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PREPARATION OF BIPHENYLENE- AND BENZOCYCLOOCTENE-FUSED HETEROCYCLES

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Abstract – Nitration of biphenylene with bismuth subnitrate and thionyl chloride give a mixture of 2-nitrobiphenylene, 2-chloro-6-nitrobiphenylene, and 5-chloro-10-nitrobenzocyclooctene. Reactions of 2-nitrobiphenylene and 5-chloro-10-nitrobenzocyclooctene with ethyl isocyanoacetate in the presence of *t*-BuOK gave the corresponding pyrimidine *N*-oxide and pyrrole, respectively.

Dedicated to Professor Yoshito Kishi on the occasion of his 70th birthday

INTRODUCTION

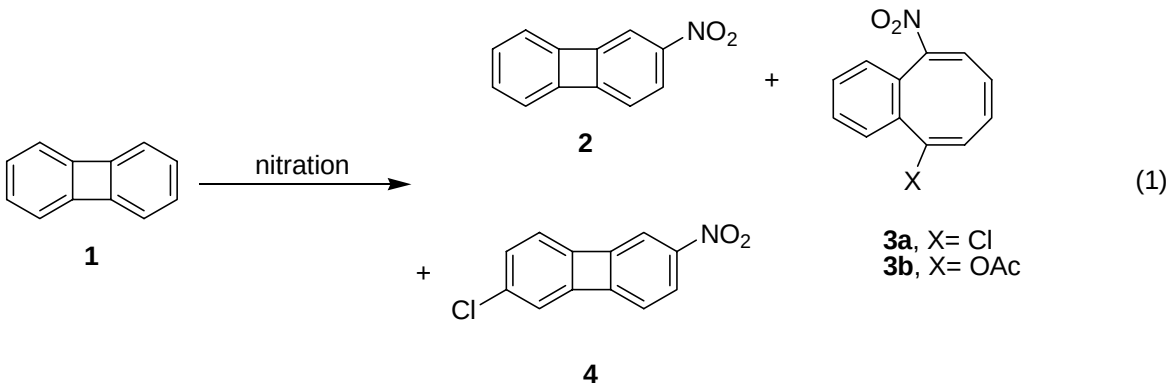
Biphenylene has a planar 12π-electron system and shows anti-aromatic property mainly due to the center cyclobutadiene moiety. When biphenylene is incorporated in other π-conjugated systems, the molecular structures and properties will be interesting from the viewpoint of anti-aromaticity effect of the incorporated cyclobutadiene moiety. Very limited numbers of biphenylene-fused heterocyclic compounds have been reported so far probably due to lack of proper synthetic methods.[1] We have explored the reaction of the nitroarenes with isocyanoacetate esters in the presence of an appropriate base gave the corresponding pyrroles and/or pyrimidne *N*-oxides depending on the natures of nitroarenes and conditions employed.[2] As the biphenylene has the low LUMO, this method would be appricable for the preparation of biphenylene-fused heterocycles. We carried out the reaction of 2-nitrobiphenylene with ethyl isocyanoacetate and a biphenylene-fused pyrimidine *N*-oxide derivative was obtained. The structures and properties of the pyrimidine *N*-oxide derivative as well as the starting compounds are discussed.

RESULTS AND DISCUSSION

Nitration of biphenylene

McOhmie and his co-workers studied the reactivity of biphenylene (**1**) and reported that the nitration of biphenylene with nitric acid occurred at 2-position to give 2-nitrobiphenylene (**2**) in rather low yield (23%)[3] together with several byproducts.[4] Recently, surprisingly selective preparation of 2-nitrobiphenylene (**2**) with bismuth subnitrate and thionyl chloride was reported by Muathen.[5] This report prompted us to use 2-nitrobiphenylene (**2**) as a starting material to biphenylene-fused heterocycles. In our hands, however, the reported result could not be achieved in spite of all of our efforts.

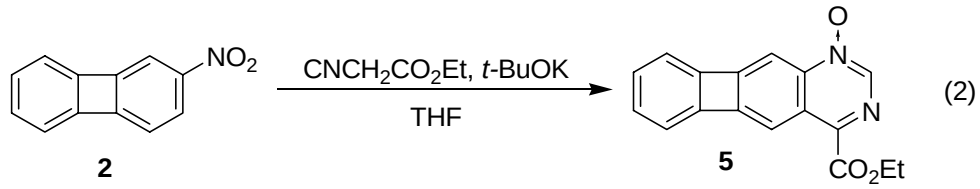
According to the reported procedure,[5] the reaction gave a crude product mixture, ^{1}H-NMR spectra of which were very complicated. After repeated chromatographic separation, 2-nitrobiphenylene (**2**) was obtained only in 17% and 5-chloro-10-nitrobenzocyclooctene (**3a**; 31%) as well as 2-chloro-6-nitrobiphenylene (**4**; 4%) was obtained (Eq 1). Structures of these products were determined by comparison with the reported spectroscopic data.[3] This result was constantly reproduced in several trials. Therefore, we examined other reported methods for the preparation of **2**. In the case of nitration of biphenylene using AcOH and HNO_3, the products obtained after chromatography on silica gel were **2** (19%) and 5-acetoxy-10-nitrobenzocyclooctene (**3b**, 25%) as they reported.



