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High level *ab initio* stabilization energies of benzene

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Summary. G2 theory is shown to be reliable for calculating isodesmic and homodesmotic stabilization energies (ISE and HSE, respectively) of benzene. G2 calculations give HSE and ISE values of 92.5 and 269.1 kJ mol^{-1} (298 K), respectively. These agree well with the experimental HSE and ISE values of 90.5 ± 7.2 and 268.7 ± 6.3 kJ mol^{-1}, respectively. We conclude that basis set superposition error corrections to the enthalpies of the homodesmotic or isodesmic reactions are not necessary in calculations of the stabilization energies of benzene using G2 theory. The calculated values of the enthalpies of formation of such molecules containing multiple bonds such as benzene and *s-trans* 1,3-butadiene, which are found from the enthalpies of isodesmic and homodesmotic reactions rather than of atomization reactions, demonstrate good performance of G2 theory. Estimates of the ΔH_f° value for benzene from the G2 calculated enthalpies of homodesmotic reaction (2) and isodesmic reaction (3) are 80.9 and 82.5 kJ mol^{-1} (298 K), respectively. These are very close to the experimental ΔH_f° value of 82.9 ± 0.3 kJ mol^{-1}. The ΔH_f° value of *s-trans* 1,3-butadiene calculated using the G2 enthalpy of isodesmic reaction (4) is 110.5 kJ mol^{-1} and is in excellent agreement with the experimental ΔH_f° value of 110.0 ± 1.1 kJ mol^{-1}.

Key words: *Ab initio* study – Stabilization energies – Aromaticity – Isodesmic and homodesmotic reactions – Benzene

1 Introduction

Isodesmic [1, 2] and homodesmotic [2, 3] reactions have been widely used in the evaluation of stabilization energies (SE) and enthalpies of formation (ΔH_f°) of many molecules [2–16]. An energetic criterion for aromaticity and antiaromaticity may be derived based on the energies of homodesmotic reactions [3, 11, 14–16]. Homodesmotic stabilization energies (HSE) have become the most dependable tool for estimates of various stabilization effects. This is explained partly by the growing amount of experimental thermodynamical data on organic compounds, but more importantly, the rapid development of *ab initio* computational methods has enabled the HSE to be calculated even when some experimental data are lacking or if a compound under question is experimentally unknown [4, 7, 11–16].

The stabilization energy of a molecule can be calculated as the difference between the standard enthalpy of atomization, ΔH_a°, or standard enthalpy of formation, ΔH_f°, of a given molecule and the same energetic parameter obtained using some additivity scheme. Homodesmotic stabilization energy is of great interest for benzene which is the key aromatic molecule [16], as it gives an estimate of the stabilization of benzene because of its aromaticity [3]. The specificity of each scheme for calculating the stabilization energy depends on the procedure employed to determine the bond energies, and for benzene these are the energies of the C–H, C–C, and C=C bonds (Eq. (1)) [17]:

$$\mathrm{SE\ (benzene)} = \Delta H_a^\circ\ \mathrm{(benzene)} - 6E(\mathrm{C{-}H}) - 3E(\mathrm{C{-}C}) - 3E(\mathrm{C{=}C}). \qquad (1)$$

The homodesmotic reaction equation for estimating aromatic stabilization energy of benzene can be obtained from Eq. (1) if the bond energies are calculated from the ΔH_a° values of reference molecules such as $H_2C{=}CH_2$ and *s-trans* 1,3-butadiene (the single =C–C= bond). The energy due to the aromatic stabilization [3, 16] may be obtained from the enthalpy of reaction (2). This stabilization energy corresponds to the stabilization caused by the cyclic delocalization of the π-electrons [18], and represents the true aromatic stabilization of benzene [3, 16, 19]:

$$\mathrm{benzene} + 3H_2C{=}CH_2 \rightarrow 3\ s\text{-}trans\ H_2C{=}CH{-}CH{=}CH_2. \qquad (2)$$

If, however, CH_4, $H_3C{-}CH_3$, and $H_2C{=}CH_2$ are taken as the reference molecules for calculations of the bond energies, Eq. (1) yields an estimation of the energy of reaction (3), which is the isodesmic stabilization energy (ISE) [1, 2]. This corresponds to the *total* stabilization energy of benzene [16]:

$$\mathrm{benzene} + 6\ CH_4 \rightarrow 3\ H_3C{-}CH_3 + 3\ H_2C{=}CH_2. \qquad (3)$$

