</sup> Conclusions derived therefrom will be compared with data obtained by application of the principle of group additivity, and by DFT calculations.

Furthermore, the standard values for the analogous carbon species, the two methylenecyclohexadienes **32** and **33**, ‘tautomers’ of toluene, are also reconsidered.

## Experimental

For experimental details on the gas-phase kinetic and product studies, see refs. 12 and 14. The classic set of group contributions was used in Benson’s group additivity method.<sup>6</sup>

DFT calculations were performed on a 350-MHz Pentium II personal computer, using the Gaussian 94 suite of programs.<sup>15</sup> Geometries and vibrational frequencies were computed at the B3LYP theoretical level,<sup>16</sup> using the 6-31G(d,p) basis set. Input geometries for DFT were obtained by optimis-

**Table 1** Experimental<sup>2,3</sup> and computed energies (SCF energy in hartree, others in kcal mol<sup>-1</sup>)

Compound	SCF Energy	ZPVE	$H_{298,DFT}$	$\Delta_f H_{298,exp}^\circ$
Methane ( <b>11</b> ) <sup>b</sup>	-40.524015282	28.24964	-25399.1	-17.9 ± 0.1
Ethane ( <b>12</b> ) <sup>b</sup>	-79.838738047	47.01336	-50050.7	-20.0 ± 0.12
Ethene ( <b>13</b> ) <sup>b</sup>	-78.593806692	32.07842	-49284.4	12.5
Propane ( <b>14</b> ) <sup>b</sup>	-119.155363472	65.07231	-74703.9	-25.02 ± 0.12
Propene ( <b>15</b> ) <sup>b</sup>	-117.916546861	50.08505	-73941.5	4.9
<i>n</i> -Butane ( <b>16</b> ) <sup>b</sup>	-158.471955492	83.00551	-99357.1	-30.4 ± 0.2
But-1-ene ( <b>17</b> ) <sup>b</sup>	-157.232788462	68.17498	-98594.3	-0.2 ± 0.2
( <i>E</i> )-But-2-ene ( <b>18</b> ) <sup>b</sup>	-157.238525281	67.84611	-98598.1	-2.6 ± 0.2
( <i>Z</i> )-But-2-ene ( <b>19</b> ) <sup>b</sup>	-157.236397401	67.91847	-98596.7	-1.8 ± 0.3
Isobutene ( <b>20</b> ) <sup>b</sup>	-157.238835279	67.82161	-98598.4	-4.29 ± 0.26
Buta-1,3-diene ( <b>21</b> ) <sup>b</sup>	-156.001660460	53.53309	-97836.5	26.38 ± 0.20
<i>n</i> -Pentane ( <b>22</b> ) <sup>b</sup>	-197.788484047	100.96318	-124010.1	-35.08 ± 0.14
Penta-1,4-diene ( <b>23</b> ) <sup>b</sup>	-195.310101942	71.27558	-122484.7	25.4 ± 0.3
( <i>E</i> )-Penta-1,3-diene ( <b>24</b> ) <sup>b</sup>	-195.324418006	71.20988	-122493.7	18.1 ± 0.2
( <i>Z</i> )-Penta-1,3-diene ( <b>25</b> ) <sup>b</sup>	-195.321984615	71.34710	-122492.0	19.8 ± 0.2
Cyclopenta-1,3-diene ( <b>26</b> ) <sup>b</sup>	-194.110691061	58.15861	-121746.1	33.2
Cyclohexane ( <b>27</b> ) <sup>b</sup>	-235.897131007	106.91808	-147918.7	-29.5 ± 0.2
Cyclohexene ( <b>28</b> ) <sup>b</sup>	-234.662678289	91.91293	-147158.9	-1.03 ± 0.23
Cyclohexa-1,3-diene ( <b>29</b> ) <sup>b</sup>	-233.430983418	76.85916	-146401.0	25.0
Cyclohexa-1,4-diene ( <b>30</b> ) <sup>b</sup>	-233.430591022	76.68920	-146400.8	25.0
Toluene ( <b>31</b> ) <sup>b</sup>	-271.578772649	80.31011	-170335.0	12.0 ± 0.2
5-Methylenecyclohexa-1,3-diene ( <b>32</b> ) <sup>b</sup>	-271.522873793	79.71549	-170300.6	47.0
				35.0 ± 3.0
3-Methylenecyclohexa-1,4-diene ( <b>33</b> ) <sup>b</sup>	-271.529033258	79.90193	-170304.4	35.0 ± 3.0
Formaldehyde ( <b>34</b> )	-114.503197699	16.76322	-71833.0	-27.7
Acetaldehyde ( <b>35</b> )	-153.835727637	34.88260	-96496.1	-40.8 ± 0.4
Crotonaldehyde ( <b>36</b> )	-231.242907604	56.30779	-145047.7	-26.2 ± 0.6
Acetone ( <b>37</b> )	-193.164211635	52.53795	-121156.9	-52.2 ± 0.1
Cyclopenta-2,4-dienone ( <b>38</b> )	-268.110180754	46.63493	-168192.4	13.2 <sup>a</sup>
Cyclohexanone ( <b>39</b> )	-309.905229971	94.83126	-194370.8	-54.5
Phenol ( <b>40</b> )	-307.478467379	65.75443	-192877.1	-23.0 ± 0.1
Cyclohexa-2,4-dione ( <b>1</b> )	-307.450347880	64.86423	-192860.2	-17.0 ± 3.0
Cyclohexa-2,5-dione ( <b>2</b> )	-307.451940248	65.09051	-192861.0	-13.0 ± 3.0

