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Quantum Chemical Characterization of Singlet and Triplet Didehydroindenes

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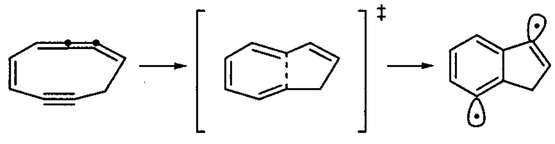
Structural and energetic properties for the lowest energy singlet and triplet states of the 19 possible didehydroindene isomers are predicted using coupled cluster, density functional, and multireference second-order perturbation theories. Singlet−triplet splittings and biradical stabilization energies provide a measure of the degree of interaction between the biradical centers. Comparisons to analogous didehydronaphthalenes are made to understand the influence of the five-membered ring. As in other didehydroarenes, proton hyperfine splittings in antecedent monoradicals are economical predictors of biradical state energy splittings.

I. Introduction

The rigid molecular frameworks imposed by aromatic systems serve as excellent scaffolds to examine electronic interactions between radicals located at different positions thereon. Hoffmann et al.[1] took advantage of this situation more than 30 years ago to illuminate the relative importance of through-space and through-bond electronic interactions for various geometric arrangements of aromatic biradicals, and that work helped to lay the foundation[2] for the analysis of electron−electron interactions in more general situations.[3−9]

More recently, the discovery that didehydrobenzene[10,11] and didehydroindene[12−14] biradicals are responsible for DNA-cleaving activity in the enediyne antibiotics[15] has fostered renewed interest in the particulars of didehydroarene electronic structure. Using gas-phase negative ion photoelectron spectroscopy, Wenthold et al.[16] have provided detailed information on the heats of formation, singlet−triplet (S−T) splittings, electron affinities, and some vibrational frequencies for the “parent” didehydrobenzenes (benzynes). Additional experimental data related to either reactivity or structure for various arynes have been derived from mass spectrometric[17−22] and matrix isolation studies.[23−27] These latter experiments have included an examination of the effects of various substituents attached to the aromatic ring(s).

Theory has also played an active role in characterizing highly reactive aryne biradicals. Focus has been almost exclusively on the benzynes,[28−43] including substituted benzynes,[27,37,44−48] annelated benzynes,[8,36,49−52] and benzynes incorporating heteroatoms in the aromatic ring.[53−57] Much less well studied have been aryl systems having rings of size other than six-membered. Some theoretical attention[58,59] has been paid to 1,5-didehydroindene (1,5-DDI) because its production by Myers−Saito electrocyclic closure of cyclonona-1,2,3,7-tetraen-5-yne forms the basis for the antitumor−antibiotic activity of neocarzinostatin (Figure 1).[14]



1,5-DDI

Figure 1. Myers−Saito cyclization of cyclonona-1,2,3,7-tetraen-5-yne to form 1,5-DDI.

In part to set a better context for prior work on 1,5-DDI, but also to examine more generally the interactions between radical sites in an aryne system including a five-membered ring, we here characterize all 19 possible DDIs (see Figure 2 for numbering convention) at several levels of theory, including multireference second-order perturbation theory (CASPT2),[60] density functional theory (DFT),[61] and coupled-cluster theory. In the case of the last theory, we have considered coupled-cluster expansions for both Hartree−Fock reference orbitals (CCSD(T))[62−64] and Brueckner orbitals (BCCD(T)).[65,66] We focus on the prediction of biradical stabilization energies (BSEs) and singlet−triplet (S−T) state energy splittings as a measure of site−site interaction in these species. In addition to evaluating the chemistry of these species, we note limitations in the various theories with respect to their application in specific situations.

II. Computational Methods

Molecular geometries for indene, the seven monodehydroindenes, and all but four DDIs were optimized at both the multiconfiguration self-consistent-field (MCSCF) and DFT levels of theory using the correlation-consistent polarized valence-double-ζ (cc-pVDZ)[67] basis set. The geometries of the four singlet m,7-DDIs ($m = 1, 2, 5, 6$) were optimized only at the MCSCF level. The MCSCF calculations were of the complete active space (CAS) variety and are described further below. The DFT calculations employed the gradient-corrected functionals of Becke[68] for exchange energy and Perdew et al.[69] for correlation energy (BPW91). All DFT geometries were confirmed as local minima by computation of analytic vibrational frequencies, and these (unscaled) frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions ($H_{298} - H_0$) for all species. In select cases, replacement of the PW91 correlation functional by the one of Lee et al.[70] (BLYP) was also examined. Gräfenstein et al. have shown that this latter level of theory compares well with experiment for unsubstituted arynes, although this agreement stems from a fortuitous cancellation of errors associated with basis set incompleteness and deficiencies in the functional.[71]

DFT calculations on doublet and triplet spin states employed an unrestricted formalism. Total spin expectation values for Slater determinants formed from the optimized Kohn−Sham

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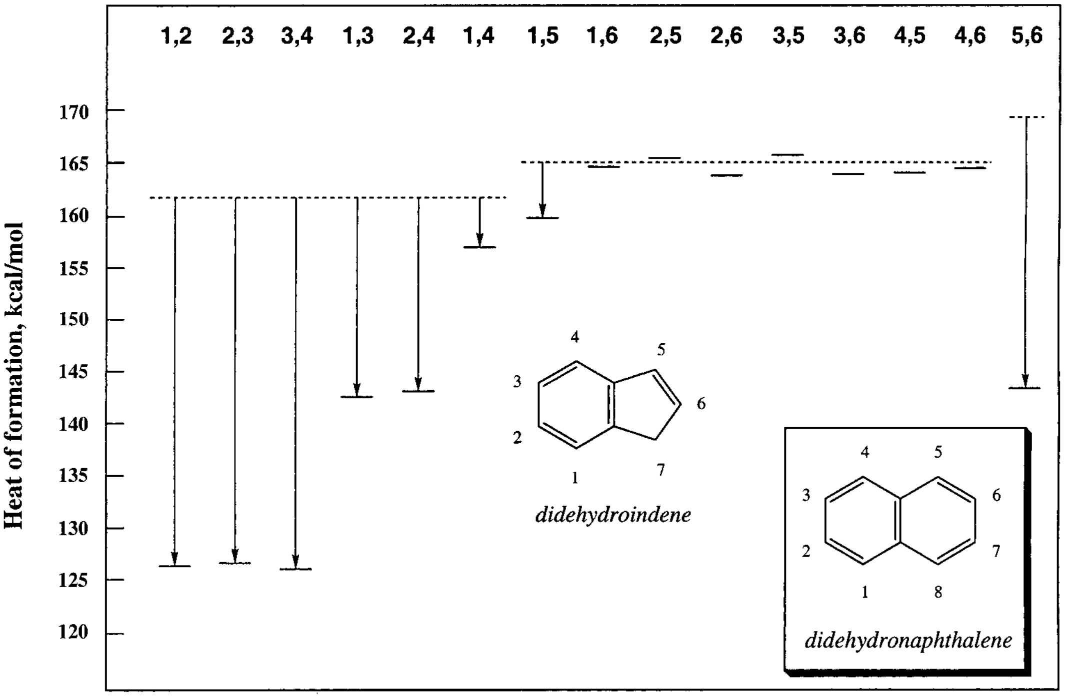

