CI Calculations on Didehydrobenzenes Predict Heats of Formation for the *Meta* and *Para* Isomers That Are Substantially Higher than Previous Experimental Values

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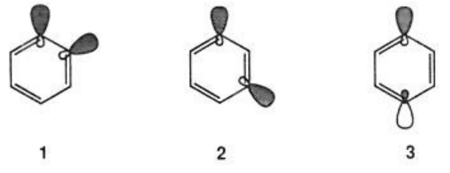
Abstract: CI calculations with the 6-311G** basis set on *o*-didehydrobenzene (**1**) predict a singlet–triplet energy difference of 34.4 kcal/mol, which is about 3 kcal/mol smaller than the value measured by Leopold, Miller, and Lineberger. Calculations at this level also predict energy differences between the singlet ground state of **1** and those of the *meta* (**2**) and *para* (**3**) isomers of respectively 15.8 and 28.4 kcal/mol. These values are both larger by about 6 kcal/mol than the values for the differences between the heats of formation obtained from the experiments of Wenthold, Paulino, and Squires. Computational evidence is presented that calculations which increased ΔE_{ST} in **1** by 3 kcal/mol would also increase the energy differences computed between **1** and **2** and **1** and **3** by about the same amount. In addition, the calculated values of ΔE_{ST} in **2** and **3** are both at least 8 kcal/mol smaller than the values estimated from two different types of experimental data for ΔH°_f for the triplets and the experimental values of ΔH°_f reported for the singlets. Calculations of the bond strengths in singlet and triplet **1** support the experimental value of $\Delta H^\circ_f = 106 \pm 3$ kcal/mol for singlet **1**, but the calculations predict bond strengths in **2** and **3** that are about 8 kcal/mol smaller than the values obtained from their experimental heats of formation. Since the bicyclic isomers (**4** and **5**) of **2** and **3** are both calculated to be higher in energy than their monocyclic counterparts, the formation of **4** and **5** in the experiments of Wenthold, Paulino, and Squires cannot reconcile the heats of formation, measured by them, with the energies for the lowest singlet states of **2** and of **3**, calculated by us. On the basis of our computational results, it is proposed that ΔH°_f for **2** and **3** is higher than that of **1** by respectively ≥18 and ≥30 kcal/mol.

Recently, Squires and co-workers have reported values for the heats of formation of *o*-, *m*-, and *p*-didehydrobenzene (**1–3**), based on energy-resolved, collision-induced dissociation measurements.[1] The values of ΔH°_f obtained for **1–3** are respectively 106 ± 3, 116 ± 3, and 128 ± 3 kcal/mol. The heat of formation of **1** is in good agreement with two other recent measurements, both of which give $\Delta H^\circ_f = 105 \pm 5$ kcal/mol,[2,3] and with an estimate of $\Delta H^\circ_f = 104 \pm 4$ kcal/mol[4] that is based on the assumption that ΔH°_f differs from bond additivity by the measured singlet–triplet splitting of $\Delta E_{ST} = 37.7 \pm 0.6$ kcal/mol in **1**.[5] The energies of **2** and **3**, relative to **1**, are in reasonable agreement with the values of 14.5 and 23.3 kcal/mol that were obtained from GVB/4-31G calculations by Noell and Newton.[6]



1 2 3

From the heat of formation of benzene (20.0 kcal/mol),[7] a value of 111 kcal/mol for its C–H bond dissociation energy (BDE),[8] and the heats of formation of **1–3** that they measured, Squires and co-workers obtained BDEs for the *ortho*, *meta*, and *para* C–H bonds in the phenyl radical of respectively 79 ± 3, 89 ± 3, and 101 ± 3 kcal/mol. The differences between the C–H BDE in benzene and these C–H BDEs in the phenyl radical may be taken as the strengths of the C–C bonds between the dehydrocarbons in **1–3**.[9] The resulting BDEs for these weak C–C bonds are respectively 32, 22, and 10 kcal/mol.[10]

The value of 10 kcal/mol for the energy of interaction between C_1 and C_4 in **3** seems surprisingly large. Because the distance between these two carbons is calculated to be on the order of 2.7 Å,[6] the dominant interaction between these carbons is via the C_2–C_3 and C_5–C_6 bonds rather than directly through space.[6,11] Calculations[12a,b,d] on 1,4-didehydrocubane,[12a,c] in which the dominant interaction between C_1 and C_4 is mediated by the highly strained C–C bonds of the cubane skeleton, find that the bond energy between these carbons amounts to only 7.4–7.6 kcal/mol.[12a,b,d] In contrast, the interaction between the dehydrocarbons in **3** is mediated by a pair of C–C σ bonds[11] that are not just unstrained but are particularly strong because they are made from atomic orbitals that are nominally sp^2 hybrids. Therefore, a bond energy of 10 kcal/mol between the dehydrocarbons in **3** would be much larger than one might have anticipated.

If it is assumed that the heats of formation of the triplet states of **2** and **3** can be estimated from bond additivity, then the C–C

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BDEs are equal to the singlet–triplet energy differences ΔE_{ST}. Making this assumption and using Squires' heats of formation,[1] Zhang and Chen obtained values of ΔE_{ST} = 26 kcal/mol for **2** and ΔE_{ST} = 14 kcal/mol for **3**.[4] These values for ΔE_{ST} are each 4 kcal/mol higher than Squires' values for the C–C BDEs only because Zhang and Chen used a value of 113 kcal/mol for the C–H BDE in benzene[10] rather than the value of 111 kcal/mol[8] that was employed by Squires.[1]

A singlet–triplet energy difference for **3** of 10–14 kcal/mol would be roughly an order of magnitude larger than the values calculated for **3**[6] and transoid tetramethylene[13] and of about the same size as the value of ΔE_{ST} computed for 1,4-didehydrocubane.[12a,b] Thus, like the C–C BDE of 10 kcal/mol, a singlet–triplet energy difference of 10–14 kcal/mol in **3** would be surprisingly high.

