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Substituent Effects on Benzdiyne: A Density Functional Theory Study

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Received November 29, 2002

Density functional theory (DFT) studies were performed to investigate the effect of substituents on the properties of benzdiyne derivatives. Twelve substituted benzdiynes—C_6X_2, where X = F, Cl, Br, Me, CF_3, CN, OH, NO_2, NH_2, OMe, NMe_2, and Ph—were considered along with the unsubstituted 1,4-benzdiyne. The structures, vibrational frequencies, and IR intensities of these benzdiynes were studied with a popular three-parameter hybrid density functional (B3LYP) combined with the split-valence 6-31G(d) basis set and Dunning's correlation-consistent polarized triple-ζ (cc-pVTZ) basis set. The relative stabilities of the substituted benzdiynes were studied with the help of reaction energies of isodesmic reactions, which showed that the electron-withdrawing groups destabilized the benzdiynes more than they did the corresponding benzenes, whereas the electron-donating groups stabilized the benzdiynes more than they did their benzene counterparts. Correlation analyses revealed that field/inductive effects played a more important role than did resonance effects. The changes in atomic charges and spin populations due to the substituents were also studied. The asymmetric $\nu(C\equiv C)$ stretching modes obtained were close to the 1500-cm^{-1} mark. Reinvestigation of the experimental results supported these results; a weak IR band at 1486 cm^{-1} was assigned to this asymmetric stretching mode in $C_6(CF_3)_2$ **F**. Some other benzdiynes also had large IR intensity values for their asymmetric $\nu(C\equiv C)$ vibrational modes due to the coupling with other vibrational modes. Heats of formation for the substituted benzdiynes were obtained from the reaction energies calculated at the B3LYP/cc-pVTZ level of theory.

I. Introduction

Because benzdiynes (tetradehydrobenzdiynes, C_6H_2) are highly unsaturated, they are challenging to study experimentally. Their existence was suggested by the final products obtained from various organic reactions[1−3] and by theoretical studies.[4−6] In 1997, we reported the first direct spectroscopic observation of a benzdiyne derivative, 3,6-bis(trifluoromethyl)-1,4-benzdiyne (**F**), by using a matrix isolation technique.[7] Prompted by our experimental work, Schaefer's group studied three possible benzdiyne (unsubstituted) isomers and **F** in 1999 by using both ab initio and density functional theory (DFT).[8] Sattelmeyer and Stanton[9] carried out theoretical studies of nine isomers of C_6H_2, including three benzdiyne isomers.

Recently, we calculated the structure and energetics of benzdiyne isomers by using both ab initio and DFT methodologies, and noted that benzdiyne has multireference character.[10] This finding is quite important for DFT computations on benzdiynes. We also pointed out that benzdiynes have large heats of formation.[10] In our earlier experiments,[11,12] we were unable to confirm the existence of unsubstituted benzdiynes. Very recently, we tried to generate benzdiynes from five kinds of precursors with different substituents, and succeeded in directly observing a new substituted benzdiyne, 3,6-difluoro-1,4-benzdiyne (**B**), as well as the previously observed benzdiyne **F**.[13] Additionally, we confirmed that benzdiynes could not be generated from the other three precursors under similar conditions. Thus, the substitution pattern of the precursors plays a vital role in the direct observation of benzdiynes.

The detection of C≡C stretching bands is an important topic in matrix isolation studies of arynes. Although we isolated both **B** and **F** in our previous experiments, we were unable to find out the asymmetric $\nu(C\equiv C)$ vibra-

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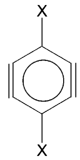

A: X = H, **B**: X = F, **C**: X = Cl,
D: X = Br, **E**: X = Me, **F**: X = CF_3,
G: X = CN, **H**: X = OH, **I**: X = NO_2,
J: X = NH_2, **K**: X = OMe,
L: X = NMe_2, **M**: X = Ph

FIGURE 1. Schematic representation of benzdiynes **A**−**M**.

tional modes because of their weak IR intensities.[7,13] Adding substituents to the benzdiynes might change the IR intensity of this important mode and thereby allow us to observe it.

In the present investigation, we used DFT to study twelve substituted benzdiynes: C_6X_2, where X = F, Cl, Br, Me, CF_3, CN, OH, NO_2, NH_2, OMe, NMe_2, and Ph (**B**−**M,** Figure 1). None of these benzdiynes (except the fluorinated ones) had previously been studied, either theoretically or experimentally. This study enabled us (1) to determine the structural changes in the benzdiynes caused by the substituents and (2) to obtain the vibrational frequencies of the benzdiynes, frequencies that should be helpful for experimental detection of these extremely unstable species. This investigation also allowed us to draw conclusions about whether one can observe the asymmetrically coupled ν(C≡C) harmonic vibrational modes by changing the substituents on the parent benzdiyne. We obtained the stabilization energies of the benzdiynes by studying isodesmic reactions, and these energies provided insight into how the substituents affected the stability of the benzdiynes. In addition, we calculated the heats of formation of the substituted benzdiynes.

