(ddd, $J_{7\text{-}anti,7\text{-}syn} \approx 5$ Hz, $J_{7\text{-}anti,1} = J_{7\text{-}anti,6} \approx 8.8$ Hz, 1 H, 7-*anti*-H), 1.11–1.29 (m, 4 H, 4-H, 5-H), 1.32–1.42 (m, 1 H, 6-H), 1.50–1.59 (m, 2 H, 3-H), 1.77–1.85 (m, 1 H, 1-H), 3.92 ($m_c$, 2 H, 8-H), 4.07 (q, $J_{2,1} = J_{2,3} = 5.7$ Hz, 1 H, 2-H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 6.95 (t, C-7), 12.5, 13.3 (d, C-1, C-6), 19.0, 23.1, 27.7 (t, C-3, C-4, C-5), 65.1 ($m_c$, C-8), 75.5 (d, C-2), 124.5 (q, C-9); MS (70 eV) *m/e* 194 (16, $M^+$), 179 (21), 166 (56), 165 (42), 152 (37), 140 (41), 139 (64), 95 (51), 94 (62), 93 (12), 91 (10), 83 (25), 81 (31), 80 (11), 79 (100), 77 (20), 69 (13), 68 (40), 67 (72), 66 (25), 65 (13), 59 (19), 57 (15), 55 (56), 54 (29), 53 (36), 43 (13), 42 (29), 41 (88), 40 (12), 39 (54), 29 (19), 28 (29), 27 (31). Anal. Calcd for $C_9H_{13}F_3O$ (194.1): C, 55.68; H, 6.75. Found: C, 55.92; H, 6.93.

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# Preparation and Chemistry of $PhI^+C{\equiv}CI^+Ph{\cdot}2^-OTf$, Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene, a Novel Difunctional Acetylene, Bis(iodonium) Species and a Stable $C_2$-Transfer Agent[†]

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*Received December 27, 1990. Revised Manuscript Received February 19, 1991*

**Abstract:** The title compound **2** is readily prepared as a stable microcrystalline solid from bis(tri-*n*-butylstannyl)acetylene and PhICN·OTf. It was fully characterized by multinuclear NMR, IR, and elemental analysis. As expected, the electron-deficient acetylene **2** reacts with a number of nucleophiles (e.g., $Ph_3P$, PhSNa, and PhOLi) providing a variety of bifunctionalized acetylenes **5**, **6**, **7**, and **9**. It also undergoes cycloaddition reactions with cyclopentadiene, furan, and other 1,3-dienes to afford useful bis(iodonium)norbornadiene-type adducts **12–14**.

As a consequence of their ready availability and the considerable versatility of their transformations, acetylenes play a key role in organic chemistry.[1] They easily add electrophiles resulting in functionalized olefins, undergo cycloadditions, possess novel photochemistry, and undergo numerous other interesting and useful transformations and rearrangements.[1,2] Most recently acetylenes and their homopolymers have attracted attention in the field of new materials; especially as potential organic conductors[3] and nonlinear optical materials.[4]

Although numerous functionalized alkynes are accessible, little is known about difunctional acetylenes, $XC{\equiv}CX$ and $XC{\equiv}CY$, with the functional groups directly attached to the triple bond. Recently, we[5] and others[6,7] have demonstrated that alkynyl(phenyl)iodonium salts **1**, the latest members of the family of multicoordinate iodine species,[8] serve as premier progenitors for a variety of monofunctional acetylenes, $RC{\equiv}CX$, and other useful transformations.

$$\underset{\mathbf{1}}{RC{\equiv}CI^+Ph{\cdot}X^-} \qquad \underset{\mathbf{2}}{PhI^+C{\equiv}CI^+Ph{\cdot}2CF_3SO_3^-}$$

In this paper we wish to report the ready preparation, characterization, and chemistry of the title compound **2**, a novel, versatile, difunctional acetylene and a unique, stable $C_2$ species.[9,10]

## Results and Discussion

**Preparation and Characterization of 2.** Alkynyliodonium salts **1** are generally prepared by one of the following common procedures: (a) reaction of terminal alkynes with [hydroxy(tosyloxy)iodo]benzene (Koser's reagent),[11] (b) reaction of (trimethylsilyl)acetylenes with PhIO/$BF_3$–etherate,[12] (c) reaction of alkynes with iodobenzene fluoroborates, fluorophosphates, or fluoroantimonates,[13] or (d) reaction of (trimethylsilyl)acetylenes with PhIO/$Tf_2O$ (Zefirov's reagent).[14] In our experience none of these methods worked for the preparation of the diiodonium acetylene **2**. Specifically, reactions of bis(trimethylsilyl)acetylene with any of the above iodine(III) reagents gave either only the monoiodonium salts under mild conditions or tar under forcing

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[†] Dedicated to Professor Ernest L. Eliel on the occasion of his 70th birthday.

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conditions. Employment of the more reactive bis(tributylstannyl)acetylene as a starting substrate resulted in the formation of only black tar even at −78 °C.

The successful synthesis of the bis(iodonium)acetylene **2** is due to our recent discovery of a new type of mixed iodobenzene sulfonate,[15] particularly (cyanophenyl)iodonium triflate **4**. This compound is a versatile reagent for the preparation of iodonium salts from stannylacetylenes via an iodonium transfer process.[16] The bis(iodonium)acetylene **2** can be prepared in a single step in 80–85% isolated yield by the reaction of the known bis(stannyl)acetylene **3**[17] and reagent **4** in $CH_2Cl_2$ under very mild conditions (eq 1). Compound **2** is a relatively stable, white microcrystalline solid that decomposes over several weeks at room temperature but may be stored for extended periods in a refrigerator without change.[18] Because of its highly ionic nature, it is insoluble in solvents such as $CH_2Cl_2$, $CHCl_3$, and ether. Polar nucleophilic solvents (e.g., $H_2O$, $CH_3OH$, EtOH, $CH_3NO_2$, DMSO, DMF) react rapidly with compound **2** with liberation of iodobenzene. It is best handled and reacted in pure, dry $CH_3CN$ where it is stable for several hours at room temperature or under heterogeneous conditions in $CH_2Cl_2$.

$$\underset{\mathbf{3}}{n\text{-}Bu_3SnC{\equiv}CSnBu_3\text{-}n} + \underset{\mathbf{4}}{2PhI(OTf)CN} \xrightarrow[-2n\text{-}Bu_3SnCN]{CH_2Cl_2,\ -78\text{ to }0\ °C,\ N_2} \underset{\mathbf{2}}{PhI^+C{\equiv}CI^+Ph{\cdot}2TfO^-} \quad (1)$$

Compound **2** was fully characterized by multinuclear NMR, IR, Raman spectrometry, and elemental analysis. The infrared spectrum is dominated by absorptions of the aromatic and ionic triflate moieties, and as expected, does not show an acetylenic stretch due to its symmetry. The Raman spectrum, however, reveals an intense alkynyl stretch at 2137 $cm^{-1}$.