The largest uncertainty in these estimates of the BDE and ΔE_{ST} in **3** is in the value of 128 kcal/mol for the heat of formation of singlet **3**.[1] Therefore, if these values for the BDE and ΔE_{ST} in **3** are, in fact, too high, the source of such an error would most likely be in a value of ΔH°_f for **3** that was too low.

The heat of formation of **3** is important not only for estimating the bond energy and the singlet–triplet gap in this diradical but also for establishing the energy of **3** relative to those of hex-3-ene-1,5-diyne and the transition state that connects these two molecules.[14] For example, using Bergman's values of 126 kcal/mol for ΔH°_f for hex-3-ene-1,5-diyne and 32 kcal/mol for $\Delta H^\ddagger$ for its rearrangement to **3**,[14] ΔH°_f = 128 ± 3 kcal/mol for **3** would make it nearly isoenergetic with the enediyne and place **3** in an energy well 30 kcal/mol deep. The finding that the mechanism of activation of several antitumor antibiotics involves the rearrangement of an enediyne to a *p*-didehydrobenzene[15] gives additional impetus to obtaining an accurate value for the heat of formation of **3**.

In order to obtain computational estimates of the energies of **2** and **3**, relative to that of **1**, and the C–C BDEs and singlet–triplet splittings in these molecules, we have performed *ab initio* calculations. In these calculations, better basis sets were used and more electron correlation was included than in the calculations of Noell and Newton.[6] Herein, we report the results of our calculations on **1–3**.

Computational Methodology

Geometries were optimized using the 6-31G*[16] basis set. For the triplet states of **1–3** and for the phenyl radical, ROHF wave functions were used,[17] but for the singlet states, because of their diradical character, two-configuration (TC) SCF wave functions were employed.[18] Vibrational analyses were carried out for both the singlet and the triplet states of **1–3**, and all were found to be minima on the C_6H_4 potential surface. These calculations were carried out with GAUSSIAN90[19] and with GAMESS.[20]

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(14) (a) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660. (b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.
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(16) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(17) We also carried out UHF geometry optimizations for the triplet states of **1–3** and for the phenyl radical. In the case of **1** and **3**, the differences between the ROHF- and UHF-optimized geometries were very small, less than 0.005 Å for bond lengths and 0.6° for bond angles. However, for triplet **2** and the phenyl radical, the differences between UHF and ROHF geometries were somewhat larger, presumably because of the substantial contamination of the UHF wave functions by higher spin states. The UHF wave functions have S^2 = 2.83 for triplet **2** and S^2 = 1.43 for the phenyl radical, whereas the pure triplet and pure doublet ROHF wave functions have respectively S^2 = 2.00 and 0.75. Nevertheless, CI calculations at the ROHF- and UHF-optimized geometries gave energies that were the same to within 0.4 kcal/mol.
(18) The optimized geometries are available as supplementary material.
(19) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN90; Gaussian, Inc.: Pittsburgh, PA, 1990.

Table I. Distances (r_{C-C}, Å) between the Dehydrocarbons at the TCSCF- and ROHF/6-31G*-Optimized Equilibrium Geometries for the Lowest Singlet and Triplet States of 1–3

	1	2	3
r_{C-C} (singlet)	1.260	2.198	2.676
r_{C-C} (triplet)	1.386	2.323	2.650

Table II. TCSCF and ROHF/6-31G* Electronic and Zero-Point Energies (ZPEs) (kcal/mol) of the Lowest Singlet and Triplet States of 1–3

	1	2	3
TCSCF (singlet)	0[a]	12.6	23.2
ROHF (triplet)	27.9	25.4	23.8
ZPE (singlet)	0[b]	–0.6	–0.5
ZPE (triplet)	–0.2	–0.4	–0.3
TCSCF + ZPE (singlet)	0	12.0	22.7
ROHF + ZPE (triplet)	27.7	25.0	23.5

[a] Relative to –229.4361 hartrees. [b] Relative to 50.9 kcal/mol.

In order to include the effects of electron correlation between the weakly bonded electron pairs and the rest of the electrons in **1–3**, CI calculations were performed. GAUSSIAN90[19] was used for most of the CI calculations involving a single reference configuration, and MELDF[21] was employed for multireference CI calculations.

Results and Discussion

The ROHF and TCSCF/6-31G* geometries for **1–3**[18] are very similar to those obtained by Noell and Newton with the 4-31G basis set.[6] The distances between the dehydrocarbons in the lowest singlet and triplet states of **1–3** are given in Table I.

In the singlet state of **1**, the C_1–C_2 bond length is calculated to be 1.260 Å, which is closer to the C–C bond length in acetylene than that in benzene. In contrast, the bond length between the dehydrocarbons in the triplet is computed to be close to the C–C bond length in benzene. The computational finding (Table II) that the TCSCF energy of singlet **1** is 27.7 kcal/mol lower than the ROHF energy for the triplet is also indicative of appreciable double-bond character in the plane of the molecule between the dehydrocarbons in the singlet.

At the TCSCF-optimized geometry for **2**, the C_1–C_3 distance is 0.13 Å shorter than that found for the lowest triplet state of **2**, again indicating some σ bonding between the dehydrocarbons in the singlet that is not present in the triplet. The fact that the TCSCF energy of the singlet is 12.8 kcal/mol lower than the ROHF energy of the triplet also supports the existence of a weak bond between these two carbons in the singlet. Moreover, the ratio of the squares of the coefficients of the two configurations in the TCSCF wave function for **2** is 3.50. This ratio is smaller than that of 8.25 in the wave function for **1** but quite different than the ratio of unity which would be expected if **2** were a true diradical.[22]

In **3**, the dehydrocarbons C_1 and C_4 are too far apart (>2.6 Å) for the atomic orbitals on them to overlap substantially. Consequently, the distances between C_1 and C_4 in the singlet and triplet are very similar, and as shown in Table II, the two states also have very similar energies. The singlet wave function of **3** also shows considerable amounts of diradical character; the ratio of the squares of the TCSCF coefficients, 1/1.43, is much closer to unity than that in **2** or **3**.

