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The Influence of Substituent Groups on the Resonance Stabilization of Benzene. An ab Initio Computational Study

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Accurate G3(MP2) calculations of the enthalpies of formation ($\Delta_f H^{298}$) of organic molecules permit replication and extension of calculations that were formerly dependent on experimental thermochemical results. A case in point is Kistiakowski's classical calculation of the total stabilization enthalpy of benzene relative to that of cyclohexene, called for many years the "resonance energy". This paper investigates extension of the classical calculation to substituted benzenes. Slight modification of the usual procedure for $\Delta_f H^{298}$ determination permits exclusion of all empirical information, leaving a purely ab initio result. Stabilization enthalpies relative to the corresponding 4-substituted cyclohexenes are presented for benzene, toluene, aniline, phenol, phenylacetylene, styrene, ethylbenzene, and phenylhydrazine. In the process of calculating these stabilization enthalpies, we have also obtained 42 values of $\Delta_f H^{298}$ for monosubstituted benzenes, cyclohexenes, and cyclohexanes, 24 of which are not in the standard reference literature. For the remaining 18 G3(MP2) results, the unsigned mean difference between calculated $\Delta_f H^{298}$ values and experimental results is ±0.91 kcal mol^{-1}.

Many simple thermochemical constructs of interest to organic chemists are limited by a lack of experimental data. With the advent of accurate molecular orbital procedures for calculating thermochemical variables, particularly enthalpies of formation ($\Delta_f H^{298}$), some familiar calculations can be revisited and extended. A case in point is modification and extension of Kistiakowsky's classic determination of the total stabilization enthalpy of benzene relative to that of cyclohexene,[1a,b] called for many years the "resonance energy". Calculations analogous to Kistiakowsky's could be repeated for any number of aromatic systems were it not for the paucity of thermochemical data and the difficulty of making the necessary calorimetric determinations.

The G-*n* family[2] of Gaussian molecular orbital calculations has produced remarkably accurate $\Delta_f H^{298}$ values of organic compounds in those cases in which experimental data exist for comparison.[3] Armed with a method of generating a very large range of accurate computed thermochemical results, one should be able to extend Kistiakowsky's method to an indefinite number of analogous systems. We shall give a few examples of the calculation of the resonance energies (RE) of aromatic compounds in which the phenyl group is perturbed by a substituent group. We shall obtain and discuss quantitative estimates of the degree of perturbation of the aromatic ring by various substituent groups. We shall find that the RE of the phenyl group is resistant to influence by substituents. In the process of calculating these RE values, we shall also obtain 42 values of $\Delta_f H^{298}$ for monosubstituted benzenes, cyclohexenes, and cyclohexanes, 24 of which are not in the standard reference literature. The drawback of the method is that each RE is calculated relative to a different 4-substituted cycloalkene rather than to a single standard as one would wish.

Theory

The theoretical foundations of the G-*n* family of molecular orbital calculations have been discussed in detail.[2] Each G-*n* method entails a different extrapolation of energies of formation calculated at lower levels of approximation to higher and presumably more accurate levels. Information on the atomization energies of the elements in their standard states at 0 K, along with a harmonic-oscillator approximation for the zero-point energy, leads to the energy of formation from the standard state at 0 K. Statistical thermodynamic temperature corrections including (harmonic oscillator) vibrational levels along with atomization energies of the elements in their standard states at 298 K, permit

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calculation of $\Delta_f H^{298}$. The G3(MP2) member of the G-*n* family is our method of choice for the work described here. The method is probably reliable to ±1 kcal mol^{-1} for hydrocarbons of six or seven carbon atoms.[3e,f]