Since isodesmic and homodesmotic stabilization energies are widely employed in chemistry [1–16], the reliability of the calculation of these energies has been the subject of intensive study, of which most have focused on the ISE and HSE of benzene [2, 11, 16, 19–28]. The best previous computational estimate of the HSE of benzene, calculated at the MP4SDTQ/6–31 *G*(*d*, *p*)//MP2/6–31 *G*(*d*, *p*) level, was 100.0 kJ mol^{-1} at 0 K [11]. Inclusion of the zero-point energy (ZPE) and thermal corrections yielded an HSE value of 105.4 kJ mol^{-1}, which is 14.9 kJ mol^{-1} above the experimental value (Table 1). This disagreement, along with previous computational results [20–27], gave rise to the suggestion that the improvement in calculations of the HSE for benzene could be achieved by applying basis set superposition error (BSSE) corrections to the homodesmotic reaction enthalpy rather than by using a high level of theory [28]. We will show, however, that BSSE corrections are not necessary at the G2 level of theory [29, 30] and the G2 calculated ISE and HSE values for benzene agree very well with the experimental values.

2 Computational methods

Standard *ab initio* molecular orbital calculations [2] were carried at the G2 level of theory [29, 30] using the GAUSSIAN-92 program [31]. This level corresponds effectively to calculations at the QCISD(T)/6–311 + *G*(3*df*,2*p*)//MP2(full)/6–31 *G*(*d*) level with the incorporation of HF/6–31*G*(*d*) scaled zero-point energies and the so-called higher-level corrections. Geometries were optimized using analytic gradient techniques [32] at MP2(full)/6–31*G*(*d*). To obtain theoretical reaction

Table 1. G2 calculated and experimental enthalpies (in kJ mol^{-1}) of reactions (2)–(4)[a]

Reaction	G2 enthalpy[b]	Experimental enthalpy
(2)	92.5	90.5 ± 7.2[c]
(3)	269.1	268.7 ± 6.3[d]
(4)	58.9	59.4 ± 4.1[e]

[a] At 298 K

[b] G2 energies of the molecules involved in reactions (2)–(4) are given in Table 2

[c] ΔH_f° (298 K) of benzene and ethylene were taken from Ref. [33], ΔH_f° (298 K) of *s-trans* 1,3-butadiene (not given in Ref. [33]) was taken from Ref. [34]

[d] Calculated using the ΔH_f° (298 K) values given in Ref. [33]

[e] All the ΔH_f° (298 K) values were taken from Ref. [33] except ΔH_f° (298 K) of *s-trans* 1,3-butadiene (not given in Ref. [33]) which was taken from Ref. [34]

enthalpies ΔH°, and formation enthalpies, ΔH_f°, at 298 K vibrational contributions to temperature corrections [2] were calculated using harmonic frequencies computed at HF/6–31*G*(*d*) and scaled by 0.8929 in accordance with G2 theory [29]. Theoretical enthalpies of formation of benzene and 1,3-butadiene were obtained from the G2 enthalpies of isodesmic and homodesmotic reactions (2)–(4) using the experimental enthalpies of formation [33, 34] of the other molecules involved in the corresponding reactions. All reaction energies reported in this paper correspond to standard reaction enthalpies (ΔH°) at 298 K.

3 Results and discussion

MP4SDTQ/6–31*G*(*d*)//HF/6–31*G*(*d*) calculations with the BSSE corrections gave a value of 89.3 kJ mol^{-1} for the HSE of benzene [28]. Tao and Pan [28] presumed that ZPE and thermal corrections to the enthalpy of reaction (2), ΔH° (2), were only + 0.8 kJ mol^{-1}. However, we calculated these corrections to be + 5.4 kJ mol^{-1} using the HF/6–31*G*(*d*) frequencies scaled by 0.8929. If these corrections are assumed, the HSE value calculated by Tao and Pan, should be 94.7 kJ mol^{-1} at 298 K, which means that the BSSE-corrected and experimental HSE values do not agree as well as was suggested [28]. This value is still better than the MP4SDTQ/6–31*G*(*d*, *p*)//MP2/6–31*G*(*d*) value [11] calculated without BSSE corrections to the reaction enthalpy. Thus, we may ask the question, do BSSE corrections have a crucial impact on the HSE value of benzene when a higher computational level is used?