<sup>a</sup> High-level (G2 value corrected by isodesmic reactions) computed value. Ref. 22. <sup>b</sup> Results from ref. 17.

ation routines on all possible conformations using the semi-empirical PM3 method, with thorough checks to identify conformations at the DFT energy minimum. Further details are described in ref. 17.

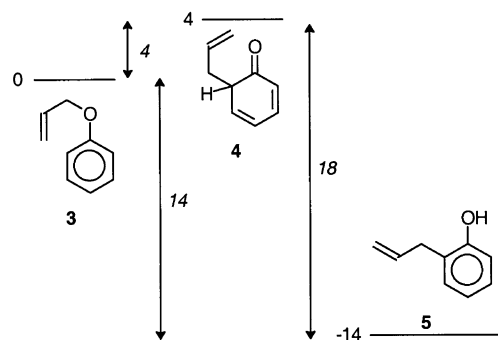
## Results and discussion

Experimental  $\Delta_f H_{298}^\circ$  values for compounds also subjected to DFT calculation are given in Table 1. Heats of formation for other relevant compounds are given throughout the text.

### 1. Kinetics of gas-phase thermolyses

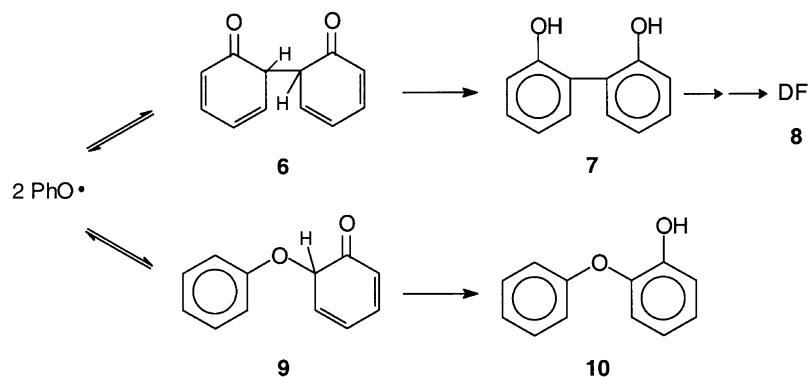
The vapour-phase thermolysis of allyl phenyl ether (**3**), at atmospheric pressure with various diluents has been studied previously.<sup>14</sup> The primary product of the well-known [3,3]-sigmatropic Claisen rearrangement is 6-allyl-cyclohexa-2,4-dienone (**4**) which—in condensed phases—is rapidly converted into *o*-allylphenol by acid-catalysed tautomerisation. This situation can also be met in the vapour phase provided that (bimolecular) enolisation, for example by adding acetic acid vapour or else by surface catalysis, can take place. Unimolecular isomerisation by a 1,3-H shift is a high-energy process due to orbital symmetry mismatch.<sup>14</sup> Indeed, thermolysis of **3** diluted with *e.g.* toluene under a nitrogen atmosphere does not lead to rearranged product but is subject to (slow) O-allyl bond homolysis—a result which was corroborated later on by the VLPP study of Colussi *et al.*<sup>18</sup> These observations mean that—while the overall process is of course *exothermic*—the first step in the Claisen rearrangement must be *endothermic*. In other words,  $\Delta_f H_{298}^\circ$  for **4** is well above that for **3**.

