Ortho-, meta-, and para-benzyne.
A comparative CCSD(T) investigation

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Geometries and energies of ortho-benzyne (1), meta-benzyne (2), and para-benzyne (3) have been calculated at the CCSD(T), GVB, GVB-LSDC, and MBPT(2) levels of theory employing the 6-31G(d, p) basis. Calculations suggest relative energies of 0, 13.7, and 25.3 kcal/mol, respectively, and $\Delta H_f^0(298)$ values of 110.8, 123.9, and 135.7 kcal/mol for 1, 2, and 3. With the $\Delta H_f^0(298)$ value of 3, the reaction enthalpy $\Delta_R H(298)$ and the activation enthalpy $\Delta H^*(298)$ for the Bergman cyclization of (Z)-hexa-1,5-diyn-3-ene to 3 are calculated to be 9.1 and 28.5 kcal/mol.

1. Introduction

Abstraction of two hydrogen atoms from benzene leads to one of the three isomeric benzynes, namely ortho-benzyne (1,2-didehydrobenzene, 1), meta-benzyne (1,3-didehydrobenzene, 2), or para-benzyne (1,4-didehydrobenzene, 3). According to their structural formula, the benzynes should possess considerable biradical character and, therefore, they are highly reactive intermediates, which have attracted considerable attention by chemists ever since the pioneering work of Wittig on arynes in the early forties [1–31]. It has been speculated that benzynes 2 and 3 can rearrange to their bicyclic isomers bicyclo[3.1.0]hexatriene (4) and bicylo[2.2.0]hexatriene (butalene, 5), but there is only indirect evidence which suggests 4 and 5 as intermediates in reactions [32–34].
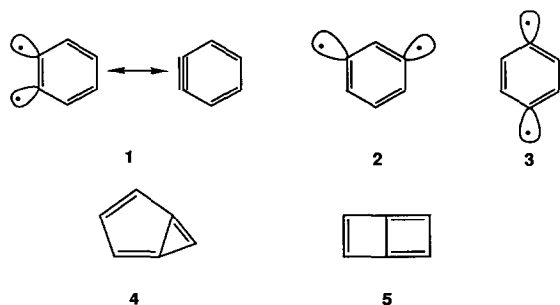
At present, research on benzynes is undergoing a renaissance triggered by the discovery of the intermediary of p-benzynes in the DNA-cleaving action of enediyne-based antitumor agents [35–37]. Enediynes such as (Z)-hexa-1,5-diyn-3-ene (6) can undergo a Bergman cyclization to form 3,

(1)
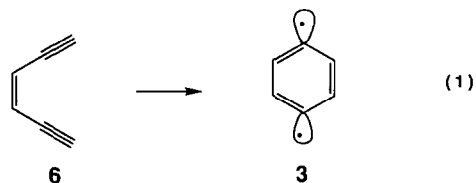
which in turn attacks DNA by abstracting H atoms from its sugar phosphate backbone. Since an understanding of the mechanism of the Bergman cyclization is a prerequisite of the enediyne antitumor activity, a number of investigations have concentrated on measuring the relative stability of the three benzyne isomers [13–17]. For example, the heat of formation $\Delta H_f^0(298)$ of 1 has been measured by Riveros, Ingemann and Nibbering [13] and independently by Guo and Grabowski [14]. Spectroscopic investigations ranging from microwave [12], infrared [6,10,11,18] to UV [5] have gathered information on 1 which has been complemented by a series of quantum chemical calculations [18,22–31] leading to the equilibrium geometry, infrared spectrum and other molecular properties.

Compared to the data available for **1**, experimental and theoretical information on **2** and **3** is rather limited [17,19–24]. Recently, the first derivative of **2** has been trapped in the matrix at low temperatures and spectroscopically investigated by Bucher and co-workers [19]. Wenthold, Paulino and Squires (WPS) [17] have determined $\Delta H_f^0(298)$ values for **1**, **2**, and **3** by energy-resolved collision-induced dissociation measurements. According to their results the relative stability of **1**, **2**, and **3** is 0, 10, and 22 kcal/mol, which partially agrees, but partially differs considerably from the few calculational predictions of the relative stability of the three isomers [22–24]. However, if the $\Delta H_f^0(298)$ values of WPS are used to derive the energetics of the Bergman cyclization (1), then large deviations up to 20 kcal/mol will be found with regard to calculated reaction energies [38,39].