II. Computational Details

All computations were performed with the Gaussian 94[14] and Gaussian 98[15] programs. The three-parameter hybrid functional (B3LYP)[16,17] was used for all the calculations. All the benzdiyne derivatives were optimized first with the split-valence 6-31G(d) basis set followed by the frequency calculations, and it was found that none of the structures have any imaginary frequencies. Second, the Dunning's[18] correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis set was used to optimize all the benzdiynes. The optimized geometries were characterized by means of harmonic vibrational frequency calculations with the same cc-pVTZ basis set, which showed no imaginary frequencies indicating that all structures were minima on the potential energy surface. As the solutions obtained with the spin-restricted DFT (RDFT) method were unstable for the substituted benzdiynes and for the parent benzdiyne, we used a symmetry-broken, spin-unrestricted DFT (UDFT) method, which has been shown to give more-accurate geometries for a number of aromatic singlet diradicals.[10,19−26] The UDFT description (exchange functionals) has been shown to cover static correlation effects (in addition to the dynamic correlation effects covered by the exchange-correlation functionals) needed for the correct treatment of critical open-shell singlet diradicals.[20]

TABLE 1. Energy Differences, Δ*E*(R−U), and $\langle S^2\rangle$ Values for Benzdiynes A−M

	$\langle S^2\rangle$		Δ*E*(R−U), kcal/mol	
benzdiyne	6-31G(d)	cc-pVTZ	6-31G(d)	cc-pVTZ
A	0.928	0.827	7.20	4.92
B	0.931	0.857	7.54	5.68
C	0.944	0.861	7.74	5.72
D	0.944	0.866	7.69	5.73
E	0.970	0.877	7.93	5.79
F	0.928	0.839	7.16	5.21
G	0.913	0.822	6.91	4.99
H	0.967	0.889	5.62	4.68
I	0.907	0.831	6.50	5.12
J	0.986	0.899	8.27	6.02
K	0.940	0.854	6.20	4.81
L	1.007	1.002	3.40	3.34
M	0.921	0.820	6.87	4.75

The relative stabilities of the substituted benzdiynes were obtained from the isodesmic reaction enthalpies. The heats of formation of the selected benzdiynes were calculated from these reaction enthalpies and the experimental heats of formation of benzene and substituted benzenes.[27−29]

The atomic charges for all the benzdiynes were derived by means of electrostatic potential (ESP)-driven charges according to the Merz−Singh−Kollman scheme.[30,31] Unpaired electron spin densities were calculated using the Mulliken population analysis (MPA) scheme.

III. Results and Discussion

A. RDFT Instability. Our previous study indicated that unsubstituted benzdiyne (**A**) has multireference character.[10] The stability tests showed that the solutions obtained for **A** with the RDFT reference were unstable and that reoptimization with the UDFT reference led to an energy lowering. The same was also true for all the substituted benzdiynes in the current study (Table 1).