In Scheme 1 the level of **4** has been taken to be 4 kcal mol<sup>-1</sup> above that of the starting compound **3** as a reasonable minimum value to acknowledge the inhibition of the rearrangement in an 'inert' environment. The value for **3** follows from simple



**Scheme 1** Enthalpy diagram (kcal mol<sup>-1</sup>) for the Claisen rearrangement of allyl phenyl ether (**3**).

group additivity: take  $\Delta_f H_{298}^\circ(\text{PhOMe}) = 16$  kcal mol<sup>-1</sup>; add an increment of  $-8.5$  to obtain PhOEt (as the typical difference going from ROME to ROEt), and then add one CH<sub>2</sub> unit ( $-5$ ) to arrive to  $-29.5$  for PhOPr; finally, add  $+30$  as the typical increment going from an alkyl to an alkenyl chain, yielding  $\Delta_f H_{298}^\circ(\mathbf{3}) = 0$  kcal mol<sup>-1</sup>. The difference of 14 kcal mol<sup>-1</sup> between **3** and **5** is the same as that for anisole and *o*-cresol.<sup>1-3</sup> The heat of ketonisation for **5**→**4** then is (at least) 18 kcal mol<sup>-1</sup>. If we were to accept the value of Shiner *et al.*<sup>13</sup> for **1** vs. phenol **40**, *i.e.*  $6 \pm 3$  kcal mol<sup>-1</sup>, to hold here as well (the allyl function will at best only lead to minor corrections in that enthalpy difference), the heat of formation of **4** would be  $8 \pm 3$  kcal mol<sup>-1</sup> lower than that of **3**. This is totally unrealistic, as it would allow the Claisen rearrangement to proceed rapidly also in the absence of enolising agents, with anything of the large equilibrium proportion of **4** left after the gas-phase reaction to enolise easily to **5** upon condensation of the product. In summary, the analysis given above implies that the hitherto accepted standard  $\Delta_f H_{298}^\circ$  value for **1** of  $-17 \pm 3$  kcal mol<sup>-1</sup>



Scheme 2 Pathways for recombination of phenoxy radicals.

must be wrong, and a value some 10 kcal mol<sup>-1</sup> higher is strongly indicated.

The very recent analysis of rates and products in the gas-phase combination of phenoxy radicals<sup>12</sup> supports this conclusion. While combination in the liquid phase leads to all 5 possible final products (diphenyl peroxide cannot exist/survive) from *O*, *ortho-C* and *para-C* coupling, in the gas phase above 700 K *o-C-o-C* combination, via **6** and **7** finally resulting in dibenzofuran (DF) **8**, becomes nearly the only productive channel. With effective bimolecular rate constants for 2 PhO•→**8** of 10<sup>8</sup>–10<sup>8.5</sup> M<sup>-1</sup> s<sup>-1</sup>, *i.e.* up to 2 orders of magnitude below that for direct radical–radical combination, formation of dimers must now be highly reversible.