The $^1H$ NMR spectrum displays the expected 2:1:2 aromatic resonances between 7.55 and 8.20 ppm typical of phenyliodonium salts. The acetylenic carbons appear at 51.8 ppm in the $^{13}C$ NMR; this falls in between the usual positions for the monoiodonium species **1** (20–40 ppm for the $\alpha$-carbons and 110–120 ppm for the $\beta$-carbons).[14] Further corroboration of the structure of **2** is provided by its chemistry.

**Reactions of Bis(iodonium) Salt 2 with Nucleophiles.** By analogy with the behavior of iodonium salts **1**,[5] compound **2** should be reactive toward nucleophiles acting as a $C_2$ transfer agent. Indeed, we have found that **2** reacts with a variety of nucleophiles under very mild conditions (−78 to −40 °C, $CH_2Cl_2$ or $CH_3CN$), but the products of these reactions cannot always be isolated because of insufficient stability. To date we have isolated and identified products in the reactions of **2** with nucleophilic reagents of four different types: phenolate and thiophenolate anions, triphenylphosphine, and the silyl enol ether of acetophenone.

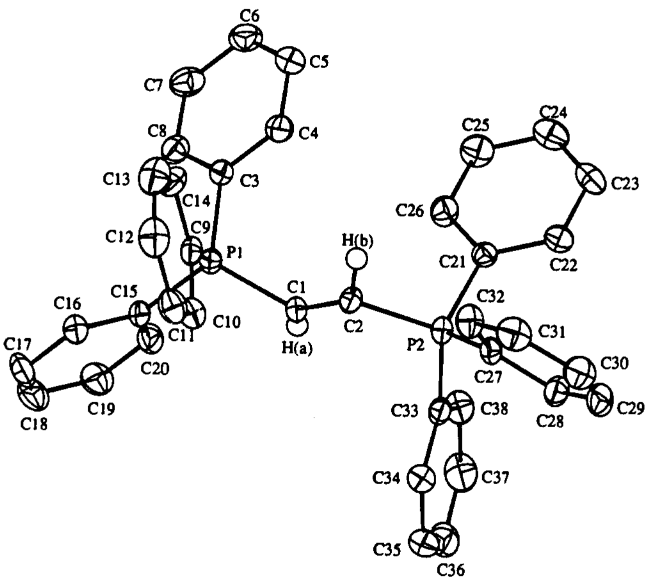
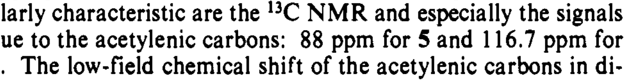


**Figure 1.** ORTEP of bis(phosphonium)ethylene **8**.

Compound **2** reacts with excess PhSNa in $CH_3CN$ or PhOLi in $CH_2Cl_2$ giving in good yield the relatively stable difunctionalized acetylenes **5** and **6**, respectively (eq 2). These products were characterized by IR, $^1H$ and $^{13}C$ NMR, and high-resolution mass spectra. Specifically, mass spectra affords in both cases the appropriate molecular ions and fragmentation patterns. Particularly characteristic are the $^{13}C$ NMR and especially the signals due to the acetylenic carbons: 88 ppm for **5** and 116.7 ppm for **6**. The low-field chemical shift of the acetylenic carbons in diphenoxyacetylene **6** may be explained by the large inductive electron-withdrawing nature of the two oxygen substituents.



Reactions of the iodonium salt **2** with 1 equiv of PhSNa or PhOLi under the same conditions resulted in compounds **5** or **6** and unreacted **2**, with none of the products of monosubstitution.

Three different products can be obtained in the reaction of **2** with $Ph_3P$ depending on the exact reaction conditions (eq 3). In the reaction with 2 equiv of $Ph_3P$ in $CCl_4$ under super dry conditions the alkynyldiphosphonium salt **7** can be prepared in 60% yield. This crystalline product is extremely hygroscopic and turns into an unidentified orange oil when exposed to air in a matter of a few minutes. The structure of compound **7** was elucidated by multinuclear NMR and high-resolution mass spectroscopy. In the FAB mass spectrum the expected peaks of the cationic part of the salt (M − $TfO^-$)$^+$ as well as further characteristic fragmentation patterns are observed. The presence of the triflate anions is confirmed by $^{19}F$ NMR. In the $^{31}P$ NMR a singlet at $\delta$ 11.8 ppm indicates the presence of an acetylenic phosphonium species.[19] The $^{13}C$ NMR consists of a group of signals charac-

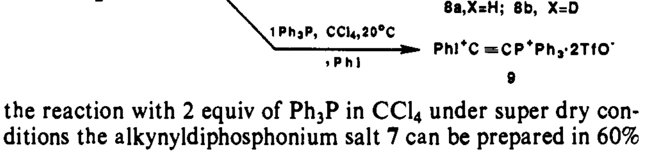


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**Table I.** Crystallographic Data for **8** and **12**