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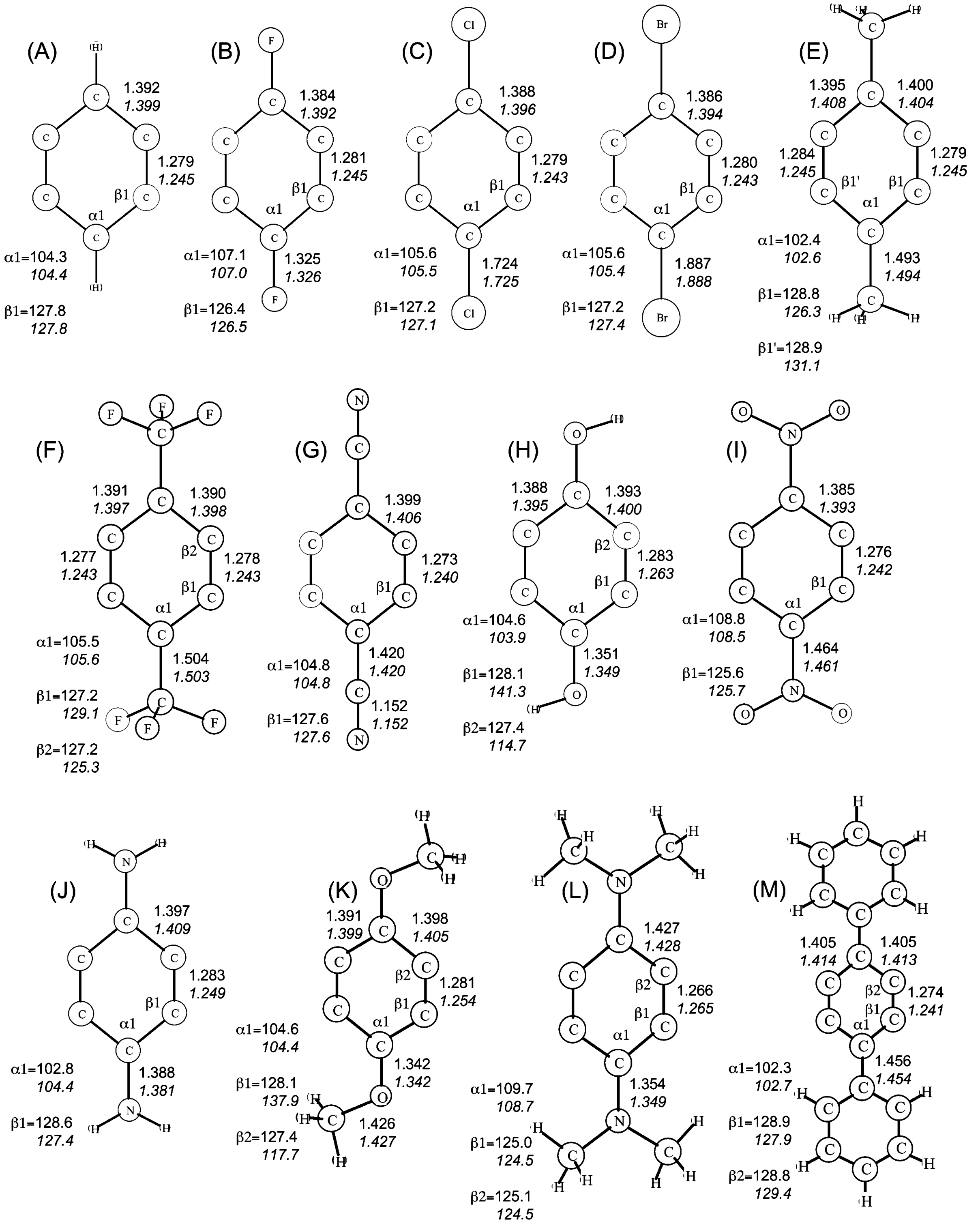

FIGURE 2. UB3LYP/cc-pVTZ optimized structures with geometrical parameters of benzdiynes **A**−**M** (the values in italics were obtained at the RB3LYP/cc-pVTZ level).

The differences between the RDFT and UDFT energies [ΔE(R−U)] and the $\langle S^2 \rangle$ values obtained for all the substituted benzdiynes with the B3LYP functional and two different basis sets are tabulated in Table 1. The benzdiyne **L** behaved somehow differently from all other benzdiynes; $\langle S^2 \rangle$ for **L** was 1.00 while for others it had the range between 0.82 and 0.90. The results obtained from the stability tests suggest that benzdiynes have multireference character, even though they are not perfect diradicals.

B. Geometries and Vibrational Frequencies. The optimized structures of the 12 substituted benzdiynes, together with the important geometrical parameters obtained with the B3LYP functional (with unrestricted as well as restricted references) with use of the cc-pVTZ basis set, are depicted in Figure 2. [Cartesian coordinates

TABLE 2. Unscaled Harmonic Vibrational Frequencies for the Asymmetric C≡C Stretch in Benzdiynes A−M, Their IR Intensities, r(C≡C) Values, Unpaired Spin Densities at $C_{\beta 1}$, Sum of the Atomic Charges of the Two Ortho Carbons (q_{ortho}), and Total Atomic Charge of the Benzdiyne Ring (q_{ring})[a]

		ν(C≡C)				
benzdiyne	r(C≡C), Å	ν, cm^{-1}	IR, km/mol	spin density, au	q_{ortho}, au	q_{ring}, au
A	1.279	1485	24.0	−0.554	−0.059	−0.295
B	1.281	1529	0.6	−0.572	−0.031	+0.141
C	1.279	1508	7.3	−0.567	+0.038	+0.048
D	1.280	1496	8.5	−0.566	+0.056	−0.013
E	1.279	1478	7.2	−0.557	−0.168	−0.063
F	1.278	1503[b]	27.9	−0.568	−0.003	−0.053
G	1.273	1528	28.4	−0.562	+0.046	−0.033
H	1.283	1505[c]	144.0	−0.568	−0.115	+0.090
I	1.276	1529[d]	7.7	−0.579	+0.067	+0.067
J	1.283	1504[e]	1.7	−0.564	−0.145	+0.078
K	1.281	1520[f]	68.2	−0.563	−0.154	+0.056
L	1.266	1680[g]	412.7	−0.203	−0.548	−0.180
M	1.274	1534[h]	8.0	−0.548	−0.132	−0.166