Should Shiner's heat of ketonisation apply, the central C–C bond of **6** (Scheme 2), with two keto groups, would be no less than 55 kcal mol<sup>-1</sup> strong, making it too long-lived to allow redissociation. Referring to ref. 12 for details, Scheme 2 just depicts one other dimer, **9**, which—when matching Shiner's heat of enolisation—would be *ca.* 12 kcal mol<sup>-1</sup> less stable than **6**. This could make the observed<sup>8</sup> very low selectivity of **10** understandable only if formation of both **6** and **9** were reversible, but this is difficult to accept together with the bond strengths in the dimers and the relative ease of the further steps to **7/8** and **10**.<sup>12</sup> The situation eases, however, when increasing the heat of enolisation (of **1** and of like species) by some 10 kcal mol<sup>-1</sup>; the C–C bond in **6** will be down to *ca.* 35 kcal mol<sup>-1</sup>, and dimer **9** is still several kcal mol<sup>-1</sup> less stable than **6** while both dimers are reversibly formed. At this point it is worthwhile to note that an important further increase of the heat of ketonisation (to for example 24 kcal mol<sup>-1</sup>, as advanced by Mahoney and Weiner<sup>19</sup>) also becomes incompatible with the data referred to above. Then, dimer **9** would be 6 kcal mol<sup>-1</sup> more stable than **6** and moreover the C–C bond of the latter would be down to only 19 kcal mol<sup>-1</sup>, which in no way can justify (selective) production of dibenzofuran at higher temperatures.

## 2. Group additivity

To approach  $\Delta_f H_{298}^\circ$  of **1** via known experimental values on structurally analogous compounds, the following is straightforward. Replace a CH<sub>2</sub> moiety in cyclohexa-1,3-diene (**29**, 26.8 kcal mol<sup>-1</sup>) by carbonyl. The increment is *ca.* -27 for *e.g.* propane (**14**)→acetone (**37**), Table 1, and also for 2-methylbutadiene (isoprene)→methyl vinyl ketone, or for ethylbenzene→acetophenone.<sup>1,2</sup> It is less (*ca.* -25) for cyclohexane (**27**)→cyclohexanone (**39**) (Table 1). So, on this basis  $\Delta_f H_{298}^\circ$  for **1** is derived to be 0–2 kcal mol<sup>-1</sup>. Full application of Benson's additivity rules leads to the same result.<sup>19</sup> With  $\Delta_f H_{298}^\circ$  for phenol (**40**) of -23 kcal mol<sup>-1</sup>, the enthalpy for tautomerisation then comes at approximately 24 kcal mol<sup>-1</sup>.

These estimates neglect any structural/conformational effects as well as additional conjugational energy, and the 'real' value is likely to be several kcal mol<sup>-1</sup> lower, as concluded in section 1 above.

The 2,5-isomer **2** is said<sup>13</sup> to be 4 kcal mol<sup>-1</sup> less stable (-13 vs. -17) than **1**, while group additivity considerations lead to a difference of 1–2 kcal mol<sup>-1</sup> only. True or not, 'crude' additivity approaches are not able to assess that difference any better.

Published data on  $\Delta_f H_{298}^\circ$  for the two cyclohexadienes **29** and **30** (Table 1) imply essentially the same values for the 1,3- and 1,4-isomers, indicating a subtle interplay of small differences in conjugative and conformational aspects due to differences in (especially C–C) bond lengths and angles. Bartmess<sup>20</sup> also obtained within experimental error the same value for **32** and **33**, the carbon analogues of **1** and **2**.

## 3. Computational results

The energy values for salient optimised structures are given in Table 1. Series of isodesmic reactions were employed to determine  $\Delta_f H_{298}^\circ$  values for the target reactants (see Table 2), applying the general equation [eqn. (1)] with the suffixes:

$$[\Sigma(\Delta H_{298,\text{DFT}})_{\text{prod}} - \Sigma(\Delta H_{298,\text{DFT}})_{\text{react}}] = [\Sigma(\Delta_f H_{298,\text{exp}}^\circ)_{\text{prod}} - \Sigma(\Delta_f H_{298,\text{exp}}^\circ)_{\text{react}}] \quad (1)$$