G3(MP2). A Hartree–Fock (HF) calculation of the internal energy of a molecule, say a 6-31G(*d*) calculation, can be improved in accuracy either by taking a larger basis set than the 6-31G(*d*) set or by extending the calculation beyond the HF level to the MP2, MP3, MP4, QCISD(T), or other post-HF levels. The calculations presented in the G3(MP2) method use both improvements. We find out how much improvement, in terms of energy, is gained by expanding the basis set from 6-31G(*d*) to a set recently published by Curtiss et al.[2f,g] called G3MP2large. The improvement (in units of hartrees) is given by the difference between the energies from the larger basis set and the smaller basis set:

$$\Delta E_{\mathrm{MP2}} = [E(\mathrm{MP2/G3MP2large})] - [E(\mathrm{MP2/6\text{-}31G}(d)]$$

where both are calculated at the MP2 level. The energy of the molecule is then calculated at the QCISD(T)/6-31G(*d*) level, and the correction obtained by basis set enlargement is added to the energy calculated at the smaller basis set but with the higher level post HF extension, QCISD(T). The obvious question is "Why do this in a stepwise fashion, when one could do a QCISD(T)/G3MP2large calculation directly?" The answer is that present machine limitations prevent us from doing the entire calculation for molecules of the size we are interested in here. The calculation must be broken into pieces and put back together later. The central assumption of additivity of energy differences has been commented upon by Pople et al.,[1a] and it is supported in this work by the unsigned mean difference (<1.0 kcal mol^{-1}) between G3MP2 results and experimental results for those instances in which experimental results are known.

The energy sum obtained in this way can, inclusive of the zero-point energy, be subjected to further treatment to give $\Delta_f H^{298}$, but we shall show that these extra terms, related to the standard states of the elements,[2d] are unnecessary for our purpose and that the essence of RE calculations is contained in the three ab initio calculations MP2/6-31G(*d*), QCISD(T)/6-31G(*d*), and MP2/G3MP2large.

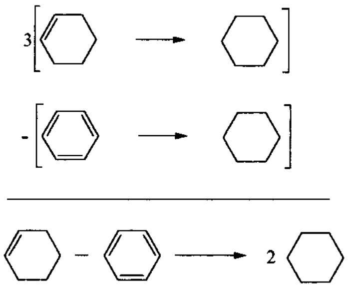
Resonance Energy. Kistiakowsky's textbook[4] determination of the RE of benzene uses the difference between three times the enthalpy of hydrogenation ($\Delta_{\mathrm{hyd}}H^{298}$) of the presumably nonresonant double bond in cyclohexene and the three "double bonds" in benzene:

$$-\mathrm{RE} = 3\Delta_{\mathrm{hyd}}H^{298}(\text{cyclohexene}) - \Delta_{\mathrm{hyd}}H^{298}(\text{benzene}) \qquad (1)$$

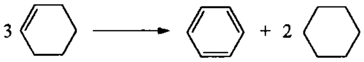
$$= 3(-28.4 \pm 0.1) - (-49.1 \pm 0.2) = -36.1 \pm 0.3\ \text{kcal mol}^{-1}$$

where the uncertainty in RE is the root-mean-square of the uncertainties of the experimental measurements. Literature values may differ slightly according to solvent and temperature corrections,[5] but the end result of RE = 36 kcal mol^{-1} (usually written with a sign reversal) is firm.

The two hydrogenation reactions in Kistiakowsky's method are shown by a Hess' law subtraction to be equivalent to one *isodesmic* reaction



which, in turn, is equivalent to



(2)

In isodesmic reactions,[6] the number of bonds of each formal type is conserved.[7] (Chesnut and Davis refer to this reaction as a *homomolecular homodesmotic* reaction and give a discussion of nomenclature and energetic implications. Suffice it to say that many errors cancel between the left and right sides of the equation, making the enthalpy of a reaction like eq 2 more reliable than the uncorrected enthalpy of atomization of any single constituent.)

The 36 kcal mol^{-1} of stabilization enthalpy found for isodesmic reaction 2 can be split into at least three component parts. First, one can note that cyclohexene has a small strain energy (1.2 kcal mol^{-1} in Benson's scheme)[8] so that 3.6 kcal mol^{-1} of the enthalpy change in reaction 2 can be ascribed to a change in strain enthalpy on going from the reactant state to the product state. Second, part of the remaining 32 kcal mol^{-1} of stabilization enthalpy would be present, as a result of conjugation, even if the molecule were acyclic. Dewar[9] separates this enthalpy from the total stabilization enthalpy, arguing that it has nothing to do with the cyclic stabilization of benzene. The remainder, 21 kcal mol^{-1}, is usually called the Dewar resonance energy. With these caveats in mind, we shall eschew the term "resonance energy" from this point on in favor of the term "total stabilization enthalpy" as minus the enthalpy change of reaction 2, $\Delta_r H^{298}$, calculated from eq 1, eq 3, or equations equivalent to eq 3.