| | **8** | **12** |
|---|---|---|
| formula | $C_{40}H_{32}F_6O_6P_2S_2$ | $C_{21}H_{16}F_6O_6S_2$ |
| formula weight, g/mol | 846.748 | 796.284 |
| space group | *Pbca* | $P2_1/n$ |
| space group no. | 61 | 1014 |
| crystal system | orthorhombic | monoclinic |
| cell constants | | |
| a, Å | 22.599 (2) | 15.9328 (10) |
| b, Å | 20.817 (1) | 13.7223 (9) |
| c, Å | 16.484 (1) | 12.7900 (8) |
| $\alpha$, deg | 90.000 | 90.00 (0) |
| $\beta$, deg | 90.000 | 103.748 (2) |
| $\gamma$, deg | 90.000 | 90.00 (0) |
| cell volume, Å$^3$ | 7754.80 | 2716.22 |
| $z$ | 4 | 4 |
| calcd density, g/cm$^3$ | 1.45 | 1.947 |
| crystal dimensions, mm | 0.28 × 0.24 × 0.20 | 0.29 × 0.22 × 0.19 |
| absorption coeff, cm$^{-1}$ | 26.788 | 25.108 |
| radiation, Å | Cu 1.54056 | Mo 0.71073 |
| reflcns measd | 8037 | 5258 |
| unique data | | 4970 |
| $2\theta$ limits, deg | 4.00–130.00 | 1.00–48.00 |
| scan technique | $\theta/2\theta$ scan | $\theta/2\theta$ scan |
| scan speed, deg/min | | 3.0 |
| scan range | $0.8000 + 1.400 (\tan\theta)^0$ | $K - 1.3$ to $K + 1.6$ |
| data coll. position | bisectic, with $\theta = 0$ | |
| absorbtion correction | empirical | empirical |
| min. % transmission | 97.1551 | 96.3100 |
| max. % transmission | 99.9668 | 99.9200 |
| av % transmission | 98.1198 | |
| highest peak in final diff Fourier, e/Å$^3$ | 0.922 | 1.266 |
| max $\rho$ value in final diff Fourier, e/Å$^3$ | 3573.88 | 1720.045 |
| weighting scheme | unit weights | non-Poisson contribution |
| data rejected | $I < 3.00\sigma(I)$, $\sin(\theta)/\lambda < 0.100$ | $I < 3.00\sigma(I)$, $\sin(\theta)/\lambda < 0.1000$ |
| no. of obsvns | 4081 | 3520 |
| no. of variables | 520 | 329 |
| data-to-parameter ratio | 7.848 | 10.699 |
| shift-to-error ratio | 0.021 | 0.024 |
| error in an obsvn of unit wt. | 4.3942 | 1.7690 |
| *R* factor | 0.0731 | 0.0504 |
| weighted *R* factor | 0.0784 | 0.0754 |

teristic for phenyls in phosphonium salts and a doublet at 135 ppm for the acetylenic carbons with a C–P coupling constant of 100 Hz. The unusual low-field chemical shift of the acetylenic carbons in compound **7** are likely due to the strong electron-withdrawing nature of the phosphonium groups.

A different product, **8**,[20] was formed in the reaction of **2** with excess $Ph_3P$ in wet $CH_3CN$. Compound **8** was isolated from the reaction mixture by crystallization in 85–90% yield and was identified by multinuclear NMR spectroscopy. Specifically, the $^{31}P$ NMR for compound **8** shows a singlet at $\delta$ 21.2 ppm, which is 10 ppm downfield from the phosphorus signal in the corresponding acetylenic salt **7**. The $^{13}C$ NMR of both compounds **7** and **8** are similar, but the signal of the olefinic carbons in **8** are shifted downfield by 5 ppm relative to the acetylenic carbons in **7**. The signal of the olefinic protons of **8** in the $^1H$ NMR are located in the same region as the aromatic protons and thus ambiguous. In order to establish the exact molecular structure of compound **8**, a single-crystal X-ray structure determination

**Table II.** Selected Bond Distances for **8**[a]

| bonds | distances (Å) | bonds | distances (Å) | bonds | distances (Å) |
|---|---|---|---|---|---|
| C1–C2 | 1.322 (4) | P1–C3 | 1.795 (3) | P2–C21 | 1.783 (3) |
| C1–P1 | 1.813 (3) | P1–C9 | 1.793 (3) | P2–C27 | 1.788 (3) |
| C2–P2 | 1.810 (3) | P1–C15 | 1.797 (3) | P2–C33 | 1.791 (3) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

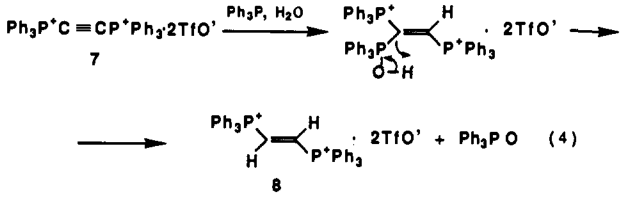
**Table III.** Selected Bond Angles for **8**[a]

| bonds | angles (deg) | bonds | angles (deg) |
|---|---|---|---|
| P1–C1–C2 | 119.9 (3) | C15–P1–C1 | 108.0 (1) |
| C1–C2–P2 | 120.3 (3) | C21–P2–C2 | 109.7 (2) |
| C3–P1–C1 | 106.5 (1) | C27–P2–C2 | 109.7 (2) |
| C9–P1–C1 | 108.0 (1) | C33–P2–C2 | 111.0 (1) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

was performed. The relevant crystal and structural data are summarized in Tables I–III, and the ORTEP is shown in Figure 1. The X-ray data indicate a typical $sp^2$ geometry for **8** with the distance between olefinic carbons being 1.322 Å and the P1–C1–C2 and P2–C2–C1 angles close to the expected 120°.

To gain insight into the formation of **8** and, in particular, the source of the two extra hydrogens in its structure, that could arise either from solvent ($CH_3CN$) in a radical process or from water as a result of a polar addition–elimination process, we carried out the same reaction in the presence of added $D_2O$. The resulting product was found to be the dideuterated derivative **8b** by $^1H$ NMR and IR. In the proton spectrum the signal of the vinylic protons in the aromatic region disappeared, and in the IR spectrum the absorption of the vinylic protons at 3000 cm$^{-1}$ shifted to the C–D region at 2230 cm$^{-1}$. Moreover, the byproduct in this reaction is $Ph_3PO$. In contrast no deuterium was incorporated when the reaction was carried out in $CD_3CN$. An additional experiment demonstrated that the diphosphonium salt **7** is the precursor in the formation of **8**. $^{31}P$ NMR monitoring of the reaction mixture showed that there was no further reaction in the mixture of **7** and $Ph_3P$ under dry conditions, but as soon as traces of $H_2O$ were added to the mixture an exothermic reaction proceeded immediately to give **8** and excess $Ph_3PO$ as the only products. These observations suggest that the most likely mechanism for the formation of **8** involves a nucleophilic addition of $Ph_3P$ and $H_2O$ to the activated triple bond in **2** and then elimination of $Ph_3PO$ (eq 4). A similar mechanism was recently proposed for the reactions of other activated alkynes with phosphines in water.[21]