In view of these discrepancies, and in view of the importance of benzynes in connection with enediyne antitumor agents [35–37], a comparative study of the three benzynes is needed. We report here a coupled cluster (CC) ab initio description of **1**, **2**, and **3** using all single (S) and double (D) excitations (CCSD) together with a perturbative treatment of all triple (T) excitations (CCSD(T)) [40]. This level of theory has proven to lead to accurate results for closed-shell problems. In this work, we will check whether the same is true for compounds with considerable multireference character. For this purpose, we have also carried out generalized valence bond (GVB) calculations with the perfect pairing (PP) restriction [41], in which we have used the equivalent of two determinants to describe the two formally single electrons of **1**, **2**, and **3** (GVB-PP(1) or shorter GVB(1)). Such an approach covers major parts of the multireference effects but not dynamic electron correlation effects. To cover the latter, we have combined the GVB approach with a simple local spin density (LSD) functional approach (GVB-LSDC) [42,43], which yields reasonable relative energies in cases with multireference character as has been shown recently [42,43].

On the basis of our CCSD(T) calculations, we are able (a) to correctly determine the geometries and relative energies of **1**, **2**, and **3**, (b) to assess the degree of biradical character for the three isomers, (c) to determine molecular properties such as dipole

moment and rotational constants, and (d) to show ways of identifying the three benzynes by spectroscopic means. We will demonstrate that experimental heats of formation published recently [17] are probably erroneous by as much as 6–8 kcal/mol. Furthermore, we will determine the energetics of the Bergman cyclization on the basis of CCSD(T) theory and will show that previous calculations of the energetics of reaction (1) [38] are erroneous by as much as 13–19 kcal/mol.

2. Results and discussion

CCSD(T) and GVB(1) geometry optimizations for **1**, **2**, and **3** have been carried out with the 6-31G(d, p) basis set [44]. In order to get starting geometries for the CC and GVB optimizations many-body perturbation theory calculations at second-order (MBPT(2)) [45] have been performed with the same basis set. Calculations have been carried out with the ACES II program [46] and the program COLOGNE, [47] which contains an extended version of GVBTWO [48] to carry out GVB-LSDC calculations [42,43].

CCSD(T)/6-31G(d, p) optimized geometries of **1**, **2**, and **3** are shown in fig. 1 (in bold print) with the corresponding GVB(1)/6-31G(d, p) and MBPT(2)/6-31G(d, p) values given in italics and normal print, respectively. In table 1, calculated energy data for **1**, **2**, and **3** are summarized while table 2 contains relevant information on the biradical character of the benzynes. Finally, in table 3, calculated dipole moments and rotational constants of the benzynes are summarized and compared with the available experimental data for **1**.

The geometry of **1** corresponds to a slightly distorted hexagon characterized by one relatively short CC bond (1.27 Å, fig. 1) while the remaining bonds have lengths close to that of the CC bond in benzene (CCSD(T): 1.40 Å). Both the CCSD(T) and MBPT(2) geometry are similar while the GVB geometry suggests somewhat shorter bond lengths. This is also true in the case of the other benzynes and, therefore, we will limit the discussion of calculated geometries to CCSD(T) results. In the case of **1**, calculated geometries suggest that a bond with partial triple bond character has been formed. This descrip-
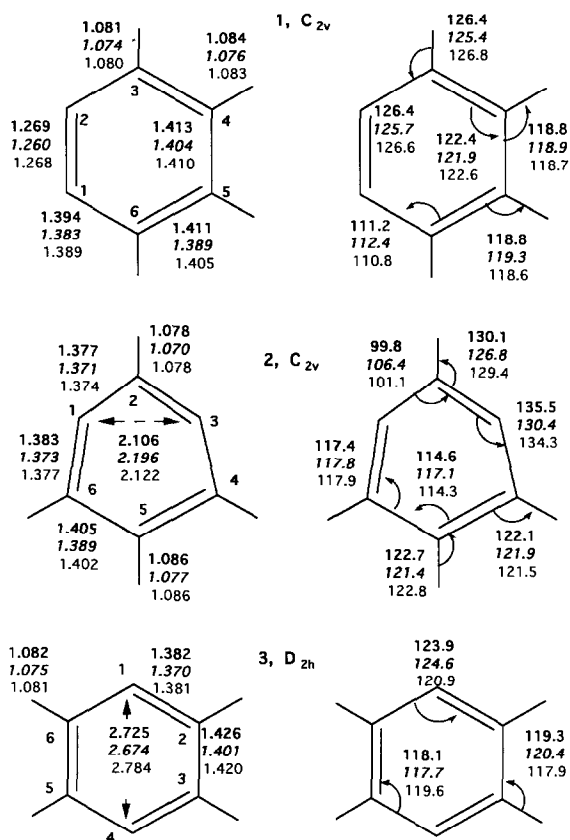
Fig. 1. CCSD(T) (in bold print), GVB(1) (in italics), and MBPT(2) (in normal print) geometries of ortho-benzyne (**1**), meta-benzyne (**2**), and para-benzyne (**3**) obtained with a 6-31G(d, p) basis. Bond lengths are given in Å, angles in deg.