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[4] Ege, S. *Organic Chemistry*, 2nd ed.; D. C. Heath: Lexington, MA, 1989.

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Substituting tabulated[5a] experimental values of $\Delta_f H^{298}$ for reaction 2, we get

$$\Delta_r H^{298} = \Delta_f H^{298}(\text{benzene}) + 2\Delta_f H^{298}(\text{cyclohexane}) - 3\Delta_f H^{298}(\text{cyclohexene}) \quad (3)$$

$$= (19.7 \pm 0.2) + 2(-29.5 \pm 0.2) - 3(-1.2 \pm 0.2) = -35.7 \pm 0.5 \text{ kcal mol}^{-1}$$

in agreement with the experimental value from hydrogenation (eq 1).

Calculating the $\Delta_f H^{298}$ of the three constituents in reaction 2 by G3(MP2), we have

$$(18.63) + 2(-29.29) - 3(-1.42) = -35.68 = -35.7 \text{ kcal mol}^{-1} \quad (4)$$

for the total stabilization enthalpy, in agreement the result of eq 3.

The full G3(MP2) procedure leading to $\Delta_f H^{298}$ contains empirical enthalpies of atomization from the standard state at 298 K of all elements in the molecule of interest, C and H in the case of benzene. This information is subject to experimental uncertainty, and it is not necessary for calculation of the enthalpy change of isodesmic reaction 2 because the number of atoms on either side of the reaction is the same and all atomic information cancels out.[10] This leaves only the G3(MP2) enthalpies,[11] H^{298}:

$$\Delta_r H^{298} = H^{298}(\text{benzene}) + 2H^{298}(\text{cyclohexane}) - 3H^{298}(\text{cyclohexene}) \quad (5)$$

$$= (-231.82430) + 2(-235.39571) - 3(-234.18629) = -5.6850 \times 10^{-2} \text{ hartrees}$$

$$= -35.67 = -35.7 \text{ kcal mol}^{-1}$$

also in agreement with eq 3, where H^{298} is the enthalpy of formation of the various molecules from isolated nuclei and electrons,[11] and the factor 627.51 is used to convert from hartrees to kcal mol^{-1}.

In the full G3(MP2) procedure, atomic spin−orbital coupling is included in obtaining H^{298} along with a "higher level correction energy" E(HLC), which is a purely empirical factor introduced into the G3(MP2) method to improve agreement with experiment.[2g] A procedural simplification can be achieved by noting that, in an isodesmic reaction, both E(HLC) and the spin−orbit coupling energy, E(SO),[2g] also cancel between the left and right sides of the equation. In ignoring E(HLC), we drop one empirical correction, and in ignoring E(SO), we are also ridding the calculation of a term which for some atoms is empirical.[10] This leaves us with a sum of four terms *none of which is empirical*, yielding a truly ab initio calculation for the molecular *energy* sum at 0 K:

$$S_E = E(\text{QCISD(T)/6-31G}(d)) + E(\text{MP2/G3MP2large}) - E(\text{MP2/6-31G}(d) + E(\text{ZPE})$$

where E(ZPE) is the zero-point energy.

The five term sum

$$S_H = S_E + H(\text{TCH})$$

is the molecular *enthalpy* sum at 298 K. H(TCH) is a thermal correction from the energy at 0 K to the enthalpy at some higher temperature, in this case to 298 K. H(TCH) is taken from statistical thermodynamics and consists of classical translational and rotational terms plus a vibrational contribution calculated using the harmonic oscillator approximation. Let us choose the latter equation, which yields S_H, as the more practical calculation, even though it contains one more term, H(TCH).