In the dominant configuration in the TCSCF wave function for singlet **3**, the antisymmetric combination ($5b_{1u}$) of atomic orbitals at C_1 and C_4, rather than the symmetric combination

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(21) Developed at the University of Washington by L. McMurchie, S. Elbert, S. Langhoff, and E. R. Davidson and modified by D. Feller and D. Rawlings.
(22) For review, see: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1–72.

($6a_g$), is preferentially occupied. This computational result is in agreement with previous findings that the interaction between C_1 and C_4 occurs principally through bonds rather than through space.[6,11] The occupation number of 1.34 for $5b_{1u}$, which is antibonding between C_1 and C_4, is responsible for the finding that in the singlet state of **3**, the distance between C_1 and C_4 is actually slightly longer than that in the triplet, where $5b_{1u}$ and $6a_g$ are each occupied by one electron.

The relative TCSCF energies in Table II are close not only to those obtained by Noell and Newton with the 4-31G basis set but also to the relative heats of formation measured by Squires and co-workers.[1] However, at the TCSCF/ROHF level of theory, the singlet–triplet gap, ΔE_{ST}, calculated for **1** is 10.0 kcal/mol smaller than the value of 37.7 kcal/mol that was measured measured directly by the photoelectron-detachment experiments of Leopold, Miller, and Lineberger.[5] This large discrepancy indicates that TCSCF calculations, not only with the 4-31G[6] basis set but also with 6-31G*, significantly overestimate the energy of the singlet state of **1** relative to the ROHF energy of the triplet. This finding also calls into question the accuracy of the TCSCF/4-31G[6] and 6-31G* energies of singlet **1** relative to the corresponding TCSCF energies of **2** and **3**.

Schaefer and co-workers have previously found in calculations with a DZP basis set that their TCSCF/ROHF value of ΔE_{ST} = 27.7 kcal/mol in **1** is increased to 32.2 kcal/mol at the CI level when all single and double excitations (CISD) are allowed from one reference configuration for the triplet and two for the singlet.[23] Application of the Davidson correction for the effect of quadruple (Q) excitations[24] increased their computed value for ΔE_{ST} to 33.3 kcal/mol. Although the CISDQ value for ΔE_{ST} is still about 4 kcal/mol below the experimental value of 37.7 ± 0.6 kcal/mol, the CISDQ value is in much better agreement with experiment than the TCSCF/ROHF value, which is 10 kcal/mol too low. Schaefer speculated that "To obtain further improvements in the theoretical accuracy, significant expansion of the basis set would most probably be needed".[23]

In order to assess how the calculated singlet–triplet gap in **1** depends on both the basis set and the type of electron correlation that is included, we carried out several calculations on *cis* bent acetylene models for **1**. In model 1, the HCC bond angles were fixed at the TCSCF and ROHF values calculated for respectively the singlet and triplet states of **1**; and the C–C and C–H bond lengths of the model were optimized at the TCSCF/ROHF level. In model 2, both the bond angles and the C–C bond lengths were fixed at the optimized values computed for the singlet and triplet states of **1** and only the C–H bond lengths of the model were optimized.

The results of the model calculations are summarized in Table III. They show that π-SD(2) and π-SD(3) CI calculations give nearly the same singlet–triplet energy gaps as CISD(2) calculations, which include *all* single and double excitations from two reference configurations for the singlet and one for the triplet. However, much smaller values of ΔE_{ST} are obtained with π-SD(1) CI calculations.

The latter calculations allow SD excitations from two reference configurations for the singlet and one reference configuration for the triplet but for only the π electrons. Therefore, the π-SD(1) CI singlet wave functions do not include correlation between the pair of electrons that form the weak σ bond and the π electrons. Thus, the finding that π-SD(1) CI calculations give a lower value of ΔE_{ST} than even TCSCF/ROHF calculations indicates the importance of including this type of electron correlation for obtaining reasonably accurate values of ΔE_{ST} for the bent acetylene models for **1**.[25]

Table III. Singlet–Triplet Energy Differences (kcal/mol) in Two *Cis* Bent Acetylene Models for **1**

calculation	basis set	model 1[a]	model 2[b]
TCSCF/ROHF[c]	6-31G*	39.4	42.6
π-SD(1) CI[d]	6-31G*	36.5	38.2
π-SD(2) CI[e]	6-31G*	45.5	46.6
π-SD(3) CI[f]	6-31G*	45.7	46.7
CISD(1)[g]	6-31G*	36.0	37.0
QCISD(1)[g,h]	6-31G*	42.4	43.4
QCISD(T)(1)[g,h]	6-31G*	45.9	46.7
CISD(2)[d]	6-31G*	45.7	47.4
π-SD(2) CI[e]	6-31G**	46.0	47.2
π-SD(2) CI[e]	6-311G*	47.3	48.2
π-SD(2) CI[e]	6-311G**	48.0	48.8
π-SD(2) CI[e]	6-311G (2d1f1p)	48.2	49.3

[a] HCC angle frozen at 125.7° for the singlet and 121.1° for the triplet and C–H and C–C bond lengths optimized at TCSCF/6-31G* for the singlet and ROHF/6-31G* for the triplet. [b] HCC angle frozen at 125.7° for the singlet and 121.1° for the triplet, C–C bond lengths frozen at 1.260 Å for the singlet and 1.386 Å for the triplet, and the C–H bond length optimized at TCSCF/6-31G* for the singlet and ROHF/6-31G* for the triplet. [c] Level of calculation for respectively the singlet and the triplet. [d] Two reference configurations, $|...4a_1^2\rangle$ and $|...3b_2^2\rangle$, for the singlet and one, $|...4a_13b_2\rangle$, for the triplet. [e] For the singlet, the calculation includes all SD excitations from the π to the π* space from the two reference configurations as well as all π-S excitations from $|...4a_13b_2\rangle$. For the triplet, it includes all SD excitations from the π to the π* space from the reference configuration as well as all π-S excitations from $|...4a_1^2\rangle$ and $|...3b_2^2\rangle$. [f] All SD excitations from the π to the π* space, requiring only that $4a_1$ and $3b_2$ are occupied by a total of two electrons. This prescription generates all SD excitations from the π to the π* space from three reference configurations for both the singlet and the triplet. [g] One reference configuration for both the singlet and the triplet. [h] See ref 26 for a discussion of this method.