tion is in line with calculated geometries reported by various other authors [25–31]. According to GVB(1) calculations, the biradical character χ of **1** is 22% [#1], which is in line with the largest D excitation amplitude a_2^D (0.24, table 2) calculated at the CCSD level of theory. However, when comparing the

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[#1] For a GVB wavefunction, one can determine the biradical character χ of a molecule from the occupation number of the natural orbitals representing an electron pair: $\chi = 1 - 2S/(1+S^2)$ with S being the overlap between the two pair orbitals. For a CCSD(T) wavefunction, we have defined the biradical character χ by $(\Sigma n_i - \Sigma n_i \text{ (ref)})$, where for a system with 2 electrons, Σn_i is defined as the sum over all occupation numbers for natural orbitals η_i with $i > n$. $\Sigma n_i (\text{ref})$ has to be taken from an appropriate reference molecule, e.g., benzene in the case of the three benzyne isomers.

later value with the corresponding amplitude for benzene (**7**, 0.12, table 2) as a suitable reference, then a considerably lower biradical character is suggested. It seems to be appropriate to consider other pairing possibilities of the two electrons that participate in the formation of the triple bond. This can be done by adding up the occupation numbers n_i of virtual natural orbitals (according to Hartree–Fock numbering) and compare the resulting value Σn_i with the corresponding sum of a suitable reference compound such as **7**. In this way, a biradical character of just 11% (table 2) is obtained for **1**, which suggests relatively little unpairing of electrons even in the case of extreme deviations from the linear geometry of a CC triple bond. Obviously, the molecule tries to retain tight pairing of electrons as much as possible.

When going from **7** to **2**, the hexagonal geometry of **7** is much more strongly distorted as in the case of **1** (fig. 1). Caused by rehybridization at atoms C1 and C3, the CC(H) bonds become shorter (CCSD(T): 1.377 and 1.383 Å, fig. 1) while the C(H)CC(H) angles widen from 120° in **7** to 135.5° in **2**. As a consequence, both the CC(H)C angle (99.8°) and the C1, C3 distance (2.106 Å) decrease thus supporting stabilizing through-space interactions between the single-electron orbitals at centres C1 and C3. The overlap between the orbitals of the GVB pair is still relatively large at 0.30 (**1**: 0.60, **3**: 0.09) indicating substantial electron pairing. Stabilizing through-space orbital interactions are supported by stabilizing through-bond interactions, [50] which provide additional possibilities for electron pairing. As a consequence, the biradical character of **2** (GVB, 44%; CCSD(T), 20%, table 2) is just twice as large as that of **1**, i.e. it is still relatively small and far from the 100% implied by the structural formula commonly used for **2** in text books (vide infra).

Because of through-space interactions, one could speculate that the bicylic isomer could be formed if the 1,3 distance decreases and the bonding overlap increases. At the Hartree–Fock level (HF/6-31G(d, p)), we find a local minimum corresponding to **4**, but at the MBPT(2), MBPT(4), and GVB(1) level of theory a local minimum representing **4** can no longer be located. Since this is in line with recent calculations by Burton and co-workers who have identified **4** as a transition state of the rearrangement of **1** to cyclopentadienylidenecarbene [51], no further

Table 1
Energies and heats of formation ΔH_f^0 (298) of ortho-benzyne (1), meta-benzyne (2), and para-benzyne (3) [a]

Method	1	2	3
MBPT(2)//MBPT(2)	−230.22343	7.5	10.3
GVB(1)//GVB(1)	−229.44325	12.5	23.2
GVB(1)-LSDC//GVB(1)	−230.77679	13.0	24.2
CCSD//CCSD(T)	−230.24387	18.0	42.5
CCSD(T)//CCSD(T)	−230.28994	13.7	25.3
exp. estimate [b]	0	10±3	22±3
heats of formation ΔH_f^0 (298)			
CCSD(T)//CCSD(T) [b]	110.8	123.9	135.7
exp. [c]	106±3	116±3	128±3
estimated error of exp. values	5	8	8