The reaction of **2** with 1 equiv of $Ph_3P$ under anhydrous conditions resulted in the formation of a mixed phosphonium iodonium acetylenic salt **9** in 76% isolated yield. Compound **9** was also characterized by high-resolution mass spectroscopy, IR, and multinuclear NMR. In the IR there is a very characteristic intense absorption at 2066 cm$^{-1}$ due to the unsymmetrical carbon–carbon triple bond. The $^{31}P$ NMR displays a singlet at $\delta$ 7.6 ppm typical for acetylenic phosphonium salts.[19] The $^{13}C$ and $^1H$ NMR are all consistent with the proposed structure. Specifically, in the $^{13}C$ NMR the carbon $\alpha$ to the $P^+$ has a chemical shift of $\delta$ 64.5 ppm, and the $\beta$-carbon has a chemical shift of $\delta$ 126 ppm, which is typical for alkynylphosphonium salts.[22]

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(19) The typical $^{31}P$ chemical shift for alkynylmonophosphonium salts is $\delta$ 6–8 ppm: Bestmann, H. J.; Kisielowski, L. *Chem. Ber.* **1983**, *116*, 1320.

(20) In the preliminary communication[9] compound **8** was incorrectly described as **7** due to the similarity of their spectral data and lack of X-ray structure for **8**.

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**Scheme 1**

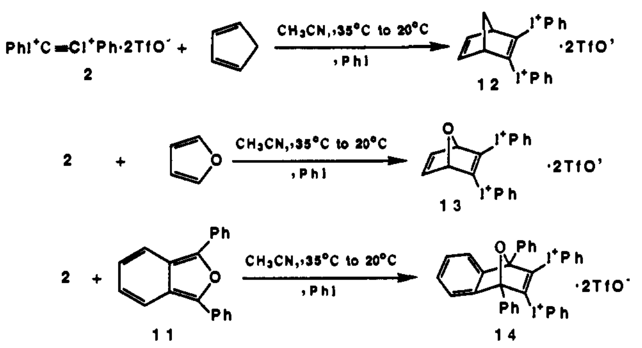

Table IV. Selected Bond Distances for **12**[a]

| bonds | distances (Å) | bonds | distances (Å) | bonds | distances (Å) |
|---|---|---|---|---|---|
| C1–C2 | 1.313 (8) | C5–C6 | 1.53 (1) | C2–I2 | 2.071 (6) |
| C1–C6 | 1.518 (8) | C6–C7 | 1.526 (9) | I2–C14 | 2.120 (7) |
| C3–C4 | 1.51 (1) | C7–C3 | 1.57 (1) | I1–C8 | 2.094 (7) |
| C4–C5 | 1.32 (1) | C1–I1 | 2.089 (6) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

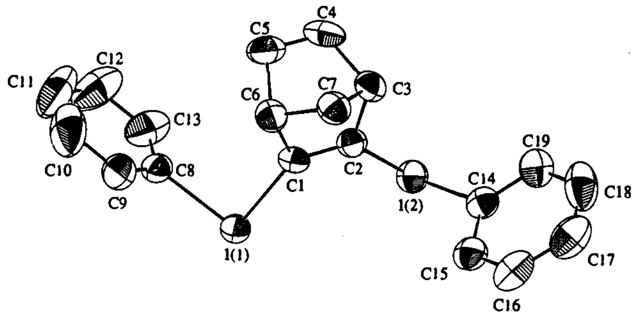

Figure 2. ORTEP of cycloadduct **12**.

Table V. Selected Bond Angles for **12**[a]

| bonds | angles (deg) | bonds | angles (deg) |
|---|---|---|---|
| C1–I1–C8 | 91.6 (2) | C4–C5–C6 | 106.0 (6) |
| C2–I2–C14 | 92.4 (2) | C2–C3–C4 | 105.0 (6) |
| I1–C1–C2 | 129.5 (4) | C1–C6–C5 | 105.1 (5) |
| I2–C2–C1 | 130.6 (4) | C1–C6–C7 | 98.3 (5) |
| C1–C2–C3 | 107.2 (5) | C2–C3–C7 | 97.5 (6) |
| C2–C1–C6 | 108.2 (6) | C7–C6–C5 | 99.6 (6) |
| C3–C4–C5 | 109.3 (7) | C7–C3–C4 | 97.7 (5) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The reaction of iodonium salts with carbon nucleophiles are of special interest because they may lead to the formation of new C–C bonds. To our knowledge there are currently only two examples known, namely, reaction of iodonium salts with lithium or sodium enolates[14,23] or alkenylcopper reagents.[24] Indeed bis(iodonium) salt **2** is highly reactive toward different carbon nucleophiles, such as sodium enolates, the silyl enol ether of cyclohexanone, lithium cyclopentadienyl, etc. However, even at −78 °C these reactions resulted largely in only black tar formation, presumably due to the instability of the expected products. In case of acetylenic nucleophiles, such as lithium acetylides and stannylacetylenes, reaction did not lead to a new C–C bond but rather proceeded like an iodonium transfer process resulting in the formation of new iodonium salts. However, the reaction of **2** with the silyl enol ether of acetophenone gave the relatively stable allene **10** as product (eq 5). Compound **10** has a strong allenic stretch in the IR at 1930–1960 cm$^{-1}$ and a carbonyl absorption at 1670 cm$^{-1}$. In the $^1$H NMR it has a complex multiplet in the aromatic region due to the two similar phenyls, two signals for the allenic CH and a broad singlet due to the CH$_2$ group. The $^{13}$C NMR is consistent with the allenic structure of **10** with a characteristic signal at 192 ppm due to the central carbon of the allene.

$$\underset{\mathbf{2}}{PhI^+C{\equiv}CI^+Ph\cdot 2TfO^-} + 2PhC(OSiMe_3){=}CH_2 \xrightarrow[-PhI]{CH_3CN,\ -35\ °C} \underset{\mathbf{10}}{PhC({=}O)CH{=}C{=}CHCH_2C({=}O)Ph} \quad (5)$$

**Cycloaddition Reactions of Iodonium Salt 2 with 1,3-Dienes.** Electron-deficient acetylenes are known to readily undergo cycloadditions.[1] Due to the strong electron-withdrawing nature of the iodonium moiety alkynyliodonium species **1** are expected to be excellent cycloaddition partners. Yet, to date little is known about the cycloadditions of these species with only one example reported,[25] namely the reaction of alkynyliodonium tosylates with 1,3-dipoles such as arylnitrile oxides.