DFT = computed, exp = experimental, prod = products, react = reactants. For example, the isodesmic value for reaction 2, Table 2, was obtained as shown in eqn. (2).

$$\Delta_f H_{298}^\circ(\mathbf{1}) = [\Delta_f H_{298,\text{exp}}^\circ(2 \times \mathbf{13} + \mathbf{34} + 4 \times \mathbf{12} - 7 \times \mathbf{11}) - [\Delta H_{298,\text{DFT}}(2 \times \mathbf{13} + \mathbf{34} + 4 \times \mathbf{12} - \mathbf{1} - 7 \times \mathbf{11})] \quad (2)$$

The choice of isodesmic reactions is limited by the availability of experimental enthalpies of formation. Furthermore, experimental data do not have the same reliability. Hence, one may either select one most reliable isodesmic reaction, or determine a mean 'best' value of a broad set. We have chosen for the latter approach, and considered for further evaluation the arithmetical mean values, which are (Table 2) -7.3 and -8.0 kcal mol<sup>-1</sup> for **1** and **2**, respectively. In doing this, we are comforted by the low standard deviation, and by the limited interval between the lowest and the highest values (4.6 for **1** and 4.0 kcal mol<sup>-1</sup> for **2**).

The arithmetical mean values for **1** and **2** are 1.2 and 1.1 kcal mol<sup>-1</sup> more negative than those obtained by tautomerisation to phenol (reactions 1, 11, Table 2)—which are not isodesmic reactions. That means that at the current level of computation the gap between an aromatic (phenol) and a conjugated system (its tautomers) is oversized. The same conclusion will be drawn for toluene (*vide infra*).

The adequacy of the present theoretical level may be argued. While recognising that higher levels could yield better results, an indirect validation was obtained by determining  $\Delta_f H_{298}^\circ$  values for **29**, **30**, and **38**, at the same level and with the same approach (details are available upon request). The results for **29** (26.6 ± 1.2 kcal mol<sup>-1</sup>) and **30** (26.2 ± 1.5 kcal mol<sup>-1</sup>) compare well with experimental data (Table 1). Hence, the current level

**Table 2**  $\Delta_f H_{298}^\circ$  values for **1** and **2** derived from isodesmic reactions (kcal mol<sup>-1</sup>)

No.	Reaction	$\Delta_f H_{298}^\circ$
1	<b>1</b> → <b>40</b>	-6.1
2	<b>1</b> + 7 <b>11</b> →2 <b>13</b> + <b>34</b> + 4 <b>12</b>	-6.9
3	<b>1</b> + <b>14</b> → <b>29</b> + <b>37</b>	-8.4
4	<b>1</b> + <b>26</b> → <b>29</b> + <b>38</b>	-7.9
5	<b>1</b> + <b>15</b> + <b>11</b> → <b>26</b> + <b>37</b> + <b>13</b>	-6.9
6	<b>1</b> + 2 <b>11</b> →2 <b>36</b> + <b>17</b>	-7.0
7	<b>1</b> + 2 <b>11</b> → <b>25</b> + <b>37</b>	-6.2
8	<b>1</b> + 4 <b>11</b> → <b>21</b> + <b>35</b> + 2 <b>12</b>	-5.5
9	<b>1</b> + <b>11</b> → <b>29</b> + <b>34</b>	-10.1
10	<b>1</b> + <b>22</b> → <b>39</b> + <b>25</b>	-7.1
	Mean value ± standard dev. <sup>a</sup>	-7.3 ± 1.4
11	<b>2</b> → <b>40</b>	-6.9
12	<b>2</b> + 7 <b>11</b> →2 <b>13</b> + <b>34</b> + 4 <b>12</b>	-7.7
13	<b>2</b> + <b>14</b> → <b>30</b> + <b>37</b>	-9.4
14	<b>2</b> + <b>26</b> → <b>30</b> + <b>38</b>	-8.9
15	<b>2</b> + <b>21</b> + <b>11</b> → <b>26</b> + <b>37</b> + 2 <b>13</b>	-8.6
16	<b>2</b> + 2 <b>11</b> →2 <b>36</b> + <b>19</b>	-7.1
17	<b>2</b> + 2 <b>11</b> → <b>23</b> + <b>37</b>	-8.7
18	<b>2</b> + <b>14</b> + 2 <b>11</b> →2 <b>19</b> + <b>37</b>	-8.0
19	<b>2</b> + <b>11</b> → <b>30</b> + <b>34</b>	-11.1
20	<b>2</b> + <b>22</b> → <b>39</b> + <b>23</b>	-9.7
21	<b>2</b> + 4 <b>11</b> →2 <b>13</b> + <b>14</b> + <b>37</b>	-8.5
	Mean value ± standard dev. <sup>b</sup>	-8.0 ± 1.0