[a] Absolute energies in hartree, relative energies in kcal/mol. The notation method 1//method 2 denotes the level of theory used for the final calculation (method 1) and the level of theory used for the geometry optimization (method 2). All calculations have been performed with the 6-31G(d, p) basis set. For 1, absolute energies are given, for 2 and 3 relative energies with respect to 1.
[b] Calculated ΔH_f^0 (298) values including ZPE and temperature corrections (see text) have been determined from hydrogenation reactions (2), (3), and (4) using the experimental ΔH_f^0 (298) value of benzene [49].
[c] Ref. [17].

Table 2
Biradical character χ (in %) of ortho-benzyne (1), meta-benzyne (2), and para-benzyne (3)

Molecule	χ [a] estimated	χ [b] GVB	$\sum n_i$ [c] CCSD(T)	χ [d] CCSD(T)	a_2^D [e] CCSD(T)
1	?	22	0.84	11	0.24
2	100	44	0.92	20	0.34
3	100	82	1.38	65	0.71
6	0		0.79	0	0.14
7	0		0.73	0	0.12

[a] Estimated biradical character is based on simple structural formulas.
[b] For a GVB wavefunction, one can determine the biradical character χ of a molecule from the occupation number of the natural orbitals representing an electron pair: $\chi = 1 - 2S/(1+S^2)$ with S being the overlap between the two pair orbitals.
[c] For a system with $2n$ electrons, $\sum n_i$ is defined as the sum over all occupation numbers for natural orbitals η_i with $i > n$.
[d] For a CCSD(T) wavefunction, we have defined the biradical character χ by $[\sum n_i - \sum n_i \text{ (ref)}]$, where 7 has been taken as a reference molecule.
[e] Largest double excitation amplitude a_2^D obtained at the CCSD level of theory.

search for 4 at the CCSD(T) level of theory has been performed in this work.

Through-space and through-bond interactions in 2, although stabilizing, are clearly weaker than the bonding 1,2-orbital interactions in isomer 1. Therefore, 2 is less stable than 1 by 13.7 kcal/mol according to CCSD(T) calculations (table 1). GVB(1) and GVB(1)-LSDC lead to comparable values of 12.5 and 13.0 kcal/mol, respectively, while both MBPT(2) and CCSD suggest unreasonably low or high energies that reflect the deficiencies of a single

determinant approach without the inclusion of T excitations. The latter are important to cover single electron, electron pair correlation effects and, thereby, some of the multireference character of the benzyne molecules.

When going from 7 to 3, the symmetry is lowered from D_{6h} to D_{2h} and only moderate distortions of the hexagonal geometry of 7 occur as can be seen from the CCSD(T) geometry of 3 (fig. 1). Rehybridization at atoms C1 and C4 increases the s-character of the bonding orbitals, which leads to shorter CC(H)

Table 3
Dipole moments μ and rotational constants A, B, and C of ortho-benzyne (1), meta-benzyne (2), and para-benzyne (3) [a]

	1	2	3
CCSD(T)/6-31G(d, p)			
μ	1.38	0.83	0
A	6920(1.0%) [b]	7264	6722
B	5678(0.5%)	5383	5602
C	3110(0.7%)	3092	3056
GVB(1)/6-31G(d, p)			
μ	1.29	0.85	0
A	6989(0.0%) [b]	7022	6950
B	5837(2.3%)	5663	5671
C	3181(1.3%)	3135	3123
MBPT(2)/6-31G(d, p)			
μ	1.68	1.21	0
A	7000(0.1%) [b]	7052	6592
B	5685(0.0%)	5434	5739
C	3137(0.1%)	3106	3068

[a] Dipole moments in Debye and rotational constants in MHz.
[b] Differences with regard to experimental values ($A_v = 6990$, $B_v = 5707$, and $C_v = 3140$ MHz, ref. [12]) are given in parentheses.

bonds (1.382 Å, CCSD(T), fig. 1), while at the same time stabilizing through-space interactions increase because of the larger p-character of the single occupied orbitals. While rehybridization and through-space interactions stabilize 3, through-bond interactions between singly occupied orbitals and bonding C(H)C(H) orbitals are destabilizing because they involve four electrons [50]. Isomer 3 is less stable than 1 by 25.3 kcal/mol (23.2 and 24.2) according to CCSD(T) (GVB(1) and GVB(1)-LSDC) calculations. Its relatively low stability is in line with its large biradical character of 82% (GVB) and 65% (CCSD(T)), respectively. Both through-bond and through-space interactions between the single electrons represent pairing possibilities, which reduce the biradical character formally from 100 to the values calculated, but since 1,4 through-space overlap (C1, C4: 2.725 Å, fig. 1) is moderate ($S = 0.09$) and through-bond interactions are destabilizing, the degree of electron pairing is smaller than in 2.

