Figure 6. Energies in kcal/mol along the reaction path from the best CI calculations.

structures **2**, **3**, and **4** are minima on the excited triplet surface (T_1). The transition state connecting **3** and **2** has not been calculated, but the reaction is similar to the reaction of **3** to **4** and of **6** to **7**, so the barrier is expected to be similar.

The structure of the triplet diradical **8** was also optimized at the STO-3G RHF level and its RHF energy recomputed with an

SVP basis. As expected, **8** seems to be a true intermediate, and it is about 4 kcal/mol more stable than **3**. Hence this diradical could be involved in the ^{3}Hg sensitized 1,3 allylic shift of **2** to **2'**. However, no attempt was made to find the transition states for closing or opening the ring in this species.

Dewar[10] has discussed the analogous ring closure of homoallyl to form the cyclobutyl radical. He also found the four-membered ring to be more stable than the three-membered ring, but the transition-state barrier to ring closure was much higher for cyclobutyl than for cyclopropylcarbinyl. The competition between formation of **8** or **3** from **2** may not be exactly analogous, however, as the terminal carbon of the double bond is being attacked in forming cyclobutyl from homoallyl while an interior carbon is being attacked in forming **8** from **2**.

Conclusion

The monoradical and diradical ring-opening reactions seem quite similar. The cyclopropyldicarbinyl diradical (**3**) does appear to be a true intermediate, and so it could be involved in the triplet di-π-methane rearrangement. Its opening to **4** is predicted to be fairly easy; however. These findings are consistent with Zimmerman's postulated mechanism for the rearrangement.

A much more complete exploration of the triplet potential surface would be necessary to rule out unequivocally a direct 1,2 vinyl shift to form **4** from **2** without the intermediacy of **3**. Needless to say, even if calculations did rule out this direct pathway from **2** to **4** in the triplet di-π-methane rearrangement of 1,4-pentadiene (**1**), they would not preclude the circumvention of a cyclopropyldicarbinyl intermediate in the bicyclic molecules studied by Paquette and Bay. Nevertheless, in light of our computational findings, the results of Paquette and Bay are most economically explained in terms of reversible formation of such an intermediate, which they suggested as an alternative interpretation of their results.

Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 3. The Valence Isomers of Benzene

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Abstract: Heats of formation and strain energies of the benzene valence isomers Dewar benzene, benzvalene, prismane, and 3,3'-bicyclopropenyl are calculated at the 6-31G*(RMP2) level with use of homodesmic reactions, including the effects of zero-point energies and changes of enthalpy with temperature. Benzvalene and Dewar benzene have similar heats of formation, with the former lower by only 4 kcal/mol. Prismane and bicyclopropenyl have nearly the same heat of formation, with that of prismane lower by ca. 1 kcal/mol. Kekulé benzene is found to be ca. 7–9 kcal/mol higher in energy than benzene.

While benzene and its valence isomers of formula $(CH)_6$ have been of theoretical and experimental interest for many years, their relative energies are incompletely known: heats of formation have been determined experimentally only for benzene (I) and benzvalene (III), that of the latter by its heat of isomerization to benzene in solution. In the present paper we use ab initio molecular orbital theory to compute accurate heats of formation of the $(CH)_6$ benzene isomers Dewar benzene (II), benzvalene (III), prismane (IV), and 3,3'-bicyclopropenyl (V).

We have found that ab initio single-configuration self-consistent-field (SCF) molecular orbital calculations with restricted Møller–Plesset second-order perturbation theory (RMP2) furnish accurate heats of reaction for strained and unstrained hydrocarbons.[1] The basis set should contain d orbitals on carbon

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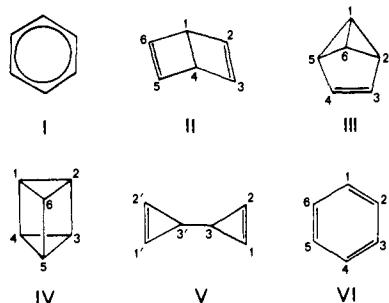
(6-31G*) and the reactions should be of the homodesmic type,[2] where reactants and products contain equal numbers of C—C and C=C bonds between nominally sp³- and sp²-hybridized carbons, as well as equal numbers of $-CH_3$, $-CH_2-$, $>CH-$, and $CH_2=$ groups. With use of these heats of reaction and experimental heats of formation for the other species, the heat of formation of the molecule of interest is obtained to 2–3 kcal/mol. Of course, zero-point energies and enthalpy corrections from 0 to 298 K are required for this accuracy. The enthalpy change of a homodesmic reaction containing unstrained systems, except for the molecule in question, is a good measure of the molecule's strain energy.[2a]