When the enthalpy sums have been obtained for each molecule in reaction 2, they are substituted into a Hess' law calculation:

$$\Delta_r H^{298} = \sum S_H(\text{products}) - \sum S_H(\text{reactants}) \quad (6)$$

$$= 627.51[2(-235.22869) + (-231.68511) - 3(-234.02854)] = -5.683 \times 10^{-2} \text{ hartrees}$$

$$= -35.69 = -35.7 \text{ kcal mol}^{-1}$$

as before.[12]

Further Approximations. Further simplification is possible based on two approximations. First, we find experimentally that hydrogenation of simple hydrocarbons is not very temperature-sensitive.[1c] Applying Hess' law to the thermal corrections for hydrogenation of benzene

$$\Delta_{\text{TCH}} H^{298} = \sum H(\text{TCH})(\text{products}) - \sum H(\text{TCH})(\text{reactants})$$

yields only −0.4 kcal mol^{-1} for the difference between $\Delta_r H^{298}$ and $\Delta_r H^0$ (strictly an energy of reaction $\Delta_r H^0 = \Delta_r E^0$). Within this difference, the thermal correction is unnecessary. For benzene $\Delta_r H^{298} \cong \Delta_r E^0$ and

$$\Delta_r H^{298} = \sum S_E(\text{products}) - \sum S_E(\text{reactants}) \quad (7)$$

(though we do not claim to have shown that this is true in general).

Second, the thermal correction is independent of the molecule except for the vibrational contribution, that is, C_p is classical for translation and rotation. Therefore, we examine the zero-point energy E(ZPE), which is proportional to the vibrational contribution to H^{298}. Applying Hess' law to E(ZPE) for reaction 2, $\Delta_r E(\text{ZPE}) = 0.7$ kcal mol^{-1}, which is opposite in sign and partly cancels with the overall thermal correction. The reaction energy for benzene, ignoring E(ZPE), is

$$\Delta_r E^0 = -36.0 \text{ kcal mol}^{-1}$$

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(10) Ochterski, J. W. Programs for Gaussian. At www.Gaussian.com, Gaussian Inc., 2000.

(11) H^{298} is the enthalpy of formation of atoms or molecules from independent nuclei and electrons in the gaseous state. Strictly speaking, this amounts to nothing more than redefining the standard state, though this standard state is energetically far removed from the usual definition of elements or compounds in their most stable form at room temperature.

(12) $\Delta_f H^{298}$ is sensitive to the number of digits carried in the calculations. The sums in eq 6 were calculated from single-point energies of 10 significant digits at double precision and rounded to 8 digits for input to eq 6. Different rounding schemes produce variations of the order of 0.01 kcal mol^{-1}

showing that the essence of the stabilization energy calculation lies in the ab initio calculations, MP2/6-31G(*d*), QCISD(T)/6-31G(*d*), and MP2/G3MP2large

$$\Delta_r H^{298} \cong \Delta_r E^0 = \sum S'_E(\text{products}) - \sum S'_E(\text{reactants}) \qquad (8)$$

where the prime indicates that the harmonic oscillator terms have been dropped from the calculation, leaving only the three ab initio terms

$$S'_E = E(\text{QCISD(T)/6-31G}(d)) + E(\text{MP2/G3MP2large}) - E(\text{MP2/6-31G}(d)) \qquad (9)$$

With these omissions, the result

$$\Delta_r H^{298} \cong -36.0 \text{ kcal mol}^{-1}$$

is robust for benzene.

Looking at the sum S'_E, one is tempted to test the Hess' law sum of the individual single-point ab initio calculations. When this is done, the QCISD(T)/6-31G(*d*) calculation gives a very respectable value of $\Delta_r H^{298} = -36.1$ kcal mol^{-1}, but neither the MP2/6-31G(*d*) nor even the MP2/G3MP2large basis set gives a satisfactory approximation to the stabilization energy of benzene (SE >42 kcal mol^{-1} for both). Evidently the stabilization energy calculation is insensitive to basis set expansion but sensitive to the post-Hartree–Fock extension. This is not surprising because the resonance part of the total stabilization is an energetic effect brought about by electron correlation.