HF/6-31G(d, p) predicts for the bicyclic isomer 5 a stationary point with three imaginary frequencies, while no stationary point at all is found on the MBPT(2)/6-31G(d, p) and GVB(1)/6-31G(d, p) surfaces. We conclude that the bicyclic isomers 4 and 5 do not exist.

Heats of formation of 1, 2, and 3. Relative energies obtained at the GVB(1)/6-31G(d, p) level of theory show the best agreement with experimentally determined stabilities of 1, 2, and 3 [17] (table 1). However, both GVB(1)-LSDC and CCSD(T) suggest higher relative energies for 2 and 3. Apart from this, both GVB and CCSD(T) calculations clearly show that MBPT(2), CCSD or even semiempirical methods (e.g. MNDO/CI or MINDO/3 [23,24]) are inappropriate for the description of benzynes. From all previously published data, only GVB−PP(1)/4-31G energies (0, 14.5, and 23.3 kcal/mol) published by Noell and Newton [22] come close to the relative energies obtained in this work.

In order to compare ab initio energies at 0 K with experimental ΔH_f^0 values usually determined at 298 K one has to calculate zero-point energies (ZPE) as well as vibrational and temperature corrections at 298 K. It is also useful to determine theoretical ΔH_f^0(298) values from calculated energies by using appropriate reference compounds and known enthalpy values. This has been done by calculating ZPE and other corrections at the GVB(1)/6-31G(d, p) level of theory. Then, CCSD(T) heats of hydrogenation (reactions (2), (3) and (4) below) have been obtained for the three benzynes using CCSD(T) re-

action energies, GVB(1)/6-31G(d, p) frequencies for 1–3 and experimental frequencies for 7 [52] and H_2 [53],

$$1 + H_2 \rightarrow 7, \tag{2}$$

$$2 + H_2 \rightarrow 7, \tag{3}$$

$$3 + H_2 \rightarrow 7. \tag{4}$$

Using the experimental heat of formation for 7 (19.8 kcal/mol [49]), $\Delta H_f^0(298)$ values of 110.8, 123.9, and 135.7 kcal/mol are obtained for 1, 2, and 3 (table 1) which are 5 (1), 8 (2) and 8 kcal/mol (3) larger than the experimental $\Delta H_f^0(298)$ values reported by WPS [17]. From comparative calculations on small alkines and alkenes with known $\Delta H_f^0(298)$ values [39], we find that CCSD(T) heats of formation of the three benzynes are too low for compounds with large biradical character, but otherwise agree rather well with experimental $\Delta H_f^0(298)$ values. In view of the reliability of CCSD(T) energies and the considerable difficulties in determining $\Delta H_f^0(298)$ for benzynes, we conclude that *experimental heats of formation published by WPS* [17] *are erroneous* and that the CCSD(T) based $\Delta H_f^0(298)$ values (table 1) can be considered as useful starting points for a refinement of experimental stabilities for 1, 2, and 3.

Dipole moments and rotational constants. Both 1 and 2 possess a finite dipole moment where the one for the *o*-isomer (1.38 Debye, CCSD(T), table 3) is larger than that for the *m*-isomer (0.83 Debye, table 3). MBPT(2) values are considerably larger (table 3) while GVB(1) dipole moments are in line with the CCSD(T) results.

In the case of 1, calculated rotational constants A_e, B_e, C_e can be compared with experimental A_v, B_v, C_v constants. The best agreement between experimental and calculated constants is obtained for MBPT(2) values, which is probably due to cancellation of errors. For CCSD(T), rotational constants agree within 1% with experimental values, while for GVB(1) deviations up to 2.3% are found (table 3), which may result from the fact that CC bond lengths are shorter at the GVB level (fig. 1). In view of the high sensitivity of rotational constants with regard to small changes in molecular geometry, the agreement between calculated and experimental values can be considered as satisfactory. Accordingly, CCSD(T)

dipole moments and rotational constants for 2 and 3 can aid the spectroscopic identification of these labile intermediates.