π-SD CI wave functions that are based on all three possible occupancies of the σ HOMO and σ* LUMO do include correlation between the pair of electrons in the high-energy σ orbitals and the π electrons. As shown in Table III, π-SD(2) CI calculations, which allow only π-S excitations from the open-shell reference configuration for the singlet and from the two closed-shell configurations for the triplet, give values of ΔE_{ST} that are the same to within 0.2 kcal/mol as those of π-SD(3) CI calculations, in which π-SD excitations are allowed from all three reference configurations. In fact, the absolute singlet and triplet energies that are obtained from these two types of CI wave functions are the same to within 0.4 kcal/mol. Because a much smaller number of spin-adapted configurations is generated in π-SD(2) CI than in π-SD(3) CI, most of our CI calculations on **1**–**3** were performed at the π-SD(2) CI level.

Full CISD calculations that are based on just one reference configuration for the singlet are less successful than π-SD(2) CI for computing the singlet–triplet energy differences. As shown in Table III, CISD(1) gives values for ΔE_{ST} that are about 10 kcal/mol smaller than those of CISD(2). A similar result was found by Schaefer and co-workers in their calculations on **1**.[23] QCISD(1) calculations, which include the effect of quadruple excitations,[26] increase ΔE_{ST} by about 6 kcal/mol but only at the QCISD(T)(1) level, which contains corrections for both triple and quadruple excitations,[26] are the values for ΔE_{ST} about the same as those obtained by both CISD(2) and π-SD(2) CI.

The results in Table III show that the calculated singlet–triplet energy gaps in the models are also dependent on the size of the basis set. As the size of the basis set is increased beyond 6-31G*,

(23) Scheiner, A. C.; Schaefer, H. F., III; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 3118. More recently, the results of calculations on other properties of **1** have also been reported; see: Scheiner, A. C.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1991**, *177*, 471.

(24) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Dordrecht: The Netherlands, 1974.

(25) We find that correlation between the π electrons and the pair that form the weak σ bond diminishes the weight of the second most important configuration, in which the σ* LUMO is doubly occupied. The presence of this configuration removes some of the ionic terms that would occur in the wave function for the high-energy pair of σ electrons if just the σ HOMO were doubly occupied.[22] Including σ–π correlation stabilizes these ionic terms, thus reducing the weight of the second configuration. Decreasing the occupation of σ* increases the strength of the bond between the dehydrocarbons.

(26) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

Table IV. π-SD(2) CI[a] Energies (kcal/mol) of the Lowest Singlet and Triplet States of 1–3 Calculated at Geometries That Were Optimized at the TCSCF/6-31G* Level for the Singlets and at the ROHF/6-31G* Level for the Triplets and Including Zero-Point Energy Differences[b]

basis set	state	1	2	3
6-31G*	S	0[c]	15.0	27.3
	T	33.2	30.7	29.6
6-311G**	S	0[d]	15.8	28.4
	T	34.4	31.8	30.7

[a] See footnote *e* in Table III for a description of this type of calculation. [b] The ZPEs are given in Table II. [c] Relative to −229.5362 hartrees. [d] Relative to −229.5880 hartrees.

the calculated values of ΔE_{ST} also increase. Adding a third, independent Gaussian (6-311G*) increases the singlet–triplet splittings by 1.6–1.8 kcal/mol; putting polarization functions on hydrogen has an effect about a third as large,[27] and adding more polarization functions (d and f orbitals) to the carbons has a still smaller effect on ΔE_{ST}.

Having found from our model calculations that π-SD(2) CI gives values of ΔE_{ST} that are close to those obtained at the full CISD(2) level, we performed π-SD(2) CI calculations on the lowest singlet and triplet states of **1** and also on those of its *meta* (**2**) and *para* (**3**) isomers. The results are given in Table IV.[28] Addition of the Davidson correction for the estimated effect of including quadruple excitations[24] provides the greatest stabilization for singlet **1** but causes only small changes in the relative energies shown in Table IV. Relative to the energy of singlet **1**, all the other energies increase by 0–0.4 kcal/mol, except for that of triplet **3**, which increases by 0.6 kcal/mol.

As discussed above, Schaefer and co-workers have previously computed the singlet–triplet gap in **1** to be 33.3 kcal/mol at the full SD CI level, with a DZP basis set, two reference configurations for the singlet, and the addition of the Davidson correction.[23] We obtain essentially the same result for **1** at the π-SD(2) CI/6-31G* level but with much less computational effort.

Also as discussed above, the value for ΔE_{ST} in **1** that was computed by Schaefer and co-workers[23] is smaller by about 4 kcal/mol than the experimental value;[5] Schaefer attributed this discrepancy to deficiencies in the size of the basis set (DZP) that was used. Not only our model calculations but also the results of our calculations on **1** support Schaefer's conjecture.

Because π-SD(2) CI calculations on **1** generate less than one-hundreth as many configurations as full CISD(2) calculations with the same number of basis functions, we were able to compare the results of π-SD(2) CI/6-31G* calculations with those obtained using the larger 6-311G** basis set. As shown in Table IV, use of this larger basis set increases the calculated value of ΔE_{ST} by 1.2 kcal/mol, thus bringing the calculated value closer to the experimental value. On the basis of the results in Table III, addition of more polarization functions to the basis set on carbon would probably result in a further decrease, albeit of smaller size, in the difference between the calculated and experimental values of ΔE_{ST} in **1**.