With two powerful electron-withdrawing groups **2** should be a first rate cycloaddition partner in [2 + 4] Diels–Alder type reactions with 1,3-dienes. Indeed, **2** reacts with cyclopentadiene, furan, and 1,3-diphenylisobenzofuran **11** in CH$_3$CN under very mild conditions (Scheme I). The respective cycloadducts **12–14** were isolated in 47–69% yield as crystalline solids and characterized by spectral and analytical means.

The structure of 2,3-bis(iodonium)norbornadiene **12** was unambiguously assigned by a single-crystal X-ray analysis. The crystal and structural data for **12** are summarized in Tables I, III, and IV, and an ORTEP representation is given in Figure 2.

The structural data reveal two normal C–C double bonds with bond lengths of 1.31 and 1.32 Å, $C_{sp^2}$–I distances of 2.09 and 2.07 Å, and C–I–C bond angles close to the 90° expected for iodonium salts and consistent with a 10-I-3 species in the J. C. Martin formalism.[26] Cycloadducts **12–14** represent a new class of bis(iodonium) alkene species ready for further synthetic elaboration by virtue of the high reactivity and easy substitution of the iodonium moiety. Vinyliodonium salts are known[27] to undergo substitution by a variety of nucleophiles, and hence **12–14** provide ready entry to diverse functionalized norbornadiene systems.

**Conclusions.** The title compound **2** can be prepared in a single step in 80–83% isolated yield from bis(stannyl)acetylene and PhICN·OTf. It represents a novel bifunctional acetylene, a bis(iodonium) species, and a stable C$_2$-transfer agent. It readily reacts with a variety of nucleophiles resulting in difunctional acetylenes such as PhSC≡CSPh, PhOC≡COPh, $Ph_3P^+C{\equiv}CP^+Ph_3\cdot 2TfO^-$, etc. Compound **2** undergoes [2 + 4] cycloadditions with a variety of dienes including cyclopentadiene and furan resulting in synthetically useful bis(iodonium)norbornadiene-type adducts. We believe that this novel bis(iodonium)acetylene will have broad and wide use in organic chemistry.

## Experimental Section

**General Methods.** Melting points (uncorrected) were obtained with a Mel-Temp capillary melting point apparatus. Infrared spectra were recorded on a Mattson FT-IR spectrophotometer. NMR spectra were recorded on a Varian XL 300 spectrometer at 300 MHz ($^1$H NMR), 75 MHz ($^{13}$C NMR), 121 MHz ($^{31}$P NMR), 282 MHz ($^{19}$F NMR). Chemical shifts for $^1$H and $^{13}$C NMR are reported in parts per million (ppm) relative to internal tetramethylsilane or the proton resonance due to the residual protons in the deuteriated NMR solvent; the chemical shifts for $^{19}$F and $^{31}$P NMR are relative to external CFCl$_3$ and 85% H$_3$PO$_4$; respectively. Mass spectra were obtained with a VG Micromass 7050E double focusing high-resolution mass spectrometer with the VG data system 2000 under positive ion fast atom bombardment (FAB)

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conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in $CH_2Cl_2$ or $CHCl_3$ as solvent, polypropylene glycol was used as a reference for peak matching. Microanalysis were performed by Atlantic Microlab Inc., Norcross, GA.

**Materials.** All commercial reagents were ACS reagent grade and used without further purification. Iodosobenzene[28] was prepared from (diacetoxy)iodobenzene and sodium hydroxide and dried in vacuum over $P_2O_5$ for 6 days. Bis(tributylstannyl)acetylene **3** was prepared by a known method[17] from dilithium acetylide and tributyltin chloride. All solvents used were dried by distillation over $CaH_2$. The reaction flasks were flame-dried and flushed with nitrogen.

**[Cyano[[(trifluoromethyl)sulfonyl]oxy]iodo]benzene (4).** Trimethylsilyl trifluoromethanesulfonate (7.75 mL, 40 mmol) was added to a stirred suspension of PhIO (8.8 g, 40 mmol) in $CH_2Cl_2$ (100 mL) at −20 °C under nitrogen. The mixture was warmed to 10 °C and stirred for 10 min until formation of a bright yellow precipitate. The reaction mixture was recooled to −30 °C, and trimethylsilyl cyanide (5.33 mL, 40 mmol) was added via a syringe resulting in an instantaneous formation of a white precipitate. The mixture was warmed to 0 °C and stirred additionally for 15 min. The precipitate was filtered, washed with ether, and dried in vacuo. The yield of **4** was 13.5 g (89%): mp 118 °C;[15] IR ($CCl_4$, cm$^{-1}$) 3099, 3066, 2182 (CN), 1249, 1257, 1208, 1182, 1034; $^1$H NMR ($\delta$, $CD_3CN$) 7.65–7.75 (m, 2 H), 7.8–7.9 (m, 1 H), 8.3–8.4 (m, 2 H); $^{19}$F NMR ($\delta$, $CD_3CN$) −76.5 (s, $CF_3$); $^{13}$C NMR ($\delta$, $CD_3CN$) 68.3 (CN), 120.8 (quart, $J$ = 118 Hz, $CF_3$), 119.6, 134.6, 135.6, 137.1 (Ph).

**Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2).** A solution of bis(tributylstannyl)acetylene **3** (3.02 g, 5 mmol) in $CH_2Cl_2$ (20 mL) was added to a stirred suspension of reagent **4** (3.79 g, 10 mmol) in $CH_2Cl_2$ (100 mL) at −78 °C under nitrogen. The mixture was allowed to warm to 0 °C and stirred for 10 min until the formation of a white microcrystalline precipitate. The precipitate was filtered under nitrogen, washed with $CH_2Cl_2$ (100 mL), and dried in vacuo. The yield of **2** was 2.96 g (81%): mp 127–128 °C (dec, recrystallized from $CH_3CN$); IR ($CCl_4$, cm$^{-1}$) 3095, 1581, 1560, 1281, 1237, 1217, 1169, 1025, 985; Raman spectrum (neat, cm$^{-1}$) 2137; $^1$H NMR ($\delta$, $CD_3CN$) 7.55–7.65 (m, 2 H), 7.7–7.8 (m, 1 H), 8.1–8.2 (m, 2 H); $^{19}$F NMR ($\delta$, $CD_3CN$) −78.93 (s, $CF_3$); $^{13}$C NMR ($\delta$, $CD_3CN$) 51.84 ($C\equiv C$), 120.5 (quart, $J$ = 318 Hz, $CF_3$), 123.65, 133.84, 134.61, 136.18 (Ph). Anal. Calcd for $C_{16}H_{10}I_2O_6S_2F_6$: C, 26.32; H, 1.38; S, 8.78. Found: C, 26.27; H, 1.39; S, 8.84.