Computational

All calculations were carried out using GAUSSIAN98.[13] The input geometry was obtained in the form of a Cartesian coordinate set by molecular mechanics with the aid of a graphical input interface as implemented in PCMODEL.[14] One can generate an input *z*-matrix using a PM3 semiempirical optimization,[3] or more conveniently, one can work directly from the geometry in Cartesian coordinates. Although recent versions of GAUSSIAN98 contain linked single-point calculations and ancillary calculations that provide E^0 and H^{298} directly, the same results can be obtained using older versions of GAUSSIAN98 or GAUSSIAN94 by a stepwise process.[2g,15]

Further information on the G-*n* series of methods is in the literature.[2] Several short, annotated BASIC programs containing necessary parameters for carrying out ancillary $\Delta_f H^{298}$ calculations are available.[15]

Results

Total stabilization enthalpies of benzene and seven substituted benzenes such as the ones calculated from eq 3, but relative to the 4-substituted cyclohexenes, e.g.,

$$\Delta_r H^{298} = \Delta_f H^{298}(\text{toluene}) + 2\Delta_f H^{298}(\text{methylcyclohexane}) - 3\Delta_f H^{298}(\text{4-methylcyclohexene}) \qquad (10)$$

are given in Table 1. In each case the calculation is carried out on the equatorial form.

Table 1. Total Stabilization Enthalpies[a]

method	H^{298}	E^0	QCISD(T)
benzene	35.7	35.3	36.1
toluene	35.9	35.8	36.6
ethylbenzene	36.4	36.1	37.4
phenylacetylene	37.7	37.3	39.0
styrene	38.4	38.1	39.6
phenol	38.4	38.0	38.6
aniline	39.8	39.5	39.6
phenylhydrazine	40.0	38.8	38.2
chlorobenzene	~32		

[a] Results in the first two columns are exact within the limits of the G3(MP2) method. Units are kcal mol^{-1}.

Total stabilization enthalpies calculated from enthalpies of formation from isolated gaseous atoms, H^{298} at 298 K are shown in column 1 of Table 1. Total stabilization enthalpies calculated from the energy of formation at 0 K from the gaseous atoms, E^0, shown in column 2 of Table 1, are approximate and assume that there is no temperature dependence of the isodesmic reaction 2. Stabilization enthalpies from the QCISD(T) single-point calculations in column 3 make this approximation and also assume that the differences between basis sets at the MP2 level

$$E(\text{MP2/G3MP2large}) - E(\text{MP2/6-31G}(d))$$

cancel across the isodesmic reaction 2. All calculations are at the MP2(full)/6-31G(*d*) geometry.

$\Delta_f H^{298}$. Once H^{298} is obtained from the G3MP2 procedure, conversion to $\Delta_f H^{298}$ is straightforward if tedious. A simple BASIC program[15] serves as a repository for essential information, avoids trivial calculational errors, and is easily extended to elements other than C, H, N, and O. Enthalpies of formation of the compounds involved in total stabilization enthalpy calculations are given in Table 2. Such experimental data as can be found in the standard resources[5a] are included for comparison. Experimental data are distinguished from calculated results by ± error bars. Calculations and experimental results have an arithmetic mean absolute difference $|(\text{exp} - \text{calc})|$ of ± 0.91 kcal mol^{-1} for 18 results. The signed arithmetic mean deviation of 0.35 kcal mol^{-1} indicates no particular trend. The largest differences are for ethylbenzene (2.2 kcal mol^{-1}) and phenylhydrazine (-2.8 kcal mol^{-1}).

Discussion

Results in Table 1 show that the stabilization energy of benzene is relatively uninfluenced upon substitution by small saturated and unsaturated alkyl groups or by simple substituents containing the electronegative atoms N and O. There is no dramatic effect (nullification, doubling, etc.) on the total stabilization enthalpy of the phenyl group brought about by monosubstitution. Trends

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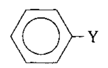
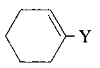
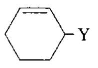
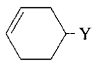
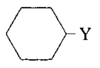
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Serena Software, Box 3076, Bloomington IN 47402-3076.

(15) Rogers, D. W. Programs for GAUSSIAN Thermochemistry. At www.MightyWords.com, search chemistry.