At the π-SD(2) CI level of theory, the singlet–triplet gap calculated for **1** is in much better agreement with experiment than that computed at the TCSCF/ROHF level. However, the energies of the singlet states of **2** and **3**, relative to that of **1**, in Table IV are rather different from those obtained at the TCSCF level of theory, which are shown in Table II. Moreover, the computed π-SD(2) CI/6-31G* energies of singlets **2** and **3**, relative to that of singlet **1**, are both higher by about 5 kcal/mol than the experimental values of respectively 10 and 22 kcal/mol.[1]

With the 6-311G** basis set, the differences between the computed and experimental values for these relative energies both increase to about 6 kcal/mol. When the basis set is expanded from 6-31G* to 6-311G**, the calculated increases in the energy differences between the lowest singlet states of **1** and **2** and **1** and **3** are respectively about 70% and 100% of the increase in the energy difference between singlet and triplet **1**. This finding suggests that further improvements in the basis set, which increased the calculated value of ΔE_{ST} in **1** by the 3 kcal/mol that is necessary to bring it into agreement with experiment, would also result in increases of about 2 kcal/mol in the energy of singlet **2** and 3 kcal/mol in the energy of singlet **3** relative to that of singlet **1**. Therefore, at still higher levels of theory, the calculated energy differences between the singlet ground states of **1** and **2** and **1** and **3** might be as much as 8–9 kcal/mol larger than the experimental values reported by Squires and co-workers.[1]

The values of ΔE_{ST} in **2** and **3** that are obtained, using Squires' experimental heats of formation for the singlet states of **1–3**, also differ by about this amount from the π-SD(2) values of ΔE_{ST} in **2** and **3**. As discussed in the introduction, Chen estimated the heats of formation of the triplet states of **2** and **3** from the heat of formation of benzene and twice the C–H BDE.[4] Using 113 kcal/mol for the C–H BDE in benzene,[10] he obtained ΔH°_f = 142 kcal/mol for these two triplets. Squires' heats of formation for the singlet states of **2** and **3** then yielded ΔE_{ST} = 26 kcal/mol in **2** and ΔE_{ST} = 14 kcal/mol in **3**.[4] These experimental values are respectively 10 and 12 kcal/mol larger than the calculated values for the singlet–triplet energy differences in Table IV.

However, if, instead of the value of 113 kcal/mol[10] used by Chen for the C–H BDE in benzene, a value of 111 kcal/mol is employed,[8] ΔH°_f = 138 kcal/mol is obtained for triplet **2** and **3**; and the estimates of ΔE_{ST} in **2** and **3** are also each reduced by 4 kcal/mol. Nevertheless, even these lower experimental estimates of ΔE_{ST} = 22 kcal/mol in **2** and ΔE_{ST} = 10 kcal/mol in **3** are respectively 6 and 8 kcal/mol larger than the calculated values for the singlet–triplet energy differences in Table IV.

Estimating the experimental heats of formation of the triplet states of **1–3** from bond additivity data gives identical energies for all three triplets. The triplet energies in Table IV confirm that, as Chen inferred[4] from the energies calculated by Noell and Newton,[6] this is not a bad approximation.[29] However, neither is it entirely correct, since the difference between the triplet energies of **1** and **3** amounts to almost 4 kcal/mol.

The heats of formation of the triplet states of **2** and **3** can also, and perhaps more reliably, be estimated from an independent experimental value for the heat of formation of triplet **1**, corrected for the calculated differences between its energy and those of triplet **2** and triplet **3**. Adding to Squires' value of ΔH°_f = 106 ± 3 kcal/mol for singlet **1**[1] the value of ΔE_{ST} = 37.6 kcal/mol in **1**, measured by photoelectron detachment,[5] gives a value of about 144 kcal/mol for the heat of formation of triplet **1**. After subtracting from this value the small calculated differences in Table IV between the energy of triplet **1** and those of the triplet states of **2** and **3**, heats of formation of respectively

(27) It should be noted that in **1**, for which bent acetylene serves as a model, there are no hydrogens attached to the dehydrocarbons. Therefore, the effect on the value of ΔE_{ST} in **1** of adding polarization functions to the hydrogens is not expected to be the same as in the model.

(28) After this study was completed, Dr. David A. Hrovat in this laboratory found that CASSCF/6-31G* calculations (MCSCF calculations with eight electrons in eight orbitals) give energy differences that are within 1 kcal/mol of those shown in Table I. QCISD(T)/6-31G* calculations, which use only one reference configuration for singlets, give ΔE_{ST} = 34.1 kcal/mol for the singlet–triplet splitting in **1** and values for the energy differences between **1** and **2** and **1** and **3** that are within 2–3 kcal/mol of those obtained at the π-SD(2) CI/6-31G* level.

(29) Zhang and Chen[4] also found that the adiabatic IP of the phenyl radical (8.1 eV) provides a good approximation to the adiabatic IP of triplet **1**. This is surprising because in triplet **1**, the least tightly bound electron occupies an antibonding rather than a nonbonding σ MO; so, one might have expected triplet **1** to have a lower IP than the phenyl radical. In fact, our QCISD(T)/6-31G* calculations do predict the vertical IP of 8.32 eV for triplet **1** to be 0.30 eV smaller than that computed for the phenyl radical. However, because the QCISD(T)/6-31G* relaxation energy of 0.83 eV for the cation formed on ionizing the phenyl radical is 0.44 eV larger than that of the radical cation formed by ionizing **1**, the phenyl radical is actually calculated to have the smaller adiabatic IP but only by 0.14 eV.