**Bis(phenylthio)acetylene (5).** Sodium thiophenolate (0.15 g, 1.1 mmol) was added to a stirred suspension of **2** (0.365 g, 0.5 mmol) in $CH_3CN$ (20 mL) at −35 °C under nitrogen. The mixture was stirred for 1 h at −35 °C until formation of a yellow solution, which was then warmed to room temperature and concentrated in vacuo. The residue (crystals of NaOTf in oil) was treated with $CH_2Cl_2$ (30 mL), the NaOTf was filtered off, and the filtrate was concentrated. Column chromatography on silica gel with hexane as eluent gave 80 mg (66%) of **5** as a colorless oil: IR (neat, cm$^{-1}$) 3058, 1579, 1477, 1023, 735, 687; $^1$H NMR ($\delta$, $CDCl_3$) 7.2–7.4 (m, 3 H), 7.5–7.6 (m, 2 H); $^{13}$C NMR ($\delta$, $CDCl_3$) 87.98 ($C\equiv C$), 126.03, 127.11, 129.28, 133.27 (Ph); mass spectrum (FAB) *m/z* (%) 242 (80), $M^+$; 139 (30), [$PhSC_2$]; 109 (53), [$PhS$]$^+$; HRMS for $C_{14}H_{10}S_2$ ($M^+$) calcd 242.02239, found 242.02212.

**Diphenoxyacetylene (6).** A solution of butyllithium in hexane (1 mL of 2.5 M solution) was added to a stirred solution of phenol (0.235 g, 2.5 mmol) in $CH_2Cl_2$ (25 mL) at −30 °C under nitrogen. A white precipitate of LiOPh formed immediately. The mixture was cooled to −78 °C, and the iodonium salt **2** was added. The reaction mixture was stirred for 15 min at −78 °C and then allowed to warm to room temperature. The resulting dark solution was filtered through silica gel (5 g), and the solvent was evaporated. Column chromatography on silica gel (50 g) with hexane as eluent gave 0.12 g (57%) of **6** as a colorless oil: IR (neat, cm$^{-1}$) 3061, 1591, 1489, 1452, 1376, 1214, 747; $^1$H NMR ($\delta$, $CDCl_3$) 7.2–7.4 m; $^{13}$C NMR ($\delta$, $CDCl_3$) 116.7 ($C\equiv C$), 122.6, 123.0, 124.9, 129.6 (Ph); mass spectrum (EI, 70 eV) *m/z* (%) 210 (100), $M^+$; HRMS for $C_{14}H_{10}O_2$ ($M^+$) calcd 210.06808, found 210.06637.

**Bis[triphenyl[[(trifluoromethyl)sulfonyl]oxy]phospho]acetylene (7).** A mixture of **2** (1.46 g, 2 mmol) and $Ph_3P$ (1 g, 3.8 mmol) in dry $CCl_4$ (30 mL) was stirred for 20 h at room temperature under nitrogen. The white solid was filtered under nitrogen and treated with $CH_2Cl_2$ (50 mL). The unreacted starting iodonium salt **2** (0.3 g) insoluble in $CH_2Cl_2$ was filtered off, and the filtrate was concentrated and crystallized by addition of ether, yielding 0.99 g (59%) of crude **7**, which was additionally purified by several recrystallizations from $CH_2Cl_2$–ether. All operations (with this extremely water-sensitive compound) were performed under dry nitrogen. For **7**: mp 164–166 °C dec; IR ($CCl_4$, cm$^{-1}$) 3055, 1584, 1486, 1435, 1286, 1105, 1024, 863, 795; $^1$H NMR ($\delta$, $CDCl_3$) 7.7–7.9 (m); $^{19}$F NMR ($\delta$, $CDCl_3$) −78.6 (s, $CF_3$); $^{31}$P NMR ($\delta$, $CDCl_3$) 11.84 (s); $^{13}$C NMR ($\delta$, $CDCl_3$) 120.5 (quart, $J$ = 318 Hz, $CF_3$), 114.05 (d, $J$ = 90 Hz), 131.1, 134.0, 136.9 (all m, Ph), 135.15 (d, $J$ = 100 Hz, $C\equiv C$); mass spectrum (FAB) *m/z* (%) 698 (4), [$M - TfO^-$]$^+$; 565 (11), [$M - TfO^- - SO_2CF_3$]$^+$; 550 (3), [$M - 2TfO^-$]$^+$; 279 (100), [$Ph_3POH$]$^+$. HRMS for $C_{38}H_{31}OP_2$ [$M - TfO^- - SO_2CF_3^+ + H^+$]$^+$ calcd 565.18502, found 565.18697.

***trans*-1,2-Bis[triphenyl[[(trifluoromethyl)sulfonyl]oxy]phospho]ethylene (8a).** Iodonium salt **2** (0.73 g, 1 mmol) was added to a stirred solution of $Ph_3P$ (0.79 g, 3 mmol) and $H_2O$ (20 mg, 1.1 mmol) in $CH_3CN$ (20 mL) at −30 °C. The resulting clear solution was allowed to warm to room temperature in 10–15 min and then concentrated in vacuo. Crystallization from $CH_2Cl_2$–ether gave 0.75 g (88%) of **8a**: mp 218–220 °C; IR ($CCl_4$, cm$^{-1}$) 3064, 3023, 2996, 1584, 1485, 1287, 1240, 1028; $^1$H NMR ($\delta$, $CD_3CN$) 7.65–7.70 (m, 2 H), 7.75–7.80 (m, 2 H), 7.91 (t, $J_{H-H}$ = 21 Hz, 2 H, CH=CH), 7.93–7.98 (m, 1 H); $^{19}$F NMR ($\delta$, $CD_3CN$) −78.65 (s, $CF_3$); $^{31}$P NMR ($\delta$, $CDCl_3$) 21.16 (s); $^{13}$C NMR ($\delta$, $CD_3CN$) 122.0 (quart, $J$ = 320 Hz, $CF_3$), 116.4, 131.8, 135.6, 137.3 (all m, Ph), 139.5 (m, HC=CH). Anal. Calcd for $C_{40}H_{32}F_6O_6P_2S_2$: C, 56.60; H, 3.80; S, 7.55. Found: C, 56.39; H, 3.82; S, 7.63. X-ray quality single crystals were obtained by slowly evaporating a solution of **8a** in $CH_3CN$ in an open air container.