The present paper extends an earlier ab initio study[3] which utilized univariate searches at the STO-3G[4a] level; no relative energies were reported, owing to the known deficiencies of the STO-3G basis in the description of strained-ring molecules. The geometries reported here were determined at the 6-31G*(SCF)[4b] level with gradient optimization.

Methods

All RMP2 calculations were performed at the 6-31G*(SCF) geometries in the frozen-core approximation[4c] with optimized programs developed by us (The Queens College Quantum Chemistry Package). Heats of reaction at 0 K are computed from the ab initio energy differences corrected for zero-point energies. In the absence of experimentally determined vibrational frequencies for prismane by which these could be calculated, the theoretical values of Dai et al.[5] were used. Enthalpies are converted from 0 to 298 K according to the equations of Hehre et al.[6] For bicyclopropenyl, the zero-point energy and enthalpy corrections were taken to be equal to those of its "homodesmer", Dewar benzene. In the final step, the desired ΔH_f(298 K) is obtained from the heats of reaction corrected to 298 K and the experimental ΔH_f(298 K)'s.

Results

Table I contains the ab initio energies of the benzene valence isomers calculated at the 6-31G*(SCF) and (RMP2) levels. The optimized geometries are given in Table II. For the geometry of Dewar benzene there is good agreement with the electron-diffraction values involving carbons alone and fair agreement for parameters involving the hydrogens.[7] For benzvalene there is good agreement with the microwave-determined values[8] and also with the carbon parameters derived from an electron-diffraction study.[9]

Calculation of heats of formation and strain energies from the homodesmic reactions described below requires heats of formation, zero-point energies, and enthalpy corrections for ethane, ethylene, propene, and isobutane; they can be found in ref 1.

For Dewar benzene we employed the homodesmic reaction

4 propene + 2 isobutane →

Dewar benzene + 2 ethylene + 5 ethane

The experimental vibrational frequencies of Dewar benzene reported by Griffith and Kent[10] furnish a zero-point energy of 59.2 kcal/mol and an enthalpy correction from 0 to 298 K of 3.5 kcal/mol. The heats of formation of Dewar benzene at the 6-31G*(SCF) and RMP2 levels are 95.7 and 92.2 kcal/mol, respectively. Since the RMP2 level has a slight tendency to underestimate the heat of formation of cyclic polyenes,[1b] a good estimate of ΔH_f of Dewar benzene is the average value, 94.0 kcal/mol. A similar value, 94.93 kcal/mol, has been obtained by the MM2 method.[11] The disproportionation of two bicyclo[2.2.0]hex-2,3-enes into Dewar benzene plus bicyclo[2.2.0]hexane is then calculated to be nearly thermally neutral,[12] which seems reasonable. With use of this value for the heat of formation of Dewar benzene, a strain energy of 63.6 kcal/mol is obtained.

A similar homodesmic reaction can be used for 3,3'-bicyclopropenyl, since the same numbers and types of CH, C—C, and C=C moieties are involved. This compound has yet to be synthesized, and no calculations of vibrational frequencies have been made. However, as we have previously shown,[13] zero-point energies of isomeric hydrocarbons are very similar; the same is true for the ΔH contributions of isomers bearing the same numbers of —CH= and >CH— groups.[14] Thus it is reasonable to take the bicyclopropenyl zero-point and ΔH corrections as those of Dewar benzene. Since V has a torsional degree of freedom about the 3–3' bond, an energetic scan at the STO-3G level was performed, using coordinates optimized in this basis for the anti (C_{2h}) form. This conformation is the most stable, although other rotomeric forms are only 1–2 kcal/mol higher in energy, an observation also reported by Greenberg and Liebman.[15] From the 6-31G*(RMP2) energy of the anti form of bicyclopropenyl we obtain a strain energy of 107.2 kcal/mol and a heat of formation of 137.6 kcal/mol (140.0 kcal/mol at the SCF level).