Table V. Values of ΔE_{ST} (kcal/mol) in **3** Calculated with the 6-31G* Basis Set at the TCSCF- and ROHF-Optimized Geometries and Including the 0.2 kcal/mol Difference in Zero-Point Energies

	TCSCF/ROHF	π-SD(2) CI[a]	σ-S, π-SD CI[b,c]	CISD(2)[c]
ΔE_{ST}	0.8	2.3[d]	1.8[e]	1.8[f]

[a] See footnote *e* in Table III for a description of this type of calculation. [b] All SD excitations from the π to the π^* space as well as all S excitations in the σ space, with the restriction that no more than two excitations were allowed at any one time. [c] Two reference configurations for the singlet and one for the triplet. [d] As shown in Table IV, this value remains unchanged when the π-SD(2) CI calculations are performed with the larger 6-311G** basis set. [e] Singlet $E = -229.7344$ hartrees. [f] Singlet $E = -230.0172$ hartrees.

141 and 140 kcal/mol are obtained for the latter two triplets. These values lie between those of 142 and 138 kcal/mol that are obtained by assuming that the heats of formation of all three triplets are the same and can be found by assuming bond additivity.[4]

Using ΔH°_f = 141 and 140 kcal/mol for respectively triplet **2** and triplet **3** and Squires' values of ΔH°_f = 116 and 128 kcal/mol for the corresponding singlets gives ΔE_{ST} = 25 kcal/mol in **2** and ΔE_{ST} = 12 kcal/mol in **3**. Our calculated π-SD(2) CI/6-311G** values of 16.0 and 2.3 kcal/mol for ΔE_{ST} in **2** and **3** are respectively 9 and 10 kcal/mol smaller than the values that are obtained using Squires' experimental heats of formation for the singlets.

Because **3** has higher symmetry (D_{2h}) than either **1** or **2**, we were able to carry out larger CI calculations on **3** than on **1** or **2**. However, as shown in Table V, the calculated singlet–triplet enery gap in **3** seems quite insensitive to the type of CI performed or whether CI is included at all. As indicated by comparison of the 6-31G* and 6-311G** results in Table IV, ΔE_{ST} in **3** also appears to be insensitive to improvements in the basis set. Thus, the 8–12 kcal/mol discrepancy between ΔE_{ST} = 10–14 kcal/mol that is obtained for **3** from Squires' experimental data and the value of $\Delta E_{ST} \approx 2$ kcal/mol that is computed by us seems very unlikely to diminish significantly at still higher levels of theory.

Since two independent ways of estimating ΔH°_f for the triplet states of **2** and **3** from different types of experimental data give very similar results, values in the range of 138–142 kcal/mol seem fairly secure. Therefore, the source of the substantial differences between the experimental and our calculated values of ΔE_{ST} in **2** and **3** appears to be Squires' values of ΔH°_f for the singlet states. Since Squires' value of $\Delta H^\circ_f = 106 \pm 3$ kcal/mol for singlet **1** also seems secure,[1–4] the equally large discrepancies between his experimental and our calculated values of the energies of singlet **2** and singlet **3**, relative to that of singlet **1**, also can be traced to Squires' values of ΔH°_f for the latter two singlet states.

If Squires' values of ΔH°_f for singlet **2** and **3** are responsible for both of these large differences between experimental and calculated energies, the strengths for the bonds between the dehydrocarbons in singlet **2** and **3** that are derived from Squires' values of ΔH°_f should also differ from those that we calculate. As discussed in the introduction, combining the heats of formation for **1–3**, reported by Squires and co-workers,[1] with the heat of formation of benzene (C_6H_6)[7] and the heat of formation for the phenyl radical ($C_6H_5\cdot$) that is based on a value of 111 kcal/mol for the C–H BDE in benzene,[8] experimental BDEs of respectively 32, 22, and 10 kcal/mol are obtained for the weak bonds between the dehydrocarbons in **1–3**.[10] Using the value of 38 kcal/mol for ΔE_{ST} in **1**[5] yields an experimental BDE of –6 kcal/mol for the triplet state of **1**. The negative sign indicates that the net interaction between parallel-spin electrons on C_1 and C_2 of **1** is destabilizing.[30]

(30) The net destabilization that occurs when bonding and antibonding combinations of localized orbitals are equally occupied has been termed "overlap repulsion"[31] because the magnitude of the destabilization depends on the overlap between the interacting orbitals.[32]

We have calculated the BDEs for the weak bonds between the dehydrocarbons in **1–3** as the energies of the same set of reactions,[9]

$$\mathbf{1}\ (\mathbf{2}\ \text{and}\ \mathbf{3}) + C_6H_6 \rightarrow 2C_6H_5\cdot \quad (1)$$

Energies of respectively –230.7889 and –230.1392 hartrees were obtained for benzene and the phenyl radical at the π-SD CI/6-31G* level; zero-point vibrational energies of respectively 67.6 and 59.0 kcal/mol were computed at their RHF- and ROHF/6-31G*-optimized geometries. Combined with the π-SD(2) CI/6-31G* energies of –229.5362 hartrees for singlet **1** and –229.4830 hartrees for triplet **1**, the electronic energies of benzene and the phenyl radical predict a BDE of 29.3 kcal/mol for singlet **1** and –4.1 kcal/mol for triplet **1**.[33] The ZPE corrections reduce the BDE of the singlet to 28.8 kcal/mol and that of the triplet to –4.4 kcal/mol.