[a] The q values were obtained at the UB3LYP/6-31G(d) level; all other values were obtained at the UB3LYP/cc-pVTZ level. [b] Mixed with C−C stretching. [c] Mixed with C−H stretching, C−O stretching, and C−O−H bending. [d] Mixed with C−C−N bending. [e] Mixed with C−C stretching. [f] Mixed with O−C−H bending, and C−O stretching. [g] Mixed with N−C−H bending. [h] Mixed with C−C−C bending.

for the optimized structures are given in the Supporting Information (SI-1).] Unsubstituted benzdiyne has a C_6 ring with D_{2h} symmetry, but substitution slightly changes the C_6 ring structure in many cases. The substituted benzdiynes can be classified into three categories on the basis of their C_6 ring structure: (1) benzdiynes with a C_6 ring with D_{2h} symmetry (**A**, **B**, **C**, **D**, **G**, and **I**); (2) benzdiynes with a planar C_6 ring (**E**, **F**, **H**, **J**, **K**, and **M**); and (3) benzdiynes with a nonplanar C_6 ring (**L**).

The benzdiynes belonging to the first group had highly symmetric planar structures, whereas the benzdiynes in the other groups had either asymmetric structures or structures in which the C_6 ring retained its planarity but some of the atoms in the substituent groups were located outside the plane. The symmetry of the C_6 ring in these benzdiynes deviated from D_{2h} symmetry; differences in r values or/and differences in β angles were noticed. The phenyl-substituted benzdiyne (**M**) was planar, unlike its benzene counterpart, which is nonplanar because of the well-known biphenyl effect[32] caused by steric interactions between the ortho hydrogens. Thus, the nature of the substituent influenced the structure of the substituted benzdiynes.

The most interesting structural parameter of the benzdiynes is the C≡C bond length, and this parameter reflected the importance of using the correct reference functional (UDFT). The calculated bond lengths (around 1.28 Å) were longer than normal for a C≡C bond, but clearly shorter than for a typical C=C bond. For all the benzdiynes (except **L**), UDFT yielded a C≡C bond that was longer (by around 0.03 Å) than that obtained with RDFT. The C≡C bond length obtained in **F** was larger by 0.034 Å than that obtained previously at the RB3LYP/TZ2P level.[8] However, there was almost no difference between the C≡C bond lengths obtained with the RDFT and UDFT references for **L**.

The calculated unpaired spin densities on $C_{\beta 1}$ (ortho carbon, see Figure 2 for notations) clearly reflected the multireference nature of most of the benzdiynes (Table 2). The total atomic charge on the C_6 ring (q_{ring}) increased (in positive scale) as the substituent's electron-withdrawing nature increased. The calculated atomic charges on the β carbons, q_{ortho} ($= q_{C\beta 1} + q_{C\beta 2}$), were also influenced by the nature of the substituent: the values had a positive value or a small negative value in benzdiynes substituted with electron-withdrawing groups, whereas the opposite was true for the benzdiynes substituted with electron-donating groups. Again **L** stands separately from all other benzdiynes; its spin density at $C_{\beta 1}$ was −0.20 while respective spin densities of all other benzdiynes were around −0.50. Also, contrary to all other benzdiynes, spin densties were located not only at β carbons but also at α carbons as well as at nitrogen atoms.

The asymmetric ν(C≡C) vibrational modes of the benzdiynes showed interesting differences. The calculated r(C≡C) values, the respective asymmetric ν(C≡C) harmonic vibrational frequencies, and their IR intensities for all the benzdiynes are tabulated in Table 2 (frequencies obtained in the present study as well as those taken from the literature for comparison purpose were not scaled). Our calculated frequency of the asymmetric ν(C≡C) vibrational mode for **A** was 1485 cm^{-1} (UB3LYP/cc-pVTZ). This frequency was 373 cm^{-1} smaller than that obtained at the B3LYP/TZ2P level by Bettinger et al.[8] The frequency for the same mode obtained at the CCSD(T)/TZ2P level[8] is 1675 cm^{-1}. Sattelmeyer and Stanton[9] studied several C_6H_2 isomers, including **A**. Their calculated value for the asymmetric ν(C≡C) mode in **A** is 1766 cm^{-1} at the SDQ-MBPT(4)/TZ2P level. For benzdiyne **F**, the frequency for the asymmetric ν(C≡C) vibrational mode (1503 cm^{-1} at UB3LYP/cc-pVTZ) differed from the value (1866 cm^{-1} at the B3LYP/TZ2P level) obtained by Bettinger et al.[8] So in both cases, the asymmetric ν(C≡C) modes obtained in the present study deviated much from those that were obtained in the previous studies.