Figure 2. The 298 K heats of formation for singlet σ,σ-DDIs calculated as described in Table 7. The dashed lines indicate the analogous systems having a BSE of zero. The inset provides the numbering used for DDN systems, to which some DDIs are compared in the text.

orbitals did not exceed 0.77 and 2.02 for doublets and triplets, respectively. For singlet biradicals, the DFT "wave function" was allowed to break spin symmetry by using an unrestricted formalism.[42,55,72] Such symmetry breaking was observed to occur to a greater or lesser extent in any system that did not involve an ortho or meta biradical (i.e., adjacent or 1,3-related on the same ring). Total spin expectation values for Slater determinants formed from the optimized Kohn−Sham orbitals in these cases ranged widely between 0.0 and 1.0. Geometry optimization using the unrestricted formalism has been shown to give more accurate geometries for a number of relevant aromatic singlet biradicals.[16,35,37,42,48,50,55,56,58,73]

To improve the molecular orbital calculations, dynamic electron correlation was accounted for using multireference second-order perturbation theory (CASPT2) for the CAS reference wave functions; these calculations were carried out for both the DFT and the CAS optimized geometries. In addition, coupled-cluster calculations including single and double excitations and a perturbative estimate for unlinked triple excitations were carried out for single-configuration reference wave functions expressed in either Hartree−Fock (CCSD(T))[63,64] or Brueckner (BCCD(T))[66] orbitals. Brueckner orbitals[65] eliminate contributions from single excitations in the coupled-cluster ansatz, and this can remove instabilities[74] associated with very large singles amplitudes in the more common CCSD(T) method that have been observed in some aryne biradicals.[48,55,59] Note that it is impossible to describe the m,7-DDI singlets with a single configuration (because the biradicals are of the σ,π-type instead of the σ,σ-type), so these species were analyzed only at the CASPT2//CAS level.

For indene, the CAS active space was formed from the eight valence π-orbitals (containing eight electrons) and the combination of C−H σ-bonds having π-symmetry at the 7-position (containing two electrons). For the 7-indenyl radical, which has all atoms coplanar, the active space is simply the nine π-orbitals (containing nine electrons); for the other indenyl radicals, the singly occupied σ-orbital and its electron were added to the active space defined for indene. Active spaces for the diradicals were derived by adding the second singly occupied orbital/electron to the active space defined for an antecedent monoradical. All molecules have C_s symmetry; all triplets, m,7-DDI singlets, and 7-dehydroindene are of electronic state symmetry A″, and all other species are of A′ symmetry. (Formally, 7-dehydroindene and 6,7-DDI are of C_{2v} symmetry and have electronic states of A_2 symmetry, but we did not enforce this in the calculations.) Acetylene and ethylene used (4,4) and (2,2) π active spaces, respectively.[8]

Isotropic hyperfine coupling constants (hfs) were calculated as[75]

$$a_X = (4\pi/3)\langle S_z\rangle^{-1} g g_X \beta \beta_X \rho(X) \qquad (1)$$

where g is the electronic g factor, β is the Bohr magneton, g_X and β_X are the corresponding values for nucleus X, and ρ(X) is the Fermi contact integral

$$\rho(X) = \sum_{\mu\nu} \mathbf{P}^{\alpha-\beta}_{\mu\nu} \phi_\mu(\boldsymbol{R}_X)\, \phi_\nu(\boldsymbol{R}_X) \qquad (2)$$

where $\mathbf{P}^{\alpha-\beta}$ is the BPW91/cc-pVDZ one-electron spin density matrix, and evaluation of the overlap between basis functions ϕ_μ and ϕ_ν is only at the nuclear position, $\boldsymbol{R}_X$.

BSEs are computed as the 298 K heat of reaction for the isodesmic process

$$m\text{-}C_9H_7 + n\text{-}C_9H_7 \rightarrow m,n\text{-}C_9H_6 + C_9H_8 \qquad (3)$$

Thus, a negative BSE implies a favorable interaction energy between the two radical centers and vice versa. Note that the 298 K S−T splitting for a given DDI is simply the difference in BSEs for the singlet and triplet states.

A different isodesmic equation that proves useful for 1,2-related diradicals (i.e., true "arynes") is

$$m,n\text{-}C_9H_6 + C_2H_4 \rightarrow C_9H_8 + C_2H_2 \qquad (4)$$

The magnitude of the typically negative reaction enthalpy

TABLE 1: Zero-Point Vibrational Energies, Thermal Contributions, and Relative H_{298} (kcal/mol) for σ,σ-DDIs

	didehydroindene														
state	1,2	1,3	1,4	1,5	1,6	2,3	2,4	2,5	2,6	3,4	3,5	3,6	4,5	4,6	5,6
	Zero-Point Vibrational Energy														
S	70.2	69.5	69.4	69.7	69.9	70.3	69.5	69.8	69.9	70.3	69.8	69.8	69.8	70.0	69.9
T	69.9	69.7	70.0	70.0	70.0	69.7	69.7	69.8	69.9	69.8	69.8	69.9	70.0	70.0	70.3
	$H_{298} - H_0$														
S	4.8	4.9	4.7	4.8	4.7	4.8	4.9	4.7	4.7	4.8	4.7	4.8	4.7	4.7	4.9
T	4.8	4.8	4.7	4.7	4.7	4.8	4.8	4.7	4.8	4.8	4.7	4.8	4.7	4.7	4.8
	H_{298} Relative to Singlet 3,4-DDI														
S	0.2[a]	10.6	20.3	22.9	27.3	1.2	11.6	28.0	27.5	0.0[b]	27.9	27.2	27.2	27.9	20.1
	0.1	13.8	18.3	21.4	27.0	0.5	14.2	28.1	26.0	0.0	28.0	26.3	27.1	27.1	15.7
	0.1	10.9	18.9	21.4	26.8	0.5	11.3	27.8	25.7	0.0	27.8	26.1	26.9	26.8	15.5
	0.0	15.0	21.8	22.4	−7.9	0.2	15.4	126.9	−315.7	0.0	140.8	−209.1	28.6	−318.9	16.1
				23.6	26.0			19.2	22.5	0.0	20.9	23.3		25.4	
T	30.9[a]	26.7	26.3	28.9	27.9	31.3	27.3	27.9	28.7	31.5	27.8	28.2	28.8	28.5	36.8
	30.2	26.6	26.2	29.0	27.5	30.2	26.9	27.7	27.9	30.6	27.8	27.5	28.6	28.0	34.9
	29.9	26.4	26.0	28.8	27.2	29.9	26.7	27.5	27.6	30.3	27.6	27.3	28.4	27.7	34.7
	32.0	32.3	28.4	32.8	33.1	32.1	32.6	33.4	31.5	32.4	30.1	33.1	34.3	30.3	36.9
				30.6	29.3			29.8	29.5		29.5	29.4		29.7	