Since 6-31G* calculations at the π-SD(2) CI level underestimate the singlet–triplet gap in **1** by slightly more than 4 kcal/mol, it is likely that they also underestimate the bond strength in singlet **1** by this amount. Adding this correction to the calculated value for the bond strength in **1** gives an estimated BDE of about 33 kcal/mol. This value is in excellent agreement with the value of 32 kcal/mol for the bond strength in singlet **1** that is obtained from experimental data, and our value of –4,4 kcal/mol for the BDE in the triplet is within 2 kcal/mol of the experimental estimate. The agreement between the computational estimates of the bond strengths in singlet and triplet **1** and those derived from the value of ΔH°_f = 106 kcal/mol for singlet **1** provides computational support for a value of ΔH°_f of about this size.[1–4]

However, the C–C BDEs that are calculated for the dehydrocarbons in singlet **2** and singlet **3** are considerably smaller than those of 22 and 10 kcal/mol that are obtained from the values of ΔH°_f for **2** and **3** reported by Squires and co-workers. From the π-SD(2) CI/6-31G* + ZPE energies in Table IV, BDE = 13.8 kcal/mol is obtained for singlet **2** and BDE = 1.5 kcal/mol is computed for singlet **3**. These calculated values are both about 8 kcal/mol lower than the BDEs that are obtained from Squires' values for ΔH°_f for **2** and **3**.

If the 6-31G* energies of **2** and **3**, relative to **1**, in Table IV were correct and if, as seems likely, the BDE of **1** is actually about 33 kcal/mol rather than the 29 kcal/mol that is obtained at the π-SD(2) CI/6-31G* level, then the calculated BDEs for **2** and **3** would each increase by about 4 kcal/mol. However, as discussed above, the data in Table IV suggest that improvements in the basis set, which improve the description of bonding in singlet **1**, increase the energy difference between it and singlets **2** and **3** by nearly the same amount. Therefore, an increase of 4 kcal/mol in the BDE of singlet **1** over the π-SD(2) CI/6-31G* value seems unlikely to be accompanied by increases of comparable size in the BDEs of the singlet states of **2** and **3**.

For the triplet states of **2** and **3**, BDEs of respectively –1.9 and –0.8 kcal/mol are obtained from the π-SD(2) CI/6-31G* + ZPE energies in Table IV. The destabilizing interaction between the parallel-spin electrons at the dehydrocarbons in **2** and **3** is calculated to be smaller than that in **1**, presumably because the overlap between the localized orbitals occupied by these electrons decreases[30] on going from **1** to **2** to **3**. The fact that the repulsive interaction between these orbitals is calculated to be close to zero in triplet **3** indicates that the energy calculated for triplet **3** is probably quite reasonable.

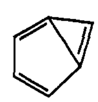
Our ability to perform CISD(2)/6-31G* calculations on **3** enabled us to recalculate the C–C BDEs in singlet and triplet **3**

(31) Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649.
(32) See, for example: Salem, L. *J. Am. Chem. Soc.* **1968**, *90*, 543. Muller, K. *Helv. Chim. Acta* **1970**, *53*, 1112. Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427.
(33) Values of 29.5 and –4.3 kcal/mol are obtained for these BDEs with CASSCF/6-31G* calculations and 31.7 and –2.4 kcal/mol with QCISD(T)/6-31G*.[28]

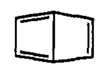
at this level and thus to test the effect on these BDEs of including more electron correlation in our calculations. The CISD(2) energies for 3 in Table V, combined with the CISD energies for benzene and the phenyl radical,[34] give, after correction for ΔZPE, a BDE of 0.9 kcal/mol for singlet 3 and –0.9 kcal/mol for triplet 3. The excellent agreement with the π-SD(2) CI results indicates that the C–C BDEs calculated for the two lowest states of 3 are unlikely to be significantly affected by inclusion of even more electron correlation. However, the calculated BDE for the singlet is about 9 kcal/mol lower than that obtained from Squires' heat of formation for singlet 3.

The significant discrepancies between theory and experiment regarding (1) the energies of singlet 2 and singlet 3 relative to that of singlet 1, (2) the values of ΔE_{ST} in 2 and 3, and (3) the BDEs in the singlet states of the latter two molecules would all disappear if Squires' values for ΔH°_f of 2 and 3 were both too low by about 8 kcal/mol. However, another possible way of reconciling our calculated energies for singlet 2 and 3 with Squires' experimental values would be to postulate that his experiments are measuring ΔH°_f for species that are different from those for which we have performed our calculations.

For example, Squires' experiments might, in principle, be measuring not the heats of formation of 2 and 3 but those of their bicyclic isomers, respectively 4 and 5. If the heats of formation of 4 and 5 were both lower by about 8 kcal/mol than those of respectively 2 and 3, our computational and Squires' experimental results would be reconciled. However, we calculate that 4 is not lower but higher in energy than 2 and that 5 is substantially higher in energy than 3.



4



5

The geometries of 4 and 5 were optimized at the RHF/6-31G* level by occupying the symmetric combinations of the AOs on the dehydrocarbons in each molecule.[18] The geometry thus optimized for 4 was planar and had a bridgehead bond length of 1.482 Å compared to 2.198 Å for this bond length in 2. The RHF-optimized C_1–C_4 bond length in 5 was 1.536 Å compared to 2.676 Å in 3.

The TCSCF/6-31G* energy at the RHF-optimized geometry for 4 was calculated to be 15.4 kcal/mol higher than that at the TCSCF-optimized geometry for 2. A search for a second minimum on the TCSCF energy surface, starting from the RHF geometry for 4, led back to the TCSCF-optimized geometry for 2.[37] A π-SD(2) CI/6-31G* calculation at the RHF-optimized geometry for 4 gave $E = -229.4936$ hartrees, which is 11.2 kcal/mol higher than the energy of 2.[38]

The TCSCF/6-31G* energy for 5 at its RHF-optimized geometry was calculated to be 60.7 kcal/mol higher than that at the TCSCF-optimized geometry for 3. At the π-SD(2) CI/6-31G* level, this energy difference was reduced to 50.8 kcal/mol.[38] Obviously, at both the TCSCF and π-SD(2) CI levels of theory, there is a huge thermodynamic driving force for ring opening of 5 to 3.