Our calculation of the ΔH° (2) value using G2 theory gives the HSE value of 92.5 kJ mol^{-1} (Table 1; G2 energies are listed in Table 2), which agrees well with the experimental HSE value of 90.5 ± 7.2 kJ mol^{-1} at 298 K. The aromatic stabilization energy of benzene is, therefore, 15.4 kJ mol^{-1} per π-electron. It is notable that cyclobutadiene, the archetypal antiaromatic molecule [16, 36] has a larger absolute value of the antiaromatic destabilization energy, which, when corrected for the strain energy of cyclobutadiene, is − 42.5 ± 1.8 kJ mol^{-1} per π-electron at

Table 2. G2 energies (in hartrees) of molecules involved in reactions (2)–(4)

Molecule	G2 E_{tot} (0 K)[a]	G2 E_{tot} (298 K)
Methane	– 40.41089	– 40.40707
Ethane	– 79.63088	– 79.62640
Ethylene	– 78.41593	– 78.41193
s-trans 1,3-butadiene	– 155.66427	– 155.65855
Benzene	– 231.78053	– 231.77508

[a] G2 energies of methane, ethylene, ethane, and of benzene were taken from Ref. [35]

the G2 level [37]. The ISE value of benzene (ΔH^0 (3)) calculated at the G2 level, is 269.1 kJ mol^{-1} and is in excellent agreement with the experimental ISE value of 268.7 ± 6.3 kJ mol^{-1} at 298 K (Table 1).

Isodesmic and homodesmotic reaction energies can be used for the calculation of enthalpies of formation [2, 19, 37–41]. Estimates of the ΔH_f^0 value for benzene from the G2 calculated enthalpies of reactions (2) and (3) are 80.9 and 82.5 kJ mol^{-1}, respectively, and both are close to the experimental value of 82.9 ± 0.3 kJ mol^{-1} at 298 K [33]. The ΔH_f^0 value of *s-trans* 1,3-butadiene calculated using the G2 enthalpy of isodesmic reaction (4) is 110.5 kJ mol^{-1} (Table 1) and agrees very well with the experimental ΔH_f^0 value of 110.0 ± 1.1 kJ mol^{-1} at 298 K [34]:

$$s\text{-}trans\ H_2C{=}CH{-}CH{=}CH_2 + 2\ CH_4 \rightarrow H_3C{-}CH_3 + 2H_2C{=}CH_2. \qquad (4)$$

The performance of G2 theory diminishes for molecules containing multiple bonds [29, 37]. This may be attributed to the necessity of including higher angular momentum functions in the basis set in order to describe these molecules properly [42]. Indeed, the ΔH_f^0 of benzene, calculated from the atomization energies using G2 theory [35, 43] differs by 18.4 kJ mol^{-1} from the experimental value. Our results show that the use of isodesmic and homodesmotic reactions, rather than the atomization reactions, to calculate enthalpies of formation of molecules with multiple bonds at the G2 level leads to error cancellation and is, therefore, somewhat similar to using corrections for multiple bonds [42].

4 Conclusions

We can draw three major conclusions from this study:

i) Homodesmotic and isodesmic stabilization energies of benzene (HSE and ISE, respectively) can be calculated accurately using a high level of theory such as the G2 level. G2 calculations gave HSE and ISE values of 92.5 and 269.1 kJ mol^{-1} (298 K), respectively. These agree well with the experimental HSE and ISE values of 90.5 ± 7.2 and 268.7 ± 6.3 kJ mol^{-1}, respectively.

ii) Basis set superposition error corrections to the enthalpies of the homodesmotic isodesmic reactions are not necessary in calculations of the stabilization energies of benzene using G2 theory.

iii) Calculations of the enthalpies of formation of such multiple-bonded molecules as benzene and *s-trans* 1,3-butadiene, which are based on isodesmic and homodesmotic reactions rather than on the atomization reactions, demonstrate good performance at the G2 level. Estimates of the ΔH_f° value for benzene, obtained from the G2 calculated enthalpies of homodesmotic reaction (2) and isodesmic reaction (3), are 80.9 and 82.5 kJ mol^{-1} (298 K), respectively, and both are close to the experimental ΔH_f° value of 82.9 ± 0.3 kJ mol^{-1}. The ΔH_f° value of *s-trans* 1,3-butadiene calculated using the G2 enthalpy of isodesmic reaction (4) is 110.5 kJ mol^{-1} and is in excellent agreement with the experimental ΔH_f° value of 110.0 ± 1.1 kJ mol^{-1}.

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