[a] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91, BCCD(T)/BPW91; the last level is reported only in select instances. [b] Absolute H_{298} (E_h) for this column: −346.292 72, −345.235 52, −345.233 99, −345.334 00, −345.333 55.

TABLE 2: Zero-Point Vibrational Energies, Thermal Contributions, and H_{298} for Indene and Indenyl Radicals[a]

property	indene	1-indenyl	2-indenyl	3-indenyl	4-indenyl	5-indenyl	6-indenyl	7-indenyl
ZPVE[b]	85.7	77.8	77.7	77.6	77.8	77.9	78.0	78.1
$H_{298} - H_0$[b]	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.6
H_{298}	−347.594 84[c]	−346.925 05	−346.924 04	−346.924 35	−346.924 24	−346.919 15	−346.918 60	−346.977 62
	−346.520 29	−345.858 46	−345.858 28	−345.858 39	−345.857 96	−345.853 24	−345.853 78	−345.908 61
	−346.518 95	−345.857 20	−345.857 02	−345.857 13	−345.856 70	−345.852 03	−345.852 62	−345.907 17
	−346.630 34	−345.960 77	−345.960 48	−345.960 61	−345.960 24	−345.955 26	−345.955 31	−346.008 94
	−346.630 15	−345.960 99	−345.960 69	−345.960 90	−345.960 49	−345.955 88	−345.956 35	
$\Delta H_{f,298}^{\circ}$	39.1 ± 0.5[d]	100.5[e]	100.5[e]	100.5[e]	100.5[e]	103.6[e]	103.6[e]	

[a] H_{298} in E_h, all other data in kcal/mol. [b] BPW91 level. [c] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91, BCCD(T)/BPW91. [d] Reference 99. [e] Estimated; see text.

TABLE 3: Zero-Point Vibrational Energies, Thermal Contributions, and Relative H_{298} (kcal/mol) for σ,π-DDIs

state	1,7	2,7	5,7	6,7
	Zero-Point Vibrational Energy			
T	70.2	70.1	70.7	70.2
	$H_{298} - H_0$			
T	4.6	4.6	4.6	4.7
	H_{298} Relative to Singlet 3,4-DDI			
S[a]	−5.3	−5.9	7.7	−4.4
T	−9.9[b]	−9.2	−7.4	−3.7
	−7.6	−7.4	−6.3	−2.2
	−7.7	−7.5	−6.2	−2.4
	−2.2	−2.0	−3.2	1.1

[a] CASPT2//CAS plus triplet thermal contributions. [b] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91.

indicates the degree to which it is more favorable to hydrogenate the triple bond of the aryne compared to the prototypical triple bond of acetylene.

Multireference and single-reference calculations were carried out with the MOLCAS[76] and Gaussian 98[77] electronic structure program suites, respectively.

III. Results

Structures, energies, and selected spectroscopic and thermochemical quantities were computed for the 19 isomeric DDIs and other molecules at several levels of theory in conjunction with the cc-pVDZ basis set. The basis set being constant, we will no longer specify it in naming a level of theory.

We consider primarily two different sets of optimized geometries—those computed at the BPW91 and CAS levels. In the case of 1,3- and 2,4-DDI, we also report various quantities computed for BLYP optimized geometries. Prior studies have empirically indicated this functional to be slightly better than BPW91 for *m*-benzyne geometries.[48,73] In the interests of brevity, we do not illustrate all of the molecular geometries, but we provide Cartesian coordinates for all species as Supporting Information. Certain key geometric parameters will be noted as appropriate in the discussion.

With respect to energies, we consider primarily five different levels of theory, namely BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)//BPW91, and BCCD(T)//BPW91. We discuss BLYP energies and/or geometries in select instances. Table 1 provides the zero-point vibrational energies, 298 K thermal contributions, and relative H_{298} values for all DDIs of σ,σ-type (i.e., the methylene position at C7 is saturated). The table also lists the absolute electronic energy for the relative zero of energy, global minimum singlet 3,4-DDI. While this permits the derivation of all electronic energies from Table 1 to within 0.1 kcal/mol, they are also included to higher precision in the Supporting Information. Table 2 lists the equivalent data for indene and the indenyl radicals. Table 3 provides the zero-point vibrational energies, 298 K thermal contributions, and relative H_{298} values for all triplet *m*,7-DDIs. In the case of the singlet *m*,7-DDIs, which have intrinsically two-determinant wave functions, only CAS optimizations were undertaken, and ZPVE and thermal contributions were assumed to be the same as those computed for the triplets (Table 1 suggests this is reasonable to within 0.2 kcal/mol or so if there is not much interaction between the two radicals, as would be expected for most of these σ,π-type biradicals). Note that 1,7-DDI, 2,7-DDI, and 5,7-DDI are indistinguishable from isomers that might be called 4,7-DDI, 3,7-DDI, and 7,7-DDI, respectively, so there are only four unique *m*,7-DDIs.