Table 2. G3MP2 Enthalpies of Formation[b]

-Y					
-H	18.6	-1.4	--	--	-29.3
	19.7±0.2	-1.2±0.2	--	--	-29.5±0.2
$-CH_3$	10.8	-10.3	-8.0	-9.1	-37.0
	12.0±0.1	-10.3±0.2	--	--	-37.0±0.2
-C≡CH	74.3	53.0	57.0	55.8	27.8
	73.3±0.4[a]				
$-CH=CH_2$	33.7	13.8	16.1	16.1	-11.9
	35.3±0.4	--	--	15.6±0.3	-11.7±0.2
	35.1±0.3[a]			16.6±0.3[a]	
$-CH_2CH_3$	4.9	-14.8	-13.5	-13.7	-41.5
	7.1±0.3	--	--	--	-41.0±0.4
-OH	-23.1	-43.8	-39.9	-41.4	-69.7
	-23.0±0.2	--	--	--	-68.4±0.5
$-NH_2$	20.4	-0.4	4.7	4.1	-24.0
	20.8±0.2	--	--	--	-25.1±0.3
$-NH-NH_2$	51.3	30.5	33.8	33.7	5.4
	48.5±0.3	--	--	--	--
-Cl	10.3	-12.0	-11.6	-12.1	--
	12.4±0.3	--	--	--	-39.1±0.9

[a] NIST compilation, ref 5e. [b] Values shown with uncertainties are experimental values. Experimental results are from ref 5a except where otherwise noted.

are, however, evident, and the largest difference, 4.3 kcal mol^{-1} between benzene and phenylhydrazine, is by no means negligible. All substituents except chlorobenzene increase calculated stabilization enthalpy relative to the total stabilization calculated for benzene. The increase is least for alkyl substitution, more for substitution by unsaturates, and most for substituents containing an electronegative atom, in this group, N or O. Stabilization by $-NH_2$ and $-NH-NH_2$ suggests considerable interaction between the lone pair of electrons on the N atom and the phenyl group.

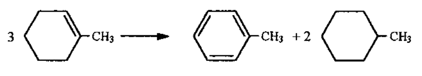
Chlorobenzene is interesting because of the electronegativity of chlorine. Unfortunately, although chlorobenzene itself and the chlorocyclohexenes are amenable to G3MP2 calculations, chlorocyclohexane exceeds our present computing capacity. The corresponding fluorinated compounds, interesting in their own right, are attractive as surrogates for chlorobenzene and the chlorocyclohexenes but it is not the MP2(full) calculations that exceed computer memory, it is the G3MP2large basis set that fails. This is a “frozen core” calculation involving valence electrons only which, of course, are the same in number for fluorine and chlorine.

One can back-calculate from the experimental value of $\Delta_f H^{298}$(chlorocyclohexane) to an estimated $H^{298} = -694.55992$ hartrees. From this value, the stabilization energy follows as

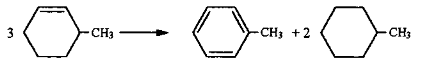
$$-690.98608 + 2(-694.55992) - 3(-693.35186) = -5.034 \times 10^{-2}\ \text{hartrees} = -31.59\ \text{kcal mol}^{-1}$$

This value has been entered into Table 1 and marked as approximate (~) to indicate the hybrid nature of the calculation, which includes both experimental and computed values of H^{298}. Stabilization energies calculated from E^0 and QCISD(T) by this method add no new information and have been omitted from the table.

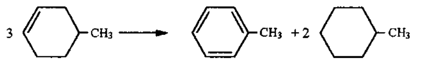
The most serious problem in these and all stabilization calculations is selection of a reference state or reference molecule. Starting with toluene, eq 2 is no longer unique because the reference molecule can be one of three possible choices:



(11-a)



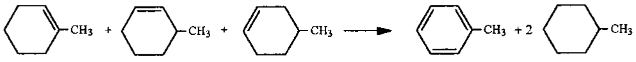
(11-b)



(11-c)

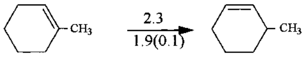
leading to $\Delta_r H^{298} = -32.3$, -39.2, and -35.9 kcal mol^{-1}.