Our experimental results on **B** and **F** made possible the evaluation of the different computational methods. Unfortunately the asymmetric ν(C≡C) vibrational mode in **B** was not observed in the experimental study.[13] This might be due to its very weak IR intensity; this mode was obtained at 1529 cm^{-1} with 0.6 km/mol IR intensity at the UB3LYP/ccp-VTZ level of theory, otherwise four intense IR bands observed in **B** (579, 929, 1174, and 1439

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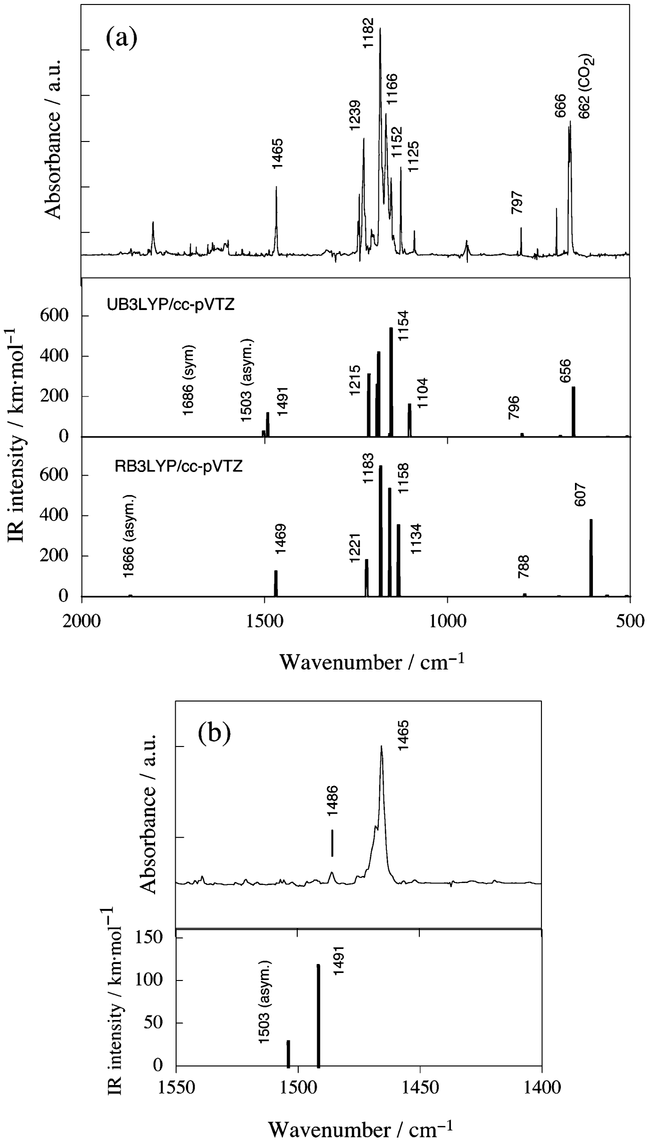

FIGURE 3. (a) Observed IR spectrum of benzdiyne **F** and theoretical IR spectra obtained by UDFT and RDFT calculations. (b) Enlarged IR spectrum around the IR band at 1486 cm^{-1} and computational results at the UB3LYP/cc-pVTZ level.