For benzvalene we used the homodesmic reaction

2 propene + 4 isobutane → benzvalene + ethylene + 7 ethane
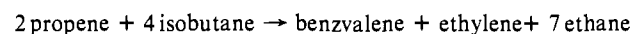
The ab initio energies in Table I yield a RMP2 strain energy of 81.3 kcal/mol and a heat of formation of 90.2 kcal/mol (88.0 kcal/mol at SCF). These values are in good agreement with the value of 87.3 kcal/mol derived from the heat of formation of benzene, 19.8 kcal/mol,[16] and the experimental heat of isomerization of benzvalene in chlorobenzene solution under silver ion catalysis.[17]

Finally, for prismane (IV), we used the homodesmic reaction

6 isobutane → prismane + 9 ethane

The ab initio energies of Table I, together with the zero-point energy and enthalpy corrections calculated from the scaled ab initio frequencies of Dai et al.,[5] furnish a strain energy of 148.9 kcal/mol

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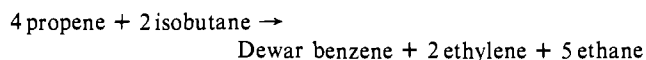
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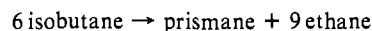(9) Bauer, S. H.; Karl, R. R., Jr. *J. Mol. Struct.* **1975**, *25*, 1.

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The Valence Isomers of Benzene

J. Am. Chem. Soc., Vol. 107, No. 18, 1985 5061

Table I. Energies of the Benzene Valence Isomers[a,b]

energy	Dewar benzene	benzvalene	prismane	3,3'-bicyclopropenyl
6-31G*(SCF)	-230.5653	-230.5708	-230.5033	-230.4948
6-31G*(RMP2)	-231.3273	-231.3372	-231.2691	-231.2549
$\Delta H_f(298\ K)^c$	94.0	90.2	136.4	137.6
strain energy[d]	63.6	81.3	148.9	107.2
zero-point energy	59.2	59.6	59.2	59.2
$H_{298\ K} - H_{0\ K}$	3.5	3.3	3.2	3.5

[a] Ab initio energies in atomic units were calculated at the 6-31G*(SCF)-optimized geometries of Table II; other energies are in kcal/mol. [b] The 6-31G*(SCF) and (RMP2) energies of benzene are -230.7031 and -231.4564 au respectively. [c] Calculated by using 6-31G*(RMP2) energies, as described in the text. [d] The calculated enthalpy change for the homodesmic reactions given in the text.

Table II Optimized Geometries of the Valence Isomers of Benzene[a,b] (Bond Lengths in Angstrom Units and Angles in Degrees)

| Dewar benzene		benzvalene[c]		prismane		bicyclopropenyl	
C_1C_2	1.525	C_1C_2	1.512(1.529)	C_1C_2	1.507	C_1C_2	1.278
C_2C_3	1.323	C_1C_6	1.432(1.452)	C_2C_3	1.549	C_1C_3	1.495
C_1C_4	1.553	C_2C_3	1.513(1.503)	C_1H_1	1.074	$C_3C_{3'}$	1.513
C_1H_1	1.082	C_3C_4	1.321(1.339)	$\angle H_1C_1C_2$	129.7	C_1H_1	1.069
C_2H_2	1.075	C_1H_1	1.072(1.078)			C_3H_3	1.086
$\angle H_2C_2C_3$	133.5	C_2H_2	1.076(1.082)			$\angle H_1C_1C_2$	149.6
$\angle H_1C_1C_4$	121.6	C_3H_3	1.073(1.078)			$\angle H_3C_3C_1$	118.8
$\angle H_3C_3C_2C_1$	177.0	$\angle H_1C_1C_6$	135.4(133.7)			$\angle C_{3'}C_3C_1$	121.6
$\angle C_2C_1C_4C_5$	117.7	$\angle H_2C_2C_3$	123.2(124.2)			$\angle H_{3'}C_3C_{3'}H_3$	180.0
		$\angle H_3C_3C_4$	129.1(128.9)				
		$\angle C_2C_3C_4$	105.5(105.7)				
		$\angle C_2C_1C_6C_5$	106.1(106.0)				

[a] Hydrogens are numbered in the same manner as the carbons to which they are attached. [b] 6-31G*(SCF)-optimized bond lengths of benzene are the following: CC, 1.386 Å; CH, 1.075 Å. [c] Numbers in parentheses are the microwave spectroscopic values reported by Suenram and Harmony (ref 8).

and a heat of formation at the RMP2 level of 136.4 kcal/mol.