Chemical relevance of calculated energies. The $\Delta H_f^0(298)$ value for 3 can be used to determine the reaction enthalpy of the Bergman cyclization. A CCSD(T)/6-31G(d, p) investigation of (Z)-hexa-1,5-diyn-3-ene (6) leads to a $\Delta H_f^0(298)$ value of 126.6 kcal/mol [*2], which compares well with thermochemical estimates of about 126 kcal/mol [54]. Accordingly, the CCSD(T) reaction enthalpy of the Bergman cyclization is 9.1 kcal/mol at 298 K.

Previous predictions of this quantity by Koga and Morokuma [38] have led to 28 (ten electron CASSCF/DZ) and 22 kcal/mol (MRD-SDCI/DZ) suggesting $\Delta H_f^0(298)$ values of $3 \leqslant 148$ kcal/mol, which are not possible in view of the discussion given above. An analysis of the CASSCF and MRD-SDCI results reveals that the large reaction energies result from an unbalanced description of the reaction partners of the Bergman cyclization. If the experimental $\Delta H_f^0(298)$ of 3 is combined with the thermochemical estimate of $\Delta H_f^0(298)$ for 6 a reaction enthalpy of 2 kcal/mol is found, which is 7 kcal /mol smaller than the CCSD(T) value.

We have checked the CCSD(T) results for reaction (1) by investigating the hypothesis (supported by experimental observations [55–57]) that (1) is spontaneous if the two triple bonds of the enediyne are pressed together to a distance of about 3 Å. CCSD(T) geometry optimization of the transition state (TS) of reaction (1) leads to an energy barrier of 29.5 kcal/mol and an activation enthalpy of 28.5 kcal/mol [39]. If the enediyne 6 is pressed together to a C1, C6 distance of 3 Å, the reaction enthalpy decreases to 0.2 kcal/mol and the activation enthalpy becomes 19.3 kcal/mol. Since reactions with an activation enthalpy lower than 21 kcal/mol proceed spontaneously, we find that CCSD(T) theory confirms experimental observations, which in turn adds reliability to CCSD(T) energy data for the Bergman cycloaromatization.

[*2] CCSD(T)/6-31G(d, p) energy of 4: −230.18734 hartree, geometry: C1C2: 1.220 Å, C2C3: 1.421 Å, C3C4: 1.357 Å, C1C2C3: 178.0°, C2C3C4: 120.6°; CCSD(T)/6-31G(d, p) energy of the TS: −230.21135 hartree, geometry: C1C2: 1.276 Å, C2C3: 1.410 Å, C3C4: 1.396 Å, C1C2C3: 133.3°, C2C3C4: 120.7°.

3. Conclusions

The following conclusions can be drawn from the CCSD(T)/6-31G(d, p) investigation of benzynes **1**, **2**, and **3**:

(1) CCSD(T)/DZ+P theory is an appropriate tool for the determination of accurate relative energies of benzynes since it covers dynamic correlation effects and some of the multireference effects. In particular, CCSD(T) covers single electron, electron pair correlation effects that are needed to correctly describe the degree of electron pairing of the single electrons of a biradical.

(2) CCSD(T)/6-31G(d, p) calculations suggest $\Delta H_f^0(298)$ values of 110.8, 123.9, and 135.7 kcal/mol for **1**, **2**, and **3**, i.e. the meta- and para-isomers are 13 and 25 kcal/mol less stable than the ortho-isomer **1**. It is likely that the experimental $\Delta H_f^0(298)$ values [17] for **1**, **2**, and **3** are 5 (**1**), 8 (**2**) and 8 (**3**) kcal/mol too low.

(3) The biradical character of the benzynes is considerably smaller than could be expected from normal structural formulas for **1**, **2**, and **3**. At the CCSD(T) level, the biradical character is predicted to be 11%, 20% and 65% indicating that considerable pairing of the single electrons occurs because of through-bond and through-space interactions.

(4) The three isomers can be identified by CCSD(T) dipole moments and rotational constants.

(5) The CCSD(T)/6-31G(d, p) reaction enthalpy of the Bergman cyclization of enediyne **6** is 9.1 kcal/mol and the corresponding activation enthalpy is 28.5 kcal/mol.

(6) Increasing the strain energy of an enediyne leads to a lowering of the reaction barrier of the Bergman cyclization. At a C1, C6 distance of 3 Å for **6**, reaction enthalpy and activation enthalpy decrease to 0.2 and 19.3 kcal/mol. This can be used for the synthetic design of anticancer drugs in enediyene research.

Acknowledgement

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