cm^{-1}) were similarly, for the most part, reproduced by both RDFT (512, 936, 1177, and 1461 cm^{-1}) and UDFT (560, 941, 1152, and 1480 cm^{-1}) references. Contrary to **B**, the corresponding asymmetric ν(C≡C) vibrational mode in benzdiyne **F** (1503 cm^{-1}) had large IR intensity, 27.9 km/mol, at the UB3LYP/cc-pVTZ level. We believed that this IR intensity was large enough to be observed in the experimental spectra. So we reanalyzed our experimental results[13] with much care, which produced a remarkable outcome. We found a weak peak at the higher wavenumber region of the ring deformation mode peak at 1465 cm^{-1} (Figure 3a). The enlarged IR spectra (Figure 3b) clearly showed a peak at 1486 cm^{-1}. The dynamic behavior of this band (Figure 4) is similar to that of the IR band that is ascribed to **F** (1465 cm^{-1}). Thus, we can assign this weak IR band to **F**: this IR band could be ascribed to the asymmetric ν(C≡C) vibrational mode in **F** predicted at 1503 cm^{-1} at the UB3LYP/cc-pVTZ level. All the other vibrational modes observed in **F** were well reproduced by the UB3LYP/cc-pVTZ level (Figure 3a). In fact the UDFT calculation reproduced the location of the IR band observed at 666 cm^{-1} well (RDFT underestimated this band by 59 cm^{-1}). By considering the fact that UB3LYP provided the most reliable account of the infrared spectrum of the highly problematic *p*-benzyne diradical as provided by the UHF-CCSD(T) and RB-CCD(T) levels over most of the high-level calculations including RHF-SDQ-MBPT(4) and RHF-CCSD(T),[34,35] we believe that the vibrational frequencies obtained for biradical-like benzdiynes in the present study are reliable and, importantly, we are able to assign the most-wanted asymmetric ν(C≡C) vibrational mode in **F** at 1486 cm^{-1}. To our knowledge, no ν(C≡C) stretching mode at such a low wavenumber has been observed previously, so this is probably the first time that such an exceptionally weak C≡C bond has been observed. There may be two reasons for this extraordinary location of the ν(C≡C) mode: (1) an exceptionally long C≡C bond length owing to the multireference character of benzdiynes and (2) the effect of the asymmetrically coupled stretching motion of two C≡C bonds. Finally, one should not forget the fact that this asymmetric ν(C≡C) mode is different from the pure ν(C≡C) mode.

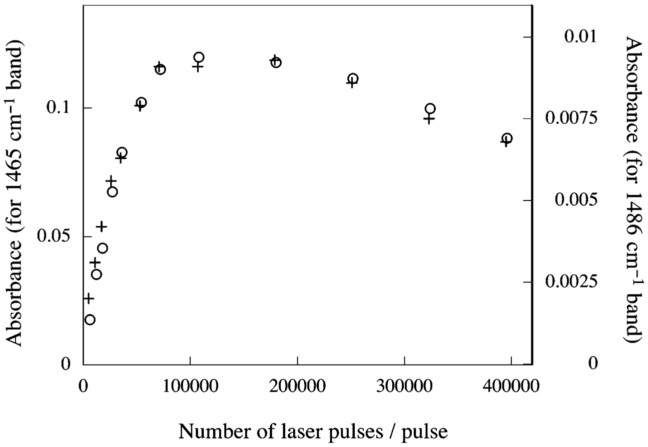

FIGURE 4. Dynamic behavior of the IR band ascribed to **F** (1465 cm^{-1}) (open circle) and that of the weak IR band at 1486 cm^{-1} (cross).

For almost all the benzdiynes, the asymmetric ν(C≡C) vibrational modes were obtained at about 1500 cm^{-1} (Table 2). The longer r and smaller ν values are clearly due to the weak C≡C bonds in diradical-like benzdiynes. Although the IR intensity obtained for the asymmetric ν(C≡C) vibrational mode in **B** was very small, the IR intensity for this mode in some other substituted benzdiynes was large due to the coupling with other vibrational modes. Considering that the vibrational modes with IR intensities of greater than 5 km/mol have been observed for 1-naphthyne in an Ar matrix in our experimental setup,[36] we believe that the asymmetric ν(C≡C) vibrational mode of these substituted benzdiynes should be experimentally observable, if they

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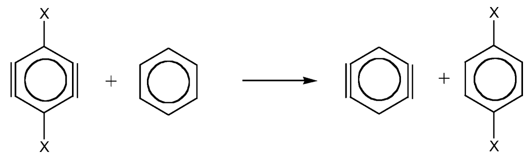
TABLE 3. Stabilization Energies (Δ*H*) and Heats of Formation ($\Delta H_f°$) at the B3LYP/cc-pVTZ Level

substituent (X)	Δ*H*, kcal/mol	$\Delta H_f°$, kcal/mol
F	−4.9	126.9
Cl	−4.1	205.4
Br	−3.3	228.7
Me	4.8	195.0
CF_3	−5.9	
CN	−7.8	288.8
OH	1.6	127.6
NO_2	−11.4	
NH_2	5.5	
OMe	5.1	241.0
NMe_2	18.6	
Ph	9.7	252.4

can be isolated in low-temperature matrixes at sufficiently high concentrations.