In summary, benzvalene and Dewar benzene have similar enthalpies of formation, 90.2 and 94.0 kcal/mol, respectively. Prismane and 3,3'-bicyclopropenyl also have similar heats of formation, 136.4 and 137.6 kcal/mol, respectively. The strain energies of the isomers are the following: Dewar benzene 63.6, benzvalene 81.3, bicyclopropenyl 107.2, and prismane 148.9 kcal/mol. The difference in strain energies of bicyclopropenyl and Dewar benzene is equal to the difference in their heats of formation, since they are referred to the same unstrained systems.

Discussion

The energies of the benzene valence isomers are easily understood. At the RMP2 level, bicyclopropenyl has a strain energy of 107.2 kcal/mol; that is almost double the strain energy of cyclopropene, 54.4 kcal/mol, calculated from the reaction

2 propene + propane → cyclopropene + ethylene + 2 ethane
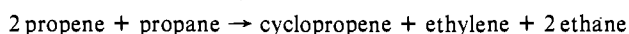
The RMP2 strain energy of Dewar benzene is 63.6 kcal/mol, also similar to twice the strain energy of cyclobutene, 31.2 kcal/mol, calculated from

2 propane + 2 propene → cyclobutene + 3 ethane + ethylene
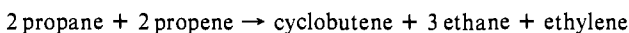
Clearly, the strain energy due to ring fusion is small. The strain energy of benzvalene is 81.3 kcal/mol. Since bicyclobutane has a RMP2 strain energy of 67.9 kcal/mol, the difference is only 13.4 kcal/mol, which is reasonably ascribed to the two cyclopentene systems. The angles at the double bonds are 105.5°, quite far from 120°. The present study is the first to predict a lower heat formation for benzvalene than for Dewar benzene. The opposite was found in a MINDO/3 study[18] and by direct comparison of 4-31G energies calculated[15a] at the STO-3G geometries.[3] Dewar benzene is also the lower-energy isomer in the hexamethyl and hexatrifluoromethyl series, by 8.0[19] and 6.4[20] kcal/mol, re-

spectively. These results are probably due to a greater amount of steric repulsion in the substituted benzvalenes than in the corresponding Dewar benzenes.

Although Kekulé benzene or cyclohexatriene (VI) is not a minimum on the C_6H_6 potential energy surface, it is interesting to know the energy of this hypothetical valence isomer relative to that of benzene itself. Assuming C=C and C—C lengths of 1.334 and 1.462 Å, respectively—the experimental values for cyclooctatetraene[21]—and a CH length of 1.075 Å, the 6-31G*-(SCF) and (RMP2) energies of VI exceed their benzene (I) counterparts by 6.8 and 8.6 kcal/mol, respectively. Similar values for Kekulé benzene at C—C and C=C bond lengths of 1.46 and 1.34 Å were recently reported by Haddon et al.[22] Let us assume that the increase in benzene total energy upon distortion is due to the additive effects of a loss of π conjugation and a decrease in energy attending return to a polyene with alternate bond lengths. An estimate of the latter can be obtained from cyclooctatetraene: three-fourths the difference in energy between a 6-31G*-(SCF)-optimized cyclooctatetraene and one with equal bond lengths (CC = 1.397 Å, CH = 1.086 Å) and the same CCC angles (126.3°) is 20 kcal/mol at the SCF level. Thus the loss in π conjugation is 27 kcal/mol. Kollmar[23] has computed a total resonance energy of 86 kcal/mol for benzene at the SCF level, a value which is derived from a wavefunction with nonconjugated π molecular orbitals. Taken together with the present SCF result, it appears that a Kekulé benzene has already lost 27/86 or about 30% of the resonance energy of benzene.

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