***trans*-1,2-Bis[triphenyl(trifluoromethyl)sulfonyl]oxy]phospho]-1,2-dideuterioethylene (8b).** The same procedure as for **6** employing $D_2O$ instead of $H_2O$ gave crystalline **8b** (80% yield): mp 215–217 °C; IR ($CCl_4$, cm$^{-1}$) 3062, 2230 (C–D), 1585, 1485, 1438, 1287, 1240, 1112, 1028, 930, 688; $^1$H NMR ($\delta$, $CD_3CN$) 7.65–7.70 (m, 2 H), 7.75–7.80 (m, 2 H), 7.93–7.98 (m, 1H).

**1-[Triphenyl[[(trifluoromethyl)sulfonyl]oxy]phospho]-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (9).** A mixture of **2** (0.365 g, 0.5 mmol) and $Ph_3P$ (0.14 g, 0.53 mmol) in dry $CCl_4$ (10 mL) was stirred for 3 h at room temperature under nitrogen. The solvent was decanted, and the residue in the flask was washed with $CCl_4$ (20 mL) and treated with $CH_2Cl_2$ (20 mL). The unreacted starting iodonium salt **2** (0.05 g) insoluble in $CH_2Cl_2$ was filtered off, and the filtrate was concentrated to give 0.3 g (76%) of crude **9** as a colorless oil, which was additionally purified by low-temperature recrystallization from $CH_2Cl_2$–ether. All operations with **9** were performed under dry nitrogen. For **9**: clear oil (crystalline solid below 0 °C); IR (neat, cm$^{-1}$) 3064, 2066 ($C\equiv C$), 1587, 1441, 1260, 1030; $^1$H NMR ($\delta$, $CDCl_3$) 7.55–7.93 (m); $^{19}$F NMR ($\delta$, $CDCl_3$) −78.1 (s, $CF_3$); $^{31}$P NMR ($\delta$, $CDCl_3$) 7.6 (s); $^{13}$C NMR ($\delta$, $CDCl_3$) 64.5 (d, $J_{C-P}$ = 178 Hz, $C\equiv CP^+$), 120.1 (quart, $J$ = 319 Hz, $CF_3$), 125.9 (d, $J$ = 107 Hz, $C\equiv CI^+$), 110.8 (d, $J$ = 29 Hz), 116.7 (d, $J$ = 100 Hz), 129.0, 130.4, 131.8, 132.9, 133.7, 135.9 (all m, Ph); mass spectrum (FAB) *m/z* (%) 287 (100) [$M + H^+ - 2TfO^- - PhI$]$^+$; HRMS for $C_{20}H_{16}P$ [$M + H^+ - 2TfO^- - PhI$]$^+$ calcd 287.09896, found 287.09986.

**1,6-Diphenylhexa-2,3-diene-1,6-dione (10).** The silyl enol ether of acetophenone (0.192 g, 1 mmol) was added to a stirred suspension of iodonium salt **2** (0.365 g, 0.5 mmol) in $CH_3CN$ (20 mL) at −35 °C under nitrogen. The reaction mixture was gradually warmed to room temperature in 15 min to give a dark yellow solution. Evaporation of the solvent followed by column chromatography on silica gel (eluent–$CH_2Cl_2$) gave 0.11 g (84%) of **10** as a yellow oil: IR (neat, cm$^{-1}$) 3058, 2982, 1955 and 1925 (C=C=C), 1654 and 1652 (C=O), 1597, 1578, 1463, 1430, 1314, 1298, 1216, 1177, 1032, 865, 756, 729, 652; $^1$H NMR ($\delta$, $CDCl_3$) 5.3 (br s, 2 H, $CH_2$), 7.05 (qd, $J$ = 6.7 and 2.6 Hz, 1 H, CH), 7.4 (d, $J$ = 6.7 Hz, 1 H, CHCO), 7.6–7.4 (m, 6 H, Ph), 8.0–7.9 (m, 4 H, Ph); $^{13}$C NMR ($\delta$, $CDCl_3$) 112.32, 116.44, 127.97, 128.23, 129.61, 131.24, 132.37, 132.44 (2Ph), 137.59 (CH), 139.19 (CH), 192.06 (=C=), 216.3 (2C=O); mass spectrum (FAB) *m/z* (%) 105 (100), [PhCO]$^+$.

**General Procedure for Reactions of Iodonium Salt 2 with Dienes.** A solution of the appropriate diene (2 mmol) in $CH_3CN$ (20 mL) was added to a stirred suspension of the iodonium salt **2** (0.73 g, 1 mmol) in $CH_3CN$ (20 mL) at −35 °C under nitrogen. The mixture was warmed to room temperature and then stirred for 1 h. The resulting yellow solution was concentrated to a volume of about 1 mL and crystallized by addition of $CH_2Cl_2$ (20 mL) and ether (10 mL). The crude products were further purified by recrystallization from $CH_3CN$–$CH_2Cl_2$–ether and dried in vacuo.

**Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]norbornadiene (12).** Cyclopentadiene (130 mg) gave by the above procedure 0.55 g (69%) of **12**: mp 177–179 °C dec; IR ($CCl_4$, cm$^{-1}$) 3087, 3065, 1568, 1472, 1445, 1281, 1242, 1225, 1204, 1162, 1022, 984; $^1$H NMR ($\delta$, $CD_3CN$) 2.02 (m, 1 H, H-7 anti), 2.42 (m, 1 H, H-7 syn), 3.99 (m, 2 H, H-3 and H-6), 6.31 (m, 2 H, H-4 and H-5), 7.59 (m, 2 H, Ph), 7.62 (m, 1 H, Ph), 8.01 (m, 2 H, Ph); $^{19}$F NMR ($\delta$, $CD_3CN$) −77.8 (s, $CF_3$); $^{13}$C NMR ($\delta$, $CD_3CN$) 61.9 (C-3 and C-6), 76.2 (C-7), 121.3 (quart, $J$ = 319 Hz, $CF_3$), 112.5, 133.4, 134.2, 137.0 (Ph), 139.2 (C-1 and C-2), 141.4 (C-4 and C-5). Anal. Calcd for $C_{21}H_{16}F_6I_2O_6S_2$: C, 31.67; H, 2.03; S, 8.05.