The harmonic vibrational frequencies of some other IR-active modes obtained for the selected benzdiynes (SI-2) clearly indicate that substituted benzdiynes have many modes with large IR intensities. We hope that if some of these molecules can be isolated, the calculated frequencies will play a vital role in identifying them.

C. Relative Stabilities and Heats of Formation. The relative stabilities of the substituted benzdiynes can be determined by means of the following isodesmic reaction:



The enthalpy changes for this reaction show whether X stabilizes or destabilizes benzdiyne more than it does benzene. The calculated energies suggest that the substituent X causes destabilization of the benzdiyne relative to benzene if the isodesmic reaction involving the substitution of X is exothermic: similarly, X causes stabilization of the benzdiyne relative to benzene if the reaction is endothermic. To calculate the reaction enthalpies (Δ*H*) at the B3LYP/cc-pVTZ level of theory, we optimized all the corresponding substituted benzenes at the B3LYP/cc-pVTZ level. We corrected the total energies of the benzdiynes and benzenes by using scaled zero-point energies (ZPE) obtained at the B3LYP/6-31G(d) level. The ZPEs were scaled by 0.9804.[37] The calculated reaction enthalpies are tabulated in Table 3. [The total energies and ZPE values for all the benzdiynes obtained at UB3LYP/cc-pVTZ level are given in the Supporting Information (SI-3).]

Replacement of two hydrogen atoms on benzene by two halogen atoms on benzdiyne led to an exothermic reaction; i.e., the halogen atom preferred to be attached to benzene rather than to benzdiyne. In other words, the addition of the substituent destabilized the benzdiyne. By considering the effects of three different halogen atoms, we found that the most electronegative halogen, fluorine, resulted in the most exothermic reaction, which indicates that fluorine destabilized benzdiyne more than the other two halogens did. The same destabilization of benzdiyne relative to benzene was also seen with other electron-withdrawing substituents. In fact, electron-withdrawing groups (NO_2, CF_3, and CN) in general destabilized the benzdiynes. In contrast, electron-donating substituents made the reaction an endothermic one; that is, electron-donating groups (such NH_2, OH, and Me) stabilized the benzdiynes. The benzdiyne stabilization increased as the electron-donating potential of the substituents increased. Thus, the benzdiynes clearly preferred electron-donating substituents over electron-withdrawing substituents. It should be noticed by considering the highly unstable nature of the benzdiynes that the small destabilization by halogen atoms and CF_3 groups (around 5 to 6 kcal/mol) might have less impact on benzdiynes.

The electronic effects of substituents can be interpreted with the help of substitution constants. Substituent effects consist mainly of field, inductive, resonance, and hyperconjugative effects. Because the peculiarity of benzdiynes arises mainly from the existence of in-plane π bonding in the C≡C bonds, we expected field/inductive effects to be more important than resonance effects. To test this expectation, we mapped the correlations between the calculated Δ*H* values and the Swain and Lupton constants, *F* and *R*, which express field/inductive effects and resonance effects,[33] respectively (Figure 5). The benzdiyne **L** was not considered for this graph since the parameters (*r*, ν, and spin density) obtained for **L** differed from those obtained for the other 12 benzdiynes. The calculated Δ*H* values showed better correlation with the constants representing inductive effects than with the constants representing resonance effects. The correlation coefficient for the Δ*H* and *R* values was smaller than 0.4, whereas the same coefficient for the Δ*H* and *F* values was moderately high (Figure 5). Hence, the σ-inductive effects of the substituent clearly played a vital role in the relative stabilization of the benzdiynes. This correlation supports our conclusion that the electron-withdrawing substituents destabilized the benzdiynes.

Heat of formation of unstable molecules is an important physical parameter for considering various organic reactions. So we calculated the heats of formation of the substituted benzdiynes by using the isodesmic reaction energies and the heats of formation of **A**, benzene, and the substituted benzenes. The heat of formation of **A** was computed from the atomization energy according to the procedure described by Curtiss et al.[38] We used higher level ab initio methodologies G2[39] and the recently developed CBS-QB3[40,41] for this purpose because highly reliable heats of formation for many molecules have been obtained with these methodologies in the past.[38,42] In addition, our previous work has shown that reliable heats of formation can be obtained for *o*-benzyne at the G2 and