<sup>a</sup> Arithmetic mean value of reactions 2–10. <sup>b</sup> Arithmetic mean value of reactions 12–21.

appears to be suitable for dienes in six-membered rings, *i.e.* similar to the structures of **1** and **2**. The value calculated for **38** (12.2 ± 0.9 kcal mol<sup>-1</sup>)—a cross-conjugated system in a ring structure—shows only a small difference from that of a higher level of computation, believed to be very reliable.

The value for **1** agrees closely with that inferred from the gas-phase kinetic results (section 1) and definitively discredits Shiner's value of -17 kcal mol<sup>-1</sup>. The  $\Delta_f H_{298}^\circ$  value for **2**, -8 kcal mol<sup>-1</sup>, is only 5 kcal mol<sup>-1</sup> above that of Shiner. Small differences between the two isomers may not be properly treated by the current DFT method, but by no means can a difference of 4 kcal mol<sup>-1</sup> between the two isomers be expected solely on the grounds of the difference between linear and cross-conjugated systems.

#### 4. Standard enthalpies of formation of the isomers of toluene

A calculational approach similar to that discussed in section 3 was applied to **32** and **33** (Table 3).

The computed value for **32**, 43 kcal mol<sup>-1</sup>, is 8 kcal mol<sup>-1</sup> above that inferred from ion cyclotron resonance spectrometry relying on bracketing of gas-phase acidities<sup>2,20</sup> (it is much closer to the 41 kcal mol<sup>-1</sup> preferred by Bally *et al.*,<sup>21</sup> who *inter alia* considered their own experimental result of 47 kcal mol<sup>-1</sup>, too high, for some unknown reason). The difference between our DFT values for **1** and **32** amounts to ~50 kcal mol<sup>-1</sup>. This is close to that known for C=O *vs.* C=CH<sub>2</sub> 'transpositions' as in *e.g.* acetone (**37**)→isobutene (**20**), or cyclohexanone (**39**)→methylenecyclohexane, *viz.* ~47 kcal mol<sup>-1</sup>, and can therefore be considered consistent within the uncertainty limits and the as yet insufficient insight into the limited differences in conjugation and—perhaps—strain energies. When 'expanding' cyclohexa-1,3-diene (**29**,  $\Delta_f H_{298}^\circ = 25$  kcal mol<sup>-1</sup>) to **32** (the increment derived from simple cases such as propane (**14**)→isobutene (**20**) being 21 kcal mol<sup>-1</sup>),  $\Delta_f H_{298}^\circ(\mathbf{32})$  is estimated at 46 kcal mol<sup>-1</sup>; 'extra' conjugation may well amount to 3 kcal mol<sup>-1</sup>, to fully agree with the DFT result of 43 kcal mol<sup>-1</sup>.