TABLE 4: BSEs and S−T Splittings (kcal/mol) for σ,σ-DDIs

	didehydroindene														
state	1,2	1,3[a]	1,4	1,5	1,6	2,3	2,4[b]	2,5	2,6	3,4	3,5	3,6	4,5	4,6	5,6
							BSE								
S	−24.0[c]	−13.3	−3.7	−4.3	−0.2	−23.4	−13.0	0.2	−0.7	−24.4	0.3	−0.8	−0.6	−0.2	−11.2
	−24.4	−10.7	−6.4	−6.3	−0.3	−24.1	−10.7	0.3	−1.5	−24.8	0.3	−1.1	−0.9	−0.5	−14.9
	−24.1	−13.4	−5.6	−6.0	−0.3	−23.8	−13.3	0.3	−1.4	−24.5	0.3	−1.0	−0.8	−0.5	−14.8
	−27.0	−12.0	−5.4	−7.9	−38.2	−27.0	−12.0	96.4	−346.2	−27.3	110.3	−239.5	−2.1	−349.5	−17.7
				−5.8	−3.1			−10.4	−6.8	−26.8	−8.6	−5.8		−4.0	
T	6.7[c]	2.7	2.3	1.7	0.3	6.7	2.6	0.0	0.5	7.0	0.2	0.2	1.1	0.4	5.5
	5.7	2.2	1.5	1.4	0.1	5.6	2.1	−0.0	0.4	5.8	0.1	0.2	0.6	0.3	4.3
	5.6	2.2	1.5	1.4	0.2	5.6	2.1	−0.0	0.4	5.8	0.1	0.2	0.7	0.3	4.4
	5.0	5.3	1.2	2.4	2.8	5.0	5.2	2.9	1.1	5.1	−0.3	2.7	3.7	−0.4	3.2
				1.2	0.2			−0.0	0.3		0.1	0.2		0.3	
							S−T Splitting								
	−30.8[d]	−16.1	−6.0	−6.0	−0.6	−30.2	−15.8	0.1	−1.2	−31.4	0.1	−1.0	−1.7	−0.6	−16.9
	−30.1	−13.0	−7.9	−7.7	−0.4	−29.8	−12.9	0.3	−1.9	−30.6	0.2	−1.2	−1.5	−0.8	−19.3
	−29.8	−15.7	−7.2	−7.4	−0.4	−29.4	−15.5	0.3	−1.8	−30.3	0.2	−1.2	−1.5	−0.8	−19.3
	−32.0	−17.4	−6.6	−10.4	−41.0	−32.0	−17.4	93.5	−347.3	−32.4	110.7	−242.2	−5.8	−349.2	−21.1
				−7.1	−3.3			−10.4	−7.0		−8.6	−6.0		−4.2	
	−30.2	−16.5	−5.8	−6.3	−0.5	−30.1	−16.5	0.1	−2.2	−30.9	−0.1	−1.1	−1.0	−1.3	−23.9

[a] When BLYP geometries are used, the column reads −13.6, −12.3, −13.4, −13.1, 2.8, 2.1, 2.2, 5.5, −16.5, −14,4, −15.7, −18.6. [b] When BLYP geometries are used, the column reads −13.4, −12.2, −13.3, −13.2, 2.7, 2.1, 2.1, 5.2, −16.2, −14,3, −15.5, −18.5. [c] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91, BCCD(T)/BPW91; the last level is reported only in select instances. [d] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91, BCCD(T)/BPW91, and the average value from two different hfs correlations (see text); the BCCD(T) level is reported only in select instances.

TABLE 5: BSEs and S−T Splittings (kcal/mol) for σ,π-DDIs

state	1,7	2,7	5,7	6,7
		BSE		
S	1.8[a]	1.2	11.6	−0.1
T	−0.4[b]	−0.3	−1.6	1.7
	−0.5	−0.4	−2.5	1.9
	−0.5	−0.4	−2.3	1.9
	1.2	1.2	−3.3	1.1
		S−T Splitting		
	2.3[c]	1.6	13.9	−2.0
	4.3	2.8	21.4	−4.2

[a] CASPT2//CAS; thermal contributions assumed equal to those of the triplet. [b] Reported from top to bottom as BPW91, CASPT2//BPW91, CASPT2//CAS, CCSD(T)/BPW91. [c] Reported from top to bottom as CASPT2//CAS and the value from hfs correlation using the 7-indenyl radical.

Tables 4 and 5 list the singlet and triplet BSEs and S−T splittings for the σ,σ-DDIs and the σ,π-DDIs, respectively. For the latter class of diradicals, the two-determinantal nature of the singlets limits the direct computation of S−T splittings to the CASPT2 level. Moreover, since we are assuming identical ZPVEs and thermal contributions to the enthalpies of the two states, the S−T splittings are effectively simply differences in electronic energies.

S−T splittings in Tables 4 and 5 are also computed by correlation with predicted proton hyperfine splittings (hfs) in monoradicals. Thus, it has been shown previously that CASPT2/cc-pVDZ S−T splittings in aryne diradicals are well correlated with BPW91/cc-pVDZ monoradical ^{1}H hfs constants,[8,36,57] where the hfs is computed for the hydrogen atom on the diradical position that is “capped” in the monoradical (while a separate correlation with experiment would be expected to be of similarly high quality, experimental data are, for the most part, not available for such an undertaking). For strongly interacting ortho- and meta-related diradicals (defined as having singlet ground states with S−T gaps larger in magnitude than −10 kcal/mol), the regression equation, which has an R value of 0.997 when computed over 11 data points for relevant benzynes,[36] pyridynes,[56] and naphthalynes,[8,36] is

$$(\text{S}-\text{T splitting, kcal/mol}) = -1.39(^1\text{H hfs, G}) - 9.48 \quad (5)$$

In the case of more weakly interacting diradical centers, the correlating equation ($R = 0.987$, nine data points) analogous to eq 5 is

$$(\text{S}-\text{T splitting, kcal/mol}) = -1.99(^1\text{H hfs, G}) - 0.30 \quad (6)$$

(The near-zero intercept for eq 6 is consistent with qualitative expectations that, if a proton does not feel any unpaired electron spin density, an electron localized in the same position would not be expected to show much preference for singlet vs triplet coupling. The nonzero intercept for eq 5 parametrically corrects for the perturbing effect of the typically large geometry differences between the individual states of the strongly interacting diradicals and/or such differences between the diradicals and their related monoradicals. Note that while the corrrelation between hfs and S−T splitting is intuitive, no formal relationship between the two has yet been established.) In Table 4, the listed value is the average from the two different monoradicals antecedent to a given diradical (e.g., the S−T splitting for 1,2-DDI may be predicted from the hfs for the proton at C(2) in 1-dehydroindene or the hfs for the proton at C(1) in 2-dehydroindene; the average absolute difference between the two predictions is only 0.1 kcal/mol over the 15 σ,σ-DDIs, which is testament to the robustness of the method). In Table 5, only hfs values from the 7-dehydroindene radical are used, since the remaining protons are better disposed geometrically to predict σ spin density than are the 7-protons to report π spin density for a σ-radical.

IV. Discussion

This remaining discussion is divided into four sections. The first two, primarily of interest to theoreticians, briefly focus on the strengths and weaknesses of the different levels of theory with respect to the prediction of electronic energies and molecular geometries, respectively. The third section outlines protocols for the estimation of the 298 K heats of formation for all of the σ,σ-diradicals and evaluates these relative to hypothetical noninteracting systems. The final section compares DDI properties to didehydronaphthalene properties to gauge the influence of the five-membered ring on the former system.