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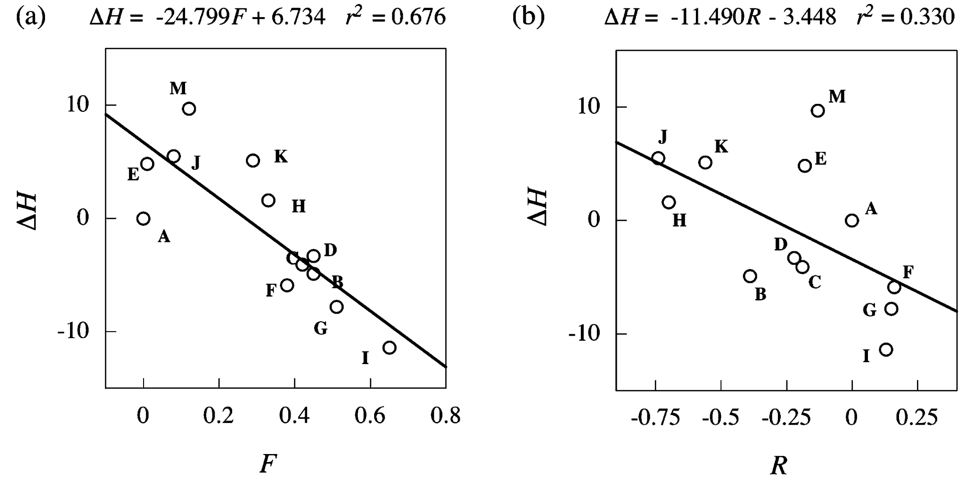

FIGURE 5. Correlation plots of the calculated ΔH values with substituent constants F and R: (a) ΔH vs F; (b) ΔH vs R.

CBS-QB3 levels of theory.[10] It is worth mentioning that heats of formation for **A** calculated at both levels were the same, 215.2 kcal/mol. To obtain the heats of formation ($\Delta H_f°$) of the substituted benzdiynes at 298.15 K, we included thermal corrections (unscaled) in the reaction energies. The calculated $\Delta H_f°$(298.15 K) values of the selected benzdiynes are listed in Table 3. The $\Delta H_f°$(298.15 K) value obtained for **B** by means of the above-mentioned atomization energy procedure (125.7 kcal/mol at the G2 level) coincided well with that obtained through isodesmic reaction energies (126.9 kcal/mol).

It is unlikely that the experimental heats of formation will soon be determined for these highly unsaturated benzdiynes, and considering the fact that studying the thermochemistry of arynes is a challenging task for theory,[43] these theoretically calculated heats of formations may be useful for understanding the chemical reactions and thermodynamic stabilities of these highly unstable intermediates.

IV. Concluding Remarks

We studied 12 substituted benzdiynes by using density functional theory, and reached the following conclusions:

All the benzdiynes had multireference character. Restricted DFT provided unstable solutions, and reoptimization with unrestricted DFT led to an energy lowering. All the benzdiynes had spin densities of about 0.5 on their β carbons.

Substitution slightly altered the structure of the benzdiyne C_6 ring. The electronic effects of the substituents influenced the atomic charges on the β carbons as well as those on the benzdiyne ring. These changes in atomic charges might ultimately affect the reactivities of the benzdiynes.

The C≡C bond lengths obtained with the unrestricted method for most of the benzdiynes, including the unsubstituted one, were around 0.03 Å longer than those obtained with the restricted method. The asymmetric ν(C≡C) vibrational frequencies obtained for all these benzdiynes were around 1500 cm^{-1}. IR intensities obtained for this important mode in some of the benzdiynes suggest that it could be observable experimentally. The asymmetric ν(C≡C) stretching vibrational mode in **F** was obtained at 1503 cm^{-1} with the intensity of 28 km/mol at the UB3LYP/cc-pVTZ level of theory. With this result, reanalyzing our experimental data made it possible to assign this asymmetric mode in **F** at 1486 cm^{-1}. Many vibrational modes with large IR intensities were predicted for all the benzdiyne derivatives. If the intermediates are ever isolated experimentally, these IR modes could be useful in assigning the observed frequencies.

We obtained the relative stabilities of the substituted benzdiynes by studying isodesmic reactions. The reaction enthalpy changes denoting the relative stability correlated well with the substitution constants expressing field/inductive effects. This result indicated that electron-withdrawing substituents such as NO_2, CN, and CF_3 destabilized benzdiyne more than they destabilized the corresponding benzenes, whereas electron-donating groups such as NH_2, Me, and OH had the opposite effect.

Acknowledgment. S.A. sincerely thanks the Science and Technology Agency (STA) of Japan for the award of a postdoctoral fellowship through a Center of Excellence (COE) project.

Supporting Information Available: Optimized Cartesian coordinates, the vibrational frequencies and IR intensities, and the total energies and the unscaled zero-point vibrational energies at the UB3LYP/cc-pVTZ level. This material is available free of charge via the Internet at http://pubs.acs.org.

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