The situation with the '*para*' isomer **33** is less clear. While Bartmess's value is equal to that of **32**,<sup>20</sup>—however each having an uncertainty of ±3 kcal mol<sup>-1</sup>—our DFT calculation (Table 3) would suggest **33** to be 4.6 kcal mol<sup>-1</sup> more stable than **32**. As yet we do not know if there is some flaw in the

**Table 3**  $\Delta_f H_{298}^\circ$  values for **32** and **33** derived from isodesmic reactions (kcal mol<sup>-1</sup>)

No.	Reaction	$\Delta_f H_{298}^\circ$
1	<b>32</b> → <b>31</b>	46.4
2	<b>32</b> + 7 <b>11</b> →3 <b>13</b> + 4 <b>12</b>	44.3
3	<b>32</b> + <b>14</b> → <b>29</b> + <b>20</b>	40.7
4	<b>32</b> + <b>12</b> → <b>26</b> + <b>20</b>	42.2
5	<b>32</b> + 2 <b>11</b> → <b>25</b> + <b>17</b>	43.0
6	<b>32</b> + 2 <b>11</b> → <b>25</b> + <b>17</b>	42.9
7	<b>32</b> + 4 <b>11</b> → <b>21</b> + <b>15</b> + 2 <b>12</b>	45.1
8	<b>32</b> + <b>11</b> → <b>29</b> + <b>13</b>	41.1
	Mean value ± standard dev. <sup>a</sup>	42.8 ± 1.6
9	<b>33</b> → <b>31</b>	42.6
10	<b>33</b> + 7 <b>11</b> →3 <b>13</b> + 4 <b>12</b>	40.5
11	<b>33</b> + <b>14</b> → <b>30</b> + <b>20</b>	36.7
12	<b>33</b> + <b>12</b> → <b>26</b> + <b>20</b>	38.4
13	<b>33</b> + <b>21</b> + 2 <b>11</b> → <b>26</b> + <b>20</b> + 2 <b>13</b>	37.6
14	<b>33</b> + 2 <b>11</b> → <b>25</b> + <b>17</b>	39.2
15	<b>33</b> + 2 <b>11</b> → <b>23</b> + <b>20</b>	37.4
16	<b>33</b> + 3 <b>11</b> →2 <b>19</b> + <b>13</b>	38.6
17	<b>33</b> + <b>14</b> + 2 <b>11</b> →2 <b>19</b> + <b>20</b>	38.2
18	<b>33</b> + 4 <b>11</b> →2 <b>13</b> + <b>20</b> + <b>14</b>	37.7
19	<b>33</b> + <b>11</b> → <b>30</b> + <b>13</b>	37.2
	Mean value ± standard dev. <sup>b</sup>	38.2 ± 1.1

<sup>a</sup> Arithmetic mean value of reactions 2–8. <sup>b</sup> Arithmetic mean value of reactions 10–19.

calculation or to what extent unrecognised stereoelectronic factors come into play. More reliable experimental data—and computation at higher levels—could help to solve this matter.

#### 5. Summarising discussion

The thermochemical-kinetic arguments (section 1) leave no doubt that the hitherto accepted value for  $\Delta_f H_{298}^\circ(\mathbf{1})$  of -17 kcal mol<sup>-1</sup>, only 6 kcal mol<sup>-1</sup> above that for phenol, is wrong, the true value being *ca.* 10 kcal mol<sup>-1</sup> higher. DFT calculations (section 3) underscore this conclusion. Accepting  $\Delta_f H_{298}^\circ(\mathbf{1}) = -7$  kcal mol<sup>-1</sup>, the difference with the heat of formation of the parent cyclohexa-1,3-diene **29** becomes 32 kcal mol<sup>-1</sup>, some 5 kcal mol<sup>-1</sup> in excess of the increment for simple pairs of (secondary) >CH<sub>2</sub> *vs.* >C=O derivatives (section 2). This may at first sight be explained simply in terms of conjugational stabilisation in **1** (note that on the basis of Shiner's value for  $\Delta_f H_{298}^\circ(\mathbf{1})$  the above-mentioned 5 kcal mol<sup>-1</sup> becomes no less than 15 kcal mol<sup>-1</sup>, which is far beyond being acceptable). However, other structural effects are likely to be involved as well. With reliable thermochemical data on analogous—unsaturated—structures such as cyclohex-3-enone lacking, and while the scarce data on non-cyclic structures are inconclusive, a more detailed discussion is as yet impossible. In this situation one can only accept that both the 'conjugated' 1,3-isomer **29** and the non-conjugated 1,4-isomer **30** have essentially the same heat of formation, and that this is also the case for their keto derivatives **1** and **2**.