A. Electronic Structure Methods. For the same (DFT) geometries, the DFT and CASPT2 energies relative to singlet

TABLE 6: H_{298} and $\Delta H_f°_{,298}$ for Acetylene, Ethylene, Benzene, Phenyl Radical, and Singlet Benzynes[a]

property	acetylene	ethylene	benzene	phenyl	*o*-benzyne	*m*-benzyne	*p*-benzyne
H_{298}	−77.289 93[b]	−78.521 03	−232.126 11	−231.455 83	−346.924 24	−230.811 64	−230.789 00
	−77.052 32	−78.264 99	−231.401 35	−230.085 36	−345.857 96	−230.102 20	−230.085 36
$\Delta H_f°_{,298}$	54.4 ± 0.2[c]	12.5 ± 0.1[c]	19.7 ± 0.2[c]	81.2 ± 0.6[d]	105.9 ± 3.3[e]	121.9 ± 3.1[e]	138.0 ± 1.0[e]
					106.0, 106.7[f]	113.9, 115.9[f]	128.1, 126.4[f]
					118.5, 118.2	126.3, 127.4	*140.5, 138.0*
					112.2, 112.4	*120.1, 121.6*	134.3, 132.2

[a] H_{298} in E_h, all other data in kcal/mol. [b] Reported from top to bottom as BPW91, CASPT2//CAS. [c] Reference 100. [d] Reference 83. [e] Reference 16. [f] BPW91, CASPT2//CAS predictions reported from top to bottom as results from isodesmic eq 4, results from isodesmic eq 3, and average of the two.

3,4-DDI tend to be in rather good agreement. In the case of the triplet σ,σ-DDIs, which should have the lowest degree of multiconfigurational character, the average absolute difference in relative H_{298} values is 0.5 kcal/mol (recall that all ZPVE and thermal contributions come from DFT, so the comparison is equivalent to electronic energies). In the case of the singlets, this increases to 1.2 kcal/mol. Some of the larger differences come from the meta 1,3-DDI and 2,4-DDI diradicals, where geometric issues arise (vide infra). In addition, a difference of 4.4 kcal/mol is predicted for the 5,6-DDI singlet. This isomer has the most strained formal triple bond, since it is found in the five-membered ring. It is difficult to decide which level of theory is likely to be the more accurate, if either. The CCSD(T) prediction is rather close to the CASPT2 one, but CCSD(T) is likely to be the most sensitive to the limited size of the basis set, so it is not obvious that it should be regarded as definitive in this instance.

The DFT methodology is technically more easily applied than the CASPT2 method. Moreover, inclusion of the full π-space in the active space for larger aromatics than indyne would pose significant challenges for CASPT2, a technical limitation that does not apply to DFT. Thus, while there are still some open issues associated with the exact nature of the spin state accessed by an unrestricted DFT calculation with broken spin-symmetry for a singlet,[42,43,71,72,75,78−81] it appears that this method holds particular promise for larger systems.

The CCSD(T) and BCCD(T) methods, on the other hand, fail dismally for most of the DDI singlets. Very large single excitation amplitudes for many of the weakly interacting singlets render the perturbative estimation of contributions from unlinked triple excitations unstable, leading to errors of hundreds of kilocalories per mole. This effect has been noted even in simple *p*-benzyne analogues.[48,55−57,59] Eliminating the single excitations by resorting to the BCCD(T) ansatz drastically reduces the degree of the error, but in several instances there is still a disagreement of up to 9 kcal/mol remaining when comparing against DFT and CASPT2. Also somewhat surprising are the differences in relative energies, sometimes as large as 4 kcal/mol, predicted by CCSD(T) and BCCD(T) for some of the DDI triplets. Crawford and Stanton have recently discussed instability in these methods in cases where second-order Jahn−Teller effects are an issue,[82] but it is not obvious that a mixing of the σ- and π-spaces in the DDI triplets would be expected to generate a strong coupling between states. Thus, while useful for aryne diradicals in select instances where CCSD(T) fails,[48,55−57,59] BCCD(T) is no panacea.

B. Molecular Geometries. As noted previously for the naphthalynes,[8] there is generally quite good agreement between the DFT- and CAS-predicted geometries of the DDIs (and indene and the indenyl radicals). At the CASPT2 level, there is a uniform preference of 0.7−0.9 kcal/mol for the DFT geometry for all σ,σ-DDIs with the exception of the meta singlets 1,3- and 2,4-DDI.

In the meta diradical cases, there is a significant difference between the various theoretical geometries with respect to the separation between the two dehydro centers. Considerable fluxionality in *m*-benzyne and analogous systems has been noted many times previously; in various instances theoretically characterized coordinates ranging from monocyclic to bicyclic structures have been found to be quite flat.[27,32,35,37,48,56,57] A general rule of thumb seems to be that BPW91 structures are too far displaced toward being bicyclic, while CAS structures tend to be too far displaced toward being monocyclic. The DDIs show trends consistent with this observation. For 1,3- and 2,4-DDI, the interdehydro separations in the singlets are 1.991 and 2.000 Å, respectively, at the BPW91 level, but 2.228 Å in each case at the CAS level. Based on comparison of predicted and experimental IR spectra[27] and energetic analysis,[48] BLYP structures seem to be optimal among a variety of functionals. At the BLYP level, the interdehydro distances are predicted to be 2.075 and 2.079 Å, respectively, i.e., in between the other two levels, but a bit closer to BPW91 than CAS.

Energetic analysis of these three geometries at the CASPT2 level indicates the BPW91 geometries to be 1.9 kcal/mol higher in energy than the CAS. The BLYP geometries are also predicted to be higher in energy, but by only 0.3 kcal/mol, indicating that in this system, too, the ring-closure coordinate is quite flat in the diradical region. When BLYP geometries are used, Table 4 indicates the BLYP, CASPT2, and CCSD(T) methods to all predict quite similar singlet BSEs. Interestingly, the BSE predicted by the BPW91 level is also similar, suggesting that there is a cancellation of errors between geometries and energies at this level.

We note that, although in any one system it is possible that *both* bicyclic and monocyclic singlets could exist as distinct minima, in those instances where such a situation has been checked reasonably carefully using a highly correlated level of theory, only a single-well potential has ever been found.[32,57] There is no reason to expect the DDI cases to be different.

