LETTERS

Heats of Formation of 1,3,5,7-Cyclooctatetraene and Bicyclo[4.2.0]octa-2,4,7-triene. A High-Level ab Initio Study

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We report herein the results of a high-level ab initio study of the D_{2d} and C_{2h} structures of 1,3,5,7-cyclooctatetraene, COT, and bicyclo[4.2.0]octa-2,4,7-triene, BOT. This information has been used to obtain, seemingly for the first time, the standard heat of formation of COT in the gas phase. Values obtained by means of standard atomization reaction are higher than the experimental value (4.7 kcal mol^{-1} at the G2 level). When isodesmic or homodesmotic reactions are used, the computational and experimental values agree well within the experimental uncertainties.

We have recently reported[1] the results of a detailed study of the potential energy surface (PES) of 1,3,5,7-cyclooctatetraene, COT, and bicyclo[4.2.0]octa-2,4,7-triene, BOT, at the CASSCF-(8,8)/6-31G(d) level of theory. Examined were in particular the species with symmetries D_{2d} (COT), C_s (BOT), C_{2h} (COT), D_4 (COT), D_{4h} (COT), and D_{8h} (COT). At this level, the first four were found to be minima on the PES. The lowest energies are those of COT (D_{2d} and C_{2h}) and BOT (C_s).

Because of our interest in this compound as well as on the more general problem of the reliabilility of thermodynamic data obtained by high-level ab initio methods, we have carried out a study at the G2(MP2) and G2 levels of BOT and the COT structures with symmetries D_{2d} and C_{2h} (see Chart 1).

Notice that while the most stable structure was found[1] to be that of D_{2d} symmetry, Paquette[2] has suggested the existence of a valence isomerization (VI) pathway between COT and BOT. Thus, a precise determination of the difference in thermodynamic stability of these species seems relevant.

Standard ab initio molecular orbital calculations[3] were performed with the Gaussian94 series of programs.[4] Energies were obtained at the G2[5] and G2(MP2)[6] levels of theory.

G2(MP2) and G2-calculated total energies at 0 K, and enthalpies at 298 K, for BOT and D_{2d} and C_{2h} structures of COT are given in Table 1. All of these structures are minima on the potential energy surface. As can be seen, D_{2d} is the most stable structure of COT, ca. 48 kcal mol^{-1} lower than that of C_{2h}.

In standard G2 theory, theoretical enthalpies of formation at 0 K are calculated through atomization reactions. In the case of COT or BOT, C_8H_8, $\Delta_f H°(0\ K)$ is calculated from the G2, or G2(MP2), energies at 0 K for the atomization reaction 1

$$C_8H_8(g) \rightarrow 8C(g) + 8H(g) \qquad (1)$$
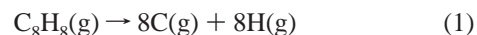
and the experimental heats of formation of C(g) and H(g).[7]

Theoretical enthalpies of formation at 298 K are calculated by correcting $\Delta_f H°(0\ K)$ as follows[9]

$$\Delta_f H°(C_8H_8, 298\ K) = \Delta_f H°(C_8H_8, 0\ K) + \Delta H_T^{calc}(C_8H_8) -$$
$$8\Delta H_T^{exp}[C(s)] - 4\Delta H_T^{exp}[H_2(g)] \quad (2)$$

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CHART 1: D_{2d} and C_{2h} Structures of 1,3,5,7-Cyclooctatetraene and C_s Structure of Bicyclo[4.2.0]octa-2,4,7-triene
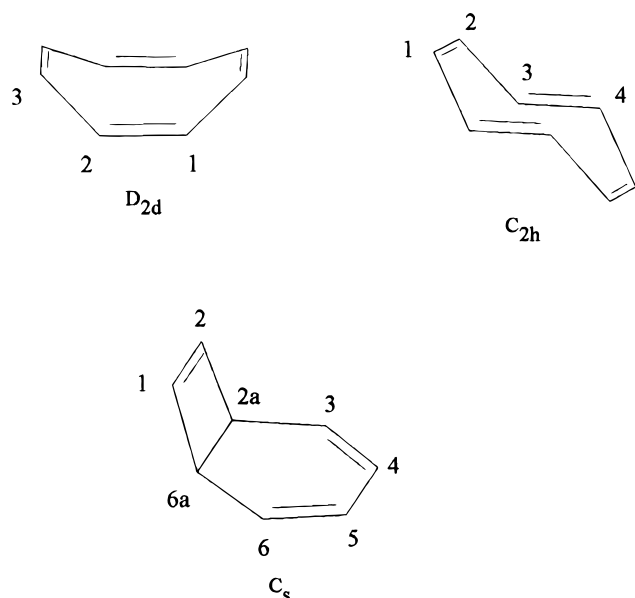
TABLE 1: G2(MP2) and G2 Total Energies at 0 K, and Enthalpies at 298 K, of 1,3,5,7-Cyclooctatetraene (COT) and Bicyclo[4.2.0]octa-2,4,7-triene (BOT)[a]

	G2(MP2)		G2	
structure	E_0	H_{298}	E_0	H_{298}
COT (D_{2d})	−308.965 03	−308.957 28	−308.970 60	−308.962 86
COT (C_{2h})	−308.889 04		−308.894 21	
BOT (C_s)	−308.952 35	−308.945 10	−308.957 97	−308.950 72

[a] All values in hartrees.