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Found: C, 31.76; H 2.06; S, 7.95. X-ray quality single crystals were obtained by slowly evaporating a solution of **12** in $CH_3CN$ in an open air container.

**Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-3,5-epoxy-1,4-cyclohexadiene (13).** Furan (140 mg) gave by the above procedure 0.58 g (73%) of **13**: mp 118-119 °C dec; IR ($CCl_4$, $cm^{-1}$) 3093, 3065, 1566, 1472, 1445, 1279, 1242, 1168, 1021, 885, 868; $^1H$ NMR ($\delta$, $CD_3CN$) 5.62 (br s, 2 H, H-3 and H-6), 6.75 (br s, 2 H, H-4 and H-5), 7.62 (m, 2 H, Ph), 7.81 (m, 1 H, Ph), 8.05 (m, 2 H, Ph); $^{19}F$ NMR ($\delta$, $CD_3CN$) −77.85 (s, $CF_3$); $^{13}C$ NMR ($\delta$, $CD_3CN$) 90.8 (C-3 and C-6), 121.2 (quart, $J$ = 319 Hz, $CF_3$), 112.4, 133.6, 134.5, 137.1 (Ph), 139.2 (C-1 and C-2), 142.7 (C-4 and C-5). Anal. Calcd for $C_{20}H_{14}F_6I_2O_7S_2$: C, 30.09; H, 1.77; S, 8.03. Found: C, 30.22; H, 1.78; S, 8.08.

**2,3-Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-1,4-epoxy-1,4-diphenylnapthalene (14).** Benzofuran **11** (540 mg) gave by the above procedure 0.47 g (47%) of **14**: mp 93-95 °C dec; IR ($CCl_4$, $cm^{-1}$) 3082, 3055, 1469, 1455, 1445, 1294, 1216, 1163, 1019, 987, 902; $^1H$ NMR ($\delta$, $CD_3CN$) 7.05-7.15 (m, 4 H, $C_6H_4$), 7.3 (m, 10 H, 2Ph), 7.6-7.9 (m, 10 H, $2PhI^+$); $^{19}F$ NMR ($\delta$, $CD_3CN$) −76.52 (s, $CF_3$); $^{13}C$ NMR ($\delta$, $CD_3CN$) 98.5 (C-1 and C-4), 121.0 (quart, $J$ = 319 Hz, $CF_3$), 113.8, 123.8, 127.8, 128.4, 130.5, 131.6, 131.9, 133.5, 134.4, 136.8 (Ar), 145.7 (C-2 and C-3), 150.1 (C-5 and C-10); mass spectrum (FAB) $m/z$ (%) 499 (25), $[M + H^+ - 2TfO^- - PhI]^+$; 295 (100), $[M + H^+ - 2TfO^- - 2PhI]^+$; HRMS for $C_{28}H_{19}IO$ $[M + H^+ - 2TfO^- - PhI]^+$ calcd 499.05581, found 499.05581.

**Acknowledgment.** This work was supported by the National Cancer Institute of NIH (2ROCA16903). We thank Dr. Atta M. Arif for the X-ray structure determinations.

**Supplementary Material Available:** Tables of X-ray crystal and structural data for compounds **8** and **12** (35 pages); tables of observed and calculated structure factors for **8** and **12** (28 pages). Ordering information is given on any current masthead page.

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# Synthesis and Characterization of Novel *p*-Terphenoquinone Analogues Involving a Central Dihydrothiophenediylidene Structure

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**Abstract:** The title quinones, 2,5-bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene and its tetraalkyl derivatives, were synthesized via 2-(4-alkoxyphenyl)thiophene and 2,5-bis(4-alkoxyphenyl)thiophene conveniently prepared by using palladium(0)-catalyzed cross coupling reaction of 4-alkoxyaryl halides and thienylzinc chloride. The ground-state structures and redox properties of these quinones were fully characterized based on spectroscopic data (IR, $^1H$ NMR, $^{13}C$ NMR, UV–vis, and MS), X-ray analysis, cyclic voltammetry, CNDO/2 calculation, and EPR spectroscopic investigation. These quinones show an intense absorption maximum in the region of 531–558 nm of their electronic spectra. Despite their three-ring system, these quinones exist in a coplanar conformation in the solid state in which the terminal six-membered rings incline 9.1° and 11.1°, respectively, from the central five-membered ring, and the twisting angle between the mean planes of the two terminal rings is 1.8°. Rotation about the intercyclic bonds does not take place at ordinary temperatures in solution. Noticeably, these quinones exhibit a half-wave oxidation potential ($E_1^{ox}$ value) of 1.26–1.46 V along with half-wave reduction potentials ($E_1^{red}$ value) of −0.11 to −0.52 V and ($E_2^{red}$ value) of −0.20 to −0.67 V vs SCE, so that they have been proven to be a new type of quinones exhibiting an amphoteric redox property undergoing two-stage one-electron reduction up to the dianions and one-electron oxidation up to the radical cations. The reduction and oxidation potentials of these quinones are in good correspondence with the calculated energy levels of the HOMO and the LUMO. Decrease in the HOMO–LUMO gap is mainly ascribed to the destabilized HOMO lying at a higher level by 0.97 eV than that of diphenoquinone. Both the cation and anion radicals were generated by the electrochemical reduction and oxidation of these amphoteric quinones and have been definitely characterized by EPR spectroscopy.

Benzoquinonoid compounds have hitherto played a most important role in the development of organic redox chemistry due to their multistage redox properties[1,2] and have attracted a great deal of attention currently not only from the scientific but also from industrial points of view since redox systems could be used for functional materials with high technological potential such as electroconductors,[3] optoelectronic display devices,[4] catalysts for electron-transfer reaction,[5] artificial photosynthetic systems,[6] and so on. Therefore, the molecular design and synthesis of novel quinonoid compounds having a different skeletal structure from the traditional ones and having unique redox properties may provide an impetus for the versatile and ensuing development of material science and material technology of topical interest.

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