C. DDI Thermochemistry. Table 6 lists H_{298} values for benzene, phenyl radical, the singlet benzynes, acetylene, and ethylene, as well as experimental 298 K heats of formation; the various electronic energies, ZPVEs, and thermal contributions have been presented elsewhere.[8,35,55] Also listed are the predicted benzyne 298 K heats of formation arrived at by computing the enthalpies of reaction for isodesmic eqs 3 and 4 and using the experimental heats of formation for all species other than the benzynes. As has been noted previously,[35] eq 3 does well at predicting $\Delta H_f°_{,298}$ for *p*-benzyne, eq 4 does very well for singlet *o*-benzyne, and an average of the two works well for singlet *m*-benzyne (optimal data in italics in Table 6). The identical protocol has also been shown to be accurate to within experimental error for predicting $\Delta H_f°_{,298}$ values for singlet 1,2-, 2,3-, and 1,4-didehydronaphthalene.[8]

Table 7 employs eq 4 to estimate the heats of formation for the ortho diradicals 1,2-, 2,3-, 3,4-, and 5,6-DDI. For the first three cases, BPW91 and CASPT2//CAS give predictions identical to within 0.8 kcal/mol. In the last case, the two levels disagree by 3.8 kcal/mol, with BPW91 predicting the higher energy. Because of its incorporation into a five-membered ring, this is the most highly strained of all the "ortho" cases, and its heat of formation is some 17 kcal/mol above the others. The degree of multiconfigurational character in the highly strained triple bond may decrease the efficacy of BPW91, but there are insufficient data to come to a firm conclusion.

For the remaining DDIs, use of eq 3 is required to estimate $\Delta H_f°_{,298}$. However, the various C−H bond strengths in indene have not been measured. Nevertheless, we feel we can estimate these bond strengths (and hence the radical heats of formation) with a reasonable degree of accuracy by making comparisons to other systems where both theory and experiment are available. In the cases of benzene[83] and naphthalene,[84] the C−H bond dissociation enthalpies (BDEs) have been measured to be 113.5 ± 0.5 and 112 ± 1.3 kcal/mol (the α- and β-naphthalene sites are essentially equivalent). The computed differences in H_{298} values for benzene and the phenyl radical at the BPW91 and CASPT2//CAS levels are 0.6833 and 0.6747 E_h, respectively. The same values for naphthalene and either of the two naphthyl radicals are 0.6833 and 0.6750, respectively. For the case of indene and any of the radicals derived from hydrogen abstraction from the six-membered ring, the same energy differences are roughly 0.6832 and 0.6747, respectively. Thus, as noted in previous theoretical studies,[85,86] the C−H bond strength for an aromatic six-membered ring is remarkably insensitive to surrounding hydrocarbon functionality, and we therefore employ the benzene value of 113.5 kcal/mol for the BDE in order to estimate $\Delta H_f°_{,298}$ for the 1-, 2-, 3-, and 4-indenyl radicals. For the 5- and 6-indenyl radicals, BPW91 and CASPT2//CAS both predict stronger C−H bonds by 3.1 kcal/mol, and we use this value to compute $\Delta H_f°_{,298}$ for these species. We note that this value of 116.6 kcal/mol agrees closely with the measurement of Broadus and Kass[87] for the BDE of the C−H bond in the five-membered ring of acenaphthyne, namely 117 ± 4 kcal/mol. The difference between the BDEs for the five- and six-membered rings is consistent with differences found by Barckholtz et al.[86] in a survey of several aromatic hydrocarbons. The remaining data in Table 7 are derived, then, from using eq 3 (and averaging with eq 4 in the case of the two *m*-DDIs).

Table 7 also provides a best estimate for the S−T splittings in the various DDIs. This S−T splitting is computed as the difference between the predicted heat of formation and the heat of formation for the hypothetical corresponding triplet where the two radicals have no formal interaction (i.e., assuming a triplet BSE of zero; thus, the heat of formation for the triplet is simply indene plus the two C−H BDEs minus the heats of formation for two hydrogen atoms). Based on experimental data for the benzynes[16] and analysis of theoretical data for the naphthalynes,[36] this approach is likely to be more accurate than relying on raw theoretical predictions, which tend to underestimate splittings in ortho and meta cases and slightly overestimate them in more weakly interacting systems. A comparison of Table 7 with Table 4 indicates that the disparities between the two approaches follow these same trends in the DDIs. We note that the S−T splitting predictions derived from hfs constants continue to agree remarkably well with CASPT2//CAS predictions (Table 4). Figure 2 plots the data in Table 7 in a way that clarifies the differences in σ,σ-DDIs having zero, one, or two radical centers in a single ring, and also groups together isomers of similar character.

We note that we can use the predicted $\Delta H_f°_{,298}$ for 1,5-DDI,

TABLE 7: Predicted Singlet $\Delta H_f°_{,298}$ and S−T Splittings (kcal/mol) for σ,σ-DDIs

	didehydroindene														
property	1,2	1,3	1,4	1,5	1,6	2,3	2,4	2,5	2,6	3,4	3,5	3,6	4,5	4,6	5,6
$\Delta H_f°_{,298}$[a]	126.1 ± 2.4[b]	142.6 ± 2.2[c]	157.2 ± 2.6[d]	159.9 ± 2.8[d]	164.7 ± 2.0[d]	126.8 ± 2.1[b]	143.1 ± 2.0[c]	165.2 ± 2.0[d]	163.9 ± 2.4[d]	126.0 ± 2.4[b]	165.3 ± 2.0[d]	164.1 ± 2.1[d]	164.3± 2.1[d]	164.6± 2.2[d]	143.7 ± 3.9[b]
ΔH_{S-T}[e]	−35.8	−19.3	−4.7	−5.1	−0.3	−35.1	−18.8	0.2	−1.1	−35.9	0.3	−0.9	−0.7	−0.4	−24.4

[a] Average of BPW91 and CASPT2 values; error range is 2.0 plus half the difference between the BPW91 and CASPT2 predictions. [b] From isodesmic eq 4. [c] From average of isodesmic eqs 3 and 4. [d] From isodesmic eq 3. [e] See text for method of computation; a reasonable error range would be that listed for $\Delta H_f°_{,298}$.

and the 298 K heat of reaction computed at a high level for the process shown in Figure 1,[58] to estimate $\Delta H_f{}^\circ{}_{,298}$ for cyclonona-1,2,3,7-tetraen-5-yne to be about 161.1 kcal/mol. As noted in the Introduction, this hydrocarbon is of interest to the extent that it is embedded in neocarzinostatin.