TABLE 2: G2(MP2)- and G2-Calculated Heats of Formation, at 298 K, of 1,3,5,7-Cyclooctatetraene (COT) and Bicyclo[4.2.0]octa-2,4,7-triene (BOT)[a]

	COT		BOT	
method	G2(MP2)	G2	G2(MP2)	G2
atomization	77.2	75.8	84.9	83.4
bond separation	72.0	71.4	79.7	79.0
homodesmotic	70.1	70.0		
experimental	71.1 ± 0.3[b]			

[a] All values in kcal mol⁻¹. [b] Value obtained from experimental $\Delta_f H°_{liquid}$ (ref 15) and $\Delta H°_{vap}$ (ref 16).

where $\Delta H_T^{calc}(C_8H_8)$ is the difference between the enthalpy at temperature T and 0 K and ΔH_T^{exp} for the elements refers to their standard states at 298 K and are taken from ref 10: 0.25 kcal mol⁻¹ for C(s) and 2.02 kcal mol⁻¹ for H₂(g).

G2(MP2)- and G2-calculated heats of formation at 298 K of COT and BOT are given in Table 2.
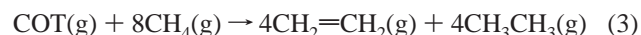
If we compare the calculated values with the experimental heat of formation of COT, we see that, at the G2(MP2) level, the calculated value for the D_{2d} structure of COT is 6.1 kcal mol⁻¹ higher than the experimental value, while these difference decrease to 4.7 kcal mol⁻¹ at the G2 level.

There has been some evidence in recent years that there is an accumulation of errors in the application of G2 theory (or similar approaches) to larger molecules.[11−13] Glukhotsev and Laiter[11] and Nicolaides and Radom[12] have shown that more accurate heats of formation can be derived using isodesmic or homodesmotic reactions[3] rather than atomization energies as in standard G2 theory. The cancellation of errors for such cases
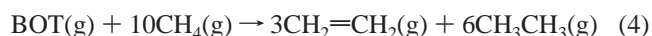
involving similar chemical bonds obviously improves the agreement with experiment.

As Raghavachari et al.[14] have pointed out, one of the deficiencies of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. These authors have very recently proposed[14] to use simpler, but better defined, reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions called "bond separation reactions", where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages, is used. The combination of such bond separation reactions with G2 theory leads to a dramatic improvement in the accuracy of theoretically evaluated heats of formation.

In our case, the bond separation reactions for COT and BOT, using their effective valence bond structure, are

$$COT(g) + 8CH_4(g) \rightarrow 4CH_2{=}CH_2(g) + 4CH_3CH_3(g) \quad (3)$$

and

$$BOT(g) + 10CH_4(g) \rightarrow 3CH_2{=}CH_2(g) + 6CH_3CH_3(g) \quad (4)$$

The bond separation reaction energies are then evaluated at G2 and G2(MP2) levels of theory using the experimentally known heats of formation for the reference molecules.[13]

G2(MP2)- and G2-calculated heats of formation using bond separation reactions 3 for COT and 4 for BOT are collected in Table 2. It is immediately obvious that there is a remarkable improvement in the performance of G2 theory when used in conjunction with isodesmic reactions, owing to better error cancellations. G2 theory is generally considered to be "semiempirical", since it has a higher level correction that is an empirically derived parameter to accommodate remaining deficiencies. However, the isodesmic scheme is nonempirical in the sense that the higher level corrections cancel exactly for isodesmic reactions.[14]

As it can be seen in Table 2, the heats of formation of COT evaluated at G2(MP2) and G2 levels using bond separation isodesmic reaction 3 are in very good agreement with the experimental value: at G2(MP2) the calculated value is 0.9 kcal mol⁻¹ higher than the experimental one, and at G2 level this difference decrease to only 0.3 kcal mol⁻¹.

The difference in the standard enthalpies of formation of 1,3,5,7-cyclooctatetraene (COT) and bicyclo[4.2.0]octa-2,4,7-triene (BOT) is 7.6 kcal mol⁻¹ at the G2 level. From a purely thermodynamic point of view, this value is sufficiently low to lend significant support to Paquette's contention[2] regarding the VI channel 1,3,5,7-cyclooctatetraene → bicyclo[4.2.0]octa-2,4,7-triene.

To calculate the heat of formation of COT we can use the following homodesmotic reaction:

$$COT(g) + 4CH_2{=}CH_2(g) \rightarrow 4CH_2{=}CHCH{=}CH_2(g) \quad (5)$$
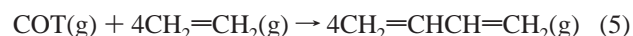
The results are collected in Table 2. As can be seen, while the agreement between the experimental and calculated (G2-(MP2) and G2) heats of formation of COT in the case of homodesmotic reaction 5 is excellent, it is slightly poorer than the agreement reached using bond separation isodesmic reaction 3.

Conclusions

We confirm that the D_{2d} structure of COT is the most stable of those examined in this work, ca. 8 kcal mol⁻¹ lower than the C_s structure of BOT at the G2 level of theory.

Theoretical heats of formation of COT evaluated from atomization reaction are higher than the experimentally determined value (6.1 and 4.7 kcal mol^{-1}, at G2(MP2) and G2 levels, respectively).

The use of bond separation isodesmic reaction permits one to obtain a very accurate heat of formation of COT, 71.4 kcal mol^{-1} at the G2 level, which differs only by 0.3 kcal mol^{-1} from the experimental value. To our knowledge, COT is the largest molecule for which this has been established at the G2 level of theory.

References and Notes

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