An alternate approximation to the reference state in eq 2 is a reference state that represents all three possible isomers, that is,



When this calculation is carried out, one obtains the arithmetic mean of the total stabilization enthalpy values from eq 11a−c, i.e., a total stabilization enthalpy of 35.8, which is within 0.1 kcal mol^{-1} of the value calculated using 4-methylcyclohexene as the reference molecule. With this in mind, we have selected 4-methylcyclohexene as the reference molecule for the total stabilization enthalpies in Table 1 in order to minimize interaction between the substituent and the double bond in the reference state.

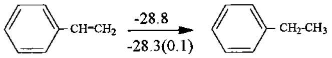
Equation 11a−c yields useful information about the interaction of the methyl group with the double bond in the 1-, 3-, and 4-methylcyclohexenes. The α methyl group in 1-methylcyclohexene stabilizes the molecule by 2.3 and 1.2 kcal mol^{-1} relative to the 3- and 4-methylcyclohexenes respectively as seen from their isomerization enthalpies



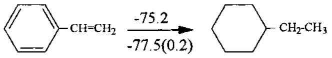
calculated from $\Delta_f H^{298}$ values in Table 2. (The experimental value is not strictly comparable, having been measured at 435 K.) The sign and magnitude of the isomerization enthalpy is not surprising in view of the "hyperconjugation enthalpy" expected in a molecule containing a methyl group α to a double bond.

An added structural complication is the possibility of axial and equatorial substitution[4] in the cyclohexenes and cyclohexane. This turns out not to be a problem for 1- and 3-methyl substitution in cyclohexene because the double bond holds the molecule flat enough that there is little or no geometric or energetic difference between the two possible orientations of the methyl group to the ring, making the terms "axial" and "equatorial" inapplicable. For the 4-isomer and for the saturated ring, however, there is a clear geometric and energetic distinction. Axial methylcyclohexane has long been known to be about 1.7 kcal mol^{-1} higher in enthalpy than the equatorial form.[4] This is confirmed by molecular mechanics calculations,[16] which also show that the other axial isomers in Table 2 have enthalpies of formation that are higher than the equatorial isomers, though the difference varies according to the size of the substituent from 0.2 kcal mol^{-1} for cyclohexylacetylene to 1.8 kcal mol^{-1} for cyclohexylethane. Where there is an energy difference between orientations, the equatorial substituent was selected for all of the calculations presented here.

$\Delta_{hyd}H^{298}$. Aside from verification through tabulated $\Delta_f H^{298}$ values, calculated results in Table 2 can also be compared to measured enthalpies of hydrogenation. For example, styrene has been hydrogenated to produce ethyl benzene under mild conditions that do not bring about

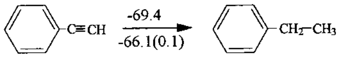


hydrogenation of the phenyl group.[17] Styrene has also been hydrogenated under more severe conditions to yield ethylcyclohexane.[18] The calculated $\Delta_{hyd}H^{298}$ from Table 2 is given above the arrow and the measured value is below it. In each case, the relative discrepancy between



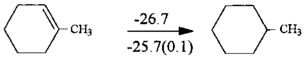
calculated and experimental values is 2−3%.

Similarly, $\Delta_{hyd}H^{298}$ can be calculated for phenylacetylene:



Here agreement with experiment[19] is not good (~5%), but much of the discrepancy can be ascribed to the calculated value of ethylbenzene. If the experimental $\Delta_{hyd}H^{298}$ for ethylbenzene is combined with the calculated value for phenylacetylene, one obtains $\Delta_{hyd}H^{298} = -67.2$ kcal mol^{-1}, in good agreement (<2%) with the direct measurement.

An enthalpy of hydrogenation is also available for 1-methylcyclohexene:



The experimental value[20] was measured in glacial acetic acid solution, not corrected for solvent effects. We have estimated these effects,[21] and we believe that the appropriate correction in the present case is about −0.7 kcal mol^{-1} such that the corrected $\Delta_{hyd}H^{298} = -26.4$ kcal mol^{-1} is in good agreement with the calculated value.

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