With respect to the *m*,7-DDIs, we do not have a good way to estimate the BDE for the sp^3-like C$-$H bond at the 7-position, so we do not attempt to compute $\Delta H_f{}^\circ{}_{,298}$ values for these species from eq 3. One could in principle add their enthalpies relative to 3,4-DDI (Table 3) to $\Delta H_f{}^\circ{}_{,298}$ for the latter, but we have not done so since the accuracy of such an approach cannot be tested against currently available experimental data. Nevertheless, there are a few interesting trends in the *m*,7-DDIs meriting discussion. In every case but 6,7-DDI, the triplet is predicted to be the preferred spin state (Tables 3 and 5). Computed isotropic hfs values for the 7-indenyl radical indicate positive spin density on all of the in-plane hydrogen atoms except for the one at the 6-position, which is consistent with this observation. The very large preference for the triplet state in 5,7-DDI and the weak preference for the singlet state in 6,7-DDI are best explained considering the 7-indenyl radical to be essentially an allyl radical annelated to a benzene ring. The allyl radical formally has all of its spin density at its termini, but π-polarization induces negative spin density at the central position.[88−91] Given the usual preference for high-spin coupling between π- and σ-systems at a single position in aromatic hydrocarbons,[92] the preferred spin state and the relative magnitudes of the preference are rationalized. Indeed, the predicted value for 5,7-DDI is not far from that predicted by Yoshimine et al.[93] for vinylmethylene, 12.0 kcal/mol, which would be the non-benzannelated analogue for 5,7-DDI. (We note that the poor performance of the hfs method in this isomer appears to derive from a large geometry change on going from the 7-indenyl radical to singlet 5,7-DDI; the former has C_{2v} symmetry and thus identical 5,6 and 6,7 C$-$C bond lengths, while the latter has bond lengths consistent with a 5,6 double bond and a 6,7 single bond, which has the effect of reducing Coulomb repulsion in the singlet by delocalizing the π-electron over the benzyl system.)[94]

An alternative comparison would be to note the similarity between the singlet and triplet states of 5,7-DDI and the analogous states of phenylnitrene.[94−96] In the latter case, the splitting has been measured to be 18 kcal/mol.[96]

D. Didehydroindenes vs Didehydronaphthalenes. One feature of indene that differentiates it from naphthalene is that there is essentially no bond alternation in the six-membered ring. Thus, the S$-$T splittings predicted for the 1,2-, 2,3-, and 3,4-DDIs are all within 0.8 kcal/mol of one another. This contrasts with the 1,2- and 2,3-DDN cases, where there is a 6.3 kcal/mol difference in ortho S$-$T gaps; this is rationalized as deriving from the significantly shorter C$-$C bond typically found at the 1,2-position compared to the 2,3.[8,36]

There is no particular difference predicted for the local geometries or S$-$T splittings of the two *m*-DDIs and the one *m*-DDN. The same is true for the para isomers of each system. Thus, the character of six-membered-ring arynes seems to be little affected by hydrocarbon ring annelation, with the exception of ortho isomers, which can show an effect *if* the annelation introduces bond length alternation.

In the DDNs π-polarization was found to operate at long ranges, giving rise to an alternating preference for singlet and triplet ground states when the two radical centers became sufficiently far from one another. However, that alternation is facilitated in DDN by the presence of rings having only an even number of atoms. In the case of DDI, polarization of the five-membered ring by spin density in the six-membered ring (and vice versa) seems negligible. Thus, there is essentially no difference in the thermochemistries of 2,5-DDI and 3,5-DDI, both of which are predicted to have very, very weak preferences for the triplet state, or between 2,6-DDI and 3,6-DDI, even though analogous diradicals show an alternating character in DDN. Thus, long-range π-polarization appears to be more effective in even-alternant hydrocarbons.

In DDN, the singlet preference over triplet for the 1,5-isomer is predicted to be 2 kcal/mol larger than that for the 1,4-isomer; this difference is rationalized by the two isomers having similar through-bond coupling mechanisms while 1,5-DDN lacks an antibonding through-space interaction present in 1,4-DDN.[8,36] In DDI, the difference between the two isomers is reduced to only 0.4 kcal/mol. This reduction probably reflects the noncollinearity now present in the 1,5-isomer, which reduces the efficiency of the through-bond interaction.

A different geometric effect identified in the DDN series was the efficiency of “W-coupling”,[8,36] which is well-known in NMR[97] and EPR[98] Thus, although π-polarization effects would be expected to render 2,7-DDN a triplet, it prefers the singlet state by about 1 kcal/mol. The analogous DDIs, 2,6 and 3,6, have essentially identical preferences, indicating that the strength of the W-coupling remains strong even though the five-membered ring somewhat distorts the ideal geometry present in the DDN case.

Finally, as noted above, 5,6-DDI is unique in being a true “aryne” with the formal triple bond in a five-membered ring. Its S$-$T splitting is substantially reduced compared to other DDI and DDN ortho arynes, as would be expected given the significantly poorer overlap for the in-plane π-system in the smaller ring.

V. Conclusions

CASPT2 and unrestricted DFT calculations (the latter being much more economical) provide predictions of structural and energetic properties for the didehydroindenes that are in good accord with one another, and are further in keeping with expectations based on theoretical and experimental results for related didehydroaromatic systems. Coupled-cluster theory suffers from instabilities when perturbative estimates for the effects of unlinked triple excitations are employed, even if Brueckner orbitals are used in the coupled-cluster ansatz.

The five-membered ring has little effect on the thermochemical properties of DDIs that are analogously related to *o*-, *m*-, or *p*-benzyne. In addition, through-bond coupling effects in DDIs are quite similar to those noted in didehydronaphthalenes. One difference between DDIs and DDNs is that long-range π-polarization does not appear to be as operative in the former case as it is in the latter, likely owing to the odd-numbered ring in the DDIs.

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Supporting Information Available: Electronic energies, geometries, and CAS configuration weights and orbital occupation numbers for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

(2) Jordan, K. *Theor. Chem. Acc.* **2000**, *103*, 286.

(3) Heilbronner, E.; Muszkat, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 3818.

(4) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(5) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.

(6) Paddon-Row, M. N. *Acc. Chem. Res.* **1992**, *15*, 245.

(7) Li, S.; Ma, J.; Jiang, Y. *J. Phys. Chem. A* **1997**, *101*, 5567.

(8) Squires, R. R.; Cramer, C. J. *J. Phys. Chem. A* **1998**, *102*, 9072.

(9) Cui, M.; Feng, J. K.; Zhang, H. X.; Ge, M. F.; Sun, C. C.; Zhang, J. P. *Synth. Met.* **1999**, *100*, 261.

(10) Lee, M. D.; Ellestad, G. A.; Borders, D. B. *Acc. Chem. Res.* **1991**, *24*, 235.

(11) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *11*, 1387.

(12) Myers, A. G. *Tetrahedron Lett.* **1987**, *28*, 4493.

(13) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995.

(14) Goldberg, I. H. *Acc. Chem. Res.* **1991**, *24*, 191.