Nevertheless, TCSCF/6-31G* geometry optimization, starting from the RHF-optimized geometry for 5, did *not* lead to the cleavage of the C_1–C_4 bond and a return to the TCSCF-optimized geometry for 3, indicating the existence of a barrier to ring opening of 5 to 3. Presumably, a barrier exists because this reaction involves a change in the symmetry of the HOMO in the dominant configuration in the TCSCF wave function. Therefore, ring opening of 5 to 3 is formally "forbidden" by orbital symmetry.[11]

The results of our calculations on 4 and 5 predict that the former does not exist and that the latter is much higher in energy than its monocyclic counterpart (3). Similar results were obtained by Noell and Newton,[6] although our π-SD(2) CI/6-31G* energy differences[38] between 2 and 4 and 3 and 5 are smaller than their TCSCF/4-31G values. Our calculations on 4 and 5 show that postulating their formation in the experiments of Squires' and co-workers does not provide a way of reconciling the heats of formation, derived from these experiments, with the energies that we calculate for 2 and 3.

Conclusions

Our calculations indicate that the experimental values for the heats of formation of 2 and 3 that were obtained by Squires and co-workers[1] are too low by at least 8 kcal/mol. Our calculations support a value of $\Delta H^\circ_f = 106 \pm 3$ kcal/mol for 1,[1–4] but they strongly suggest values of ΔH°_f that are higher than that of 1 by ≥18 kcal for 2 and ≥30 kcal/mol for 3. Postulating the formation of 4 and 5 in Squires' experiments does not provide a viable means for reconciling his results with ours. Additional measurements of ΔH°_f for 2 and 3 certainly seem warranted.[39]

Our calculations also reveal the importance of including dynamic correlation between electrons in weak bonds and the other electrons in a molecule. For example, in 1 and in the bent acetylene models for 1, inclusion of σ–π correlation stabilizes the singlet, relative to the triplet, by 5–6 kcal/mol on going from the TCSCF/ROHF level to π-SD(2) CI. The TCSCF/6-31G* energy differences between bicyclic compounds 4 and 5 and their bond-cleaved, monocyclic isomers (2 and 3) of respectively 15.4 and 60.7 kcal/mol are also reduced at the π-SD(2) CI level to respectively 11.2 and 50.8 kcal/mol.[38] Since transition states often contain weak bonds, inclusion of dynamic electronic correlation is likely to be important in calculating accurate energy barriers for at least some reactions.[41]

(34) When ROHF orbitals are used in the CI calculation (RCISD) on the phenyl radical, the CISD energies of the phenyl radical and benzene are respectively $E = -230.6847$ and -231.3536 hartrees.[35]

(35) The results of these CISD/6-31G* calculations support a value close to 111 kcal/mol for the C–H BDE in benzene. The CISD energy difference between benzene and the phenyl radical is 0.3 kcal/mol smaller than the difference between ethylene ($E = -78.2910$ hartrees) and the vinyl radical ($E = -77.6216$ hartrees). The difference of 8.6 kcal/mol between the ROHF ZPEs of benzene and the phenyl radical is 0.7 kcal/mol smaller than that between ethylene (ZPE = 34.4 kcal/mol) and the ethyl radical (ZPE = 25.1 kcal/mol), so that the C–H BDE in benzene is predicted to be 0.4 kcal/mol larger than that in ethylene. Since the best experimental value for the C–H BDE in ethylene at 298 K is 111 kcal/mol,[36] our finding of only a 0.4 kcal/mol difference between the calculated C–H BDEs in benzene and ethylene indicates that the C–H BDE in benzene is also about 111 kcal/mol. However, if UHF orbitals are used in the CI calculations (UCISD) on the radicals, a very different result is obtained. Due to the large amount of spin contamination in the UHF wave function for the phenyl radical,[17] its UCISD energy is higher by 0.0086 hartrees than its RCISD energy, whereas the UCISD energy of the vinyl radical is only 0.0020 hartrees higher than its RCISD energy. Thus, if the UCISD energies are employed, the C–H BDE of benzene is computed to be 4.8 kcal/mol higher than that of ethylene. This latter result appears to be spurious and cautions against the use of UCISD calculations for open-shell molecules in which spin contamination of the UHF wave functions is large.

(36) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(37) Similar results have been obtained in calculations on 2,4-didehydrophenol; see: Bucher, G.; Sander, W.; Kraka, E.; Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1230.

(38) Because π-SD(2) CI calculations correlate the pair of electrons in only one of the strained σ bonds of 4 and 5, QCISD(T) calculations, which correlate all the electrons, are likely to provide better estimates of the energy differences between 4 and 5 and their monocyclic isomers respectively 2 and 3. However, the QCISD(T)/6-31G* energy of 4 (–230.1965 hartrees) is still 4.6 kcal/mol above that of 2, and the QCISD(T)/6-31G* energy of 5 (–230.1265 hartrees) is 37.0 kcal/mol above that of 3.

(39) After our calculations were essentially complete, we learned that Wierschke, Nash, and Squires had also performed *ab initio* calculations on 1–3 with highly correlated wave functions and reached conclusions similar to ours regarding the energies of 2 and 3 relative to that of 1.[40] More recently, Professor Squires has informed us that new experimental data from his group lead to values of ΔH°_f for 2 and 3 that are in excellent agreement with those that we have calculated.

(40) Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.*, following paper in this issue.

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Supplementary Material Available: TCSCF- and ROHF/6-31G*-optimized geometries for the lowest singlet and triplet states of **1–3** and RHF/6-31G*-optimized geometries for the lowest singlet states of **4** and **5** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(41) For example, CASSCF/6-31G* calculations[42] not only give an energy of activation for the Cope rearrangement that is higher than the experimental value[43] by 12.5 kcal/mol but also place a diradical intermediate at nearly the same energy as the concerted transition state. Both of these failures are remedied by calculations that include dynamic correlation between the six "active" electrons, which form the weak bonds in the concerted transition state, and the rest of the valence electrons; see: Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.*, submitted for publication.

(42) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756.

(43) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.