Turning to the carbon analogue **32**, it is understandable that Shiner *et al.*,<sup>13</sup> comparing their result for **1** (-17 kcal mol<sup>-1</sup>) with that of Bartmess for **32** (35 kcal mol<sup>-1</sup>),<sup>20</sup> could judge both values consistent: the difference (52 kcal mol<sup>-1</sup>) is approximately correct (section 4) but both absolute values are some 10 kcal mol<sup>-1</sup> too low. One other way to demonstrate this is to consider heats of hydrogenation. For cyclohexa-1,3-diene ( $\Delta_f H_{298}^\circ(\mathbf{29}) = 25$  kcal mol<sup>-1</sup>)→cyclohexane ( $\Delta_f H_{298}^\circ(\mathbf{27}) = -29.5$  kcal mol<sup>-1</sup>) this is (-)54.5 kcal mol<sup>-1</sup>. Accepting  $\Delta_f H_{298}^\circ(\mathbf{32}) = 43$  kcal mol<sup>-1</sup>, conversion to methylenecyclohexane ( $\Delta_f H_{298}^\circ = -6$  kcal mol<sup>-1</sup>)<sup>3</sup> is 49 kcal mol<sup>-1</sup> exothermic, some 5 kcal mol<sup>-1</sup> less than in the case of the parent cyclohexadiene. This may be seen again as a reflection of a loss in conjugational stabilisation of the triene system of **32** (Bartmess's value for **32** would make the heat of hydrogenation as low as (-)41 kcal mol<sup>-1</sup>, far beyond reality).

The present level of knowledge is insufficient to provide a well-defined answer to the question about the enthalpy difference between **32** and **33**. There are not even literature values available for the methylenecyclohexenes, which could give insight into the importance of *e.g.* conjugation in diene moieties. Which of the two is more stable remains a puzzle but their absolute values, in our view, cannot possibly be below 40 kcal mol<sup>-1</sup>.

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- 10 The increment for biphenyl ( $\Delta_f H_{298}^\circ = +43.5$  kcal mol<sup>-1</sup>) to its *meta*-OH derivative (*m*-hydroxybiphenyl, **I**) should be almost equal to that for benzene (+20 kcal mol<sup>-1</sup>) to phenol (-23 kcal mol<sup>-1</sup>), to arrive at  $\Delta_f H_{298}^\circ$  (**I**)  $\approx 0.5$  kcal mol<sup>-1</sup>, rather than Bertholon's value of +5.0 kcal mol<sup>-1</sup> (ref. 9). Likewise, for *p*-hydroxybiphenyl the discrepancy is 8 kcal mol<sup>-1</sup>. Analogous checks on the values reported for alkylphenols show that the data for R = Me, Et, Pr<sup>i</sup> are in accordance with expectation, but for *m*- (and *p*-) *tert*-butylphenol, they are (again) some 4 kcal mol<sup>-1</sup> above that derived *via* introducing OH in the hydrocarbon.
- 11 With  $\Delta_f H_{298}^\circ$  for diphenylmethane (ref. 3) =  $37 \pm 0.5$  kcal mol<sup>-1</sup> (a value tallying reasonably well with that inferred from transplanting benzyl head-on to benzene, or by exchanging R in PhCH<sub>2</sub>R for Ph, for which values come out at  $\sim 39$  kcal mol<sup>-1</sup>), introduction of OH at the *meta*-position (increment for benzene  $\rightarrow$  phenol of -43 kcal mol<sup>-1</sup>, or more closely related, from toluene (12.4)  $\rightarrow$  *m*-cresol (-31.6), -44 kcal mol<sup>-1</sup>), yields a heat of formation of gaseous *m*-PhCH<sub>2</sub>PhOH of *ca.* -7 kcal mol<sup>-1</sup>, rather than +11.5 kcal mol<sup>-1</sup> as advanced by Bertholon *et al.* The situation with the *para*-isomer (reported value: +15 kcal mol<sup>-1</sup>) is even worse.
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