(15) *Enediyne Antibiotics as Antitumor Agents*; Borders, D. B., Doyle, T. W., Eds.; Marcel Dekker: New York, 1995.

(16) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279.

(17) Grützmacher, H. F.; Lohmann, J. *Liebigs Ann. Chem.* **1970**, *733*, 88.

(18) Grützmacher, H. F.; Lehmann, W. R. *Liebigs Ann. Chem.* **1975**, 2023.

(19) Linnert, H. V.; Riveros, J. M. *Int. J. Mass Spectrom. Ion Processes* **1994**, *140*, 163.

(20) Thoen, K. K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1997**, *119*, 3832.

(21) Thoen, K. K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1999**, *121*, 800.

(22) Diau, E. W. G.; Casanova, J.; Roberts, J. D.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 1376.

(23) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134.

(24) Weimer, H. A.; McFarland, B. J.; Li, S.; Weltner, W. *J. Phys. Chem.* **1995**, *99*, 1824.

(25) Sander, W.; Bucher, G.; Wandel, H.; Kraka, E.; Cremer, D.; Sheldrick, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 10660.

(26) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669.

(27) Sander, W.; Exner, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2285.

(28) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

(29) Scheiner, A. C.; Schaefer, H. F., III; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 3118.

(30) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 11951.

(31) Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958.

(32) Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1994**, *116*, 4929.

(33) Lindh, R.; Persson, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4963.

(34) Lindh, R.; Lee, T. J.; Bernhardsson, A.; Persson, B. J.; Karlström, G. *J. Am. Chem. Soc.* **1995**, *117*, 7186.

(35) Cramer, C. J.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, *277*, 311.

(36) Cramer, C. J.; Squires, R. R. *J. Phys. Chem. A* **1997**, *101*, 9191.

(37) Kraka, E.; Cremer, D.; Bucher, G.; Wandel, H.; Sander, W. *Chem. Phys. Lett.* **1997**, *268*, 313.

(38) Lindh, R.; Ryde, U.; Schütz, M. *Theor. Chem. Acc.* **1997**, *97*, 203.

(39) Chen, W.-C.; Chang, N.-y.; Yu, C.-h. *J. Phys. Chem. A* **1998**, *102*, 2584.

(40) Lindh, R.; Bernhardsson, A.; Schütz, M. *J. Phys. Chem. A* **1999**, *103*, 9913.

(41) Galbraith, J. M.; Schreiner, P. R.; Harris, N.; Wei, W.; Wittkopp, A.; Shaik, S. *Chem. Eur. J.* **2000**, *6*, 1446.

(42) Gräfenstein, J.; Hjerpe, A. M.; Kraka, E.; Cremer, D. *J. Phys. Chem. A* **2000**, *104*, 1748.

(43) de Visser, S. P.; Filatov, M.; Shaik, S. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5046.

(44) Bucher, G.; Sander, W.; Kraka, E.; Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *35*, 746.

(45) Marquardt, R.; Sander, W.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 746.

(46) Davico, G. E.; Schwartz, R. L.; Ramond, T. M.; Lineberger, W. C. *J. Am. Chem. Soc.* **1999**, *121*, 6047.

(47) Cramer, C. J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2273.

(48) Johnson, W. T. G.; Cramer, C. J. *J. Am. Chem. Soc.*, in press.

(49) Ford, G. P.; Biel, E. R. *Tetrahedron Lett.* **1995**, *36*, 3663.

(50) Schreiner, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 4184.

(51) Schreiner, P. R. *Chem. Commun.* **1998**, 483.

(52) Koseki, S.; Fujimura, Y.; Hirama, M. *J. Phys. Chem. A* **1999**, *103*, 7672.

(53) Nam, H. H.; Leroi, G. E.; Harrison, J. F. *J. Phys. Chem.* **1991**, *95*, 6514.

(54) Hoffner, J.; Schottelius, M. J.; Feichtinger, D.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 376.

(55) Cramer, C. J. *J. Am. Chem. Soc.* **1998**, *120*, 6261.

(56) Cramer, C. J.; Debbert, S. *Chem. Phys. Lett.* **1998**, *287*, 320.

(57) Debbert, S. L.; Cramer, C. J. *Int. J. Mass Spectrom.* **2000**, *201*, 1.

(58) Cramer, C. J.; Squires, R. R. *Org. Lett.* **1999**, *1*, 215.

(59) Schreiner, P. R.; Prall, M. *J. Am. Chem. Soc.* **1999**, *121*, 8615.

(60) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(61) *Chemical Applications of Density Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Symposium Series 629; American Chemical Society: Washington, DC, 1996.

(62) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(63) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(64) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(65) Brueckner, K. A. *Phys. Rev.* **1954**, *96*, 508.

(66) Handy, N.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185.

(67) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(68) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(69) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.

(70) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(71) Gräfenstein, J.; Cremer, D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2091.

(72) Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1998**, *288*, 593.

(73) Sander, W.; Wandel, H.; Bucher, G.; Gräfenstein, J.; Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1998**, *120*, 8480.

(74) Stanton, J. F. *Chem. Phys. Lett.* **1997**, *281*, 130.

(75) Lim, M. H.; Worthington, S. E.; Dulles, F. J.; Cramer, C. J. In *Density-Functional Methods in Chemistry*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Symposium Series 629; American Chemical Society: Washington, DC, 1996; p 402.

(76) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS*, Version 4; Lund University: Lund, Sweden, 1997.

(77) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. A.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(78) Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261.

(79) Noodleman, L.; Post, D.; Baerends, E. J. *Chem. Phys.* **1982**, *64*, 159.

(80) Cramer, C. J.; Dulles, F. J.; Giesen, D. J.; Almlöf, J. *Chem. Phys. Lett.* **1995**, *245*, 165.

(81) Davidson, E. *Int. J. Quantum Chem.* **1998**, *69*, 241.

(82) Crawford, T. D.; Stanton, J. F. Preprint.

(83) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

(84) Reed, D. R.; Kass, S. R. *J. Mass Spectrom.* **2000**, *35*, 534.

(85) Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261.

(86) Barckholtz, C.; Barckholtz, T. A.; Hadad, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 491.

(87) Broadus, K. M.; Kass, S. M. To be published.

(88) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(89) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

(90) Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26*, 259.

(91) Yoshizawa, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 6921.

(92) Salem, L. *Electrons in Chemical Reactions*; John Wiley and Sons: New York, 1982; Chapter 7.

(93) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785.

(94) Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8698.

(95) Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1992**, *114*, 5349.

(96) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 8699.

(97) Sternhell, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 236.

(98) King, F. W. *Chem. Rev.* **1976**, *76*, 157.

(99) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986.

(100) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1991; Vol. 2, Parts 1 and 2.