Reaction of 2-nitrobipheylene (2) with ethyl isocyanoacetate

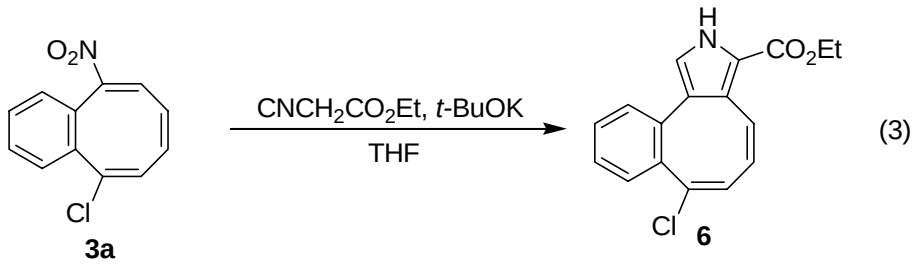
Although we could get the aimed compound **2** only in low yield, we decided to conduct the reactions of the obtained nitro compounds with ethyl isocyanoacetate in the presence of a base.[2] We carried out reactions of 2-nitrobiphenylene and ethyl isocyanoacetate in the presence of DBU, *t*-butyliminotri(1-pyrrolidinyl)phosphine (BTPP), or *t*-BuOK. Reactivity of 2-nitrobiphenylene toward an isocyanoacetate anion was low and the starting material was only consumed by the treatment with *t*-BuOK for 30 h at room temperature. The product was separated by chromatography on silica gel and

assigned as 4-(ethoxycarbonyl)benzocyclobutadieno[5,6-g]quinazoline 1-oxide (**5**) by spectroscopic data (Eq 2). The yield was 29%.



Reaction of 5-chloro-10-nitrobenzocyclooctatetraene (3a) with ethyl isocyanoacetate

We next carried out the reaction of 5-chloro-10-nitrobenzocyclooctene (**3a**) and ethyl isocyanoacetate. 5-Chloro-10-nitrobenzocyclooctene (**3a**) was treated with ethyl isocyanoacetate in the presence of *t*-BuOK for 24 h at room temperature to give ethyl 7-chlorobenzocycloocteno[5,6-c]pyrrole-3-carboxylate (**6**) in 30% yield (Eq 3). The structure of **6** was determined by spectroscopic data including the NOE experiments for the positional determination of the ester moiety.



Structural analysis

Single crystals of benzocyclooctenes (**3a**, **3b**, and **6**) and biphenylenes (**4** and **5**) were obtained by the slow evaporation of the solvent ($CHCl_3$) and were subject to X-ray analysis. The crystallographic data were summarized in Table 1.[6] In the cases of 5-chloro-10-nitrobenzocyclooctene (**3a**) and 2-chloro-6-nitrobiphenylene (**4**), the molecules occupy special positions of *-1* and *m* symmetries, respectively. Therefore, chloro and nitro substituents are completely disordered and halves of the molecules are found in their asymmetric units. This phenomenon is attributable to the similar van der Waals volumes of chloro and nitro groups. Packing of 5-acetoxy-10-nitrobenzocyclooctene (**3b**) shows heavy disorder. The only 4 atoms of nitrogen and acetyl group of the major (85.8%) and the minor (14.2%) molecules occupy the same space. Relationship between the major and minor molecules is a mirror image from the plane including the four common atoms. Ortep drawings of the measured compounds are illustrated in Figure 1 and only the major molecules are shown in the cases of the disordered structures.

Table 1. Crystallographic summary

	3a	**3b**	**4**	**5**	**6**
MF	$C_{12}H_8ClNO_2$	$C_{14}H_{11}NO_4$	$C_{12}H_6ClNO_2$	$C_{17}H_{12}N_2O_3$	$C_{17}H_{14}ClNO_2$
FW	233.65	257.25	231.64	292.29	299.76
Space group	*Pnma*	*P2₁/a*	*P2₁/n*	*C2/c*	*P-1*
a/Å	6.982(4)	7.5375(16)	3.6978(15)	22.588(15)	7.4293(14)
b/Å	13.052(8)	12.859(3)	7.324(3)	5.236(3)	9.2283(18)
c/Å	11.764(7)	13.089(3)	18.092(8)	23.211(19)	10.652(2)
α	90	90	90	90	100.751(5)
β	90	103.149(2)	93.435(9)	104.528(7)	94.262(4)
γ	90	90	90	90	92.645(4)
V/Å^3	1072.1(11)	1235.4(5)	489.1(4)	2657(3)	714.2(2)
Z	4	4	2	8	2
Unique	1262	2801	1104	2949	3198
Obs.	895	2419	1071	1452	2497
Param.	93	233	93	200	191
R_1 (>2σ)	0.0988	0.0579	0.0898	0.1349	0.0479
wR_2 (all)	0.2416	0.1240	0.1872	0.3427	0.1305
GOF	1.157	1.169	1.320	1.138	1.125
T/ºC	-173	-173	-170	-123	-123
CCDC No	627553	627549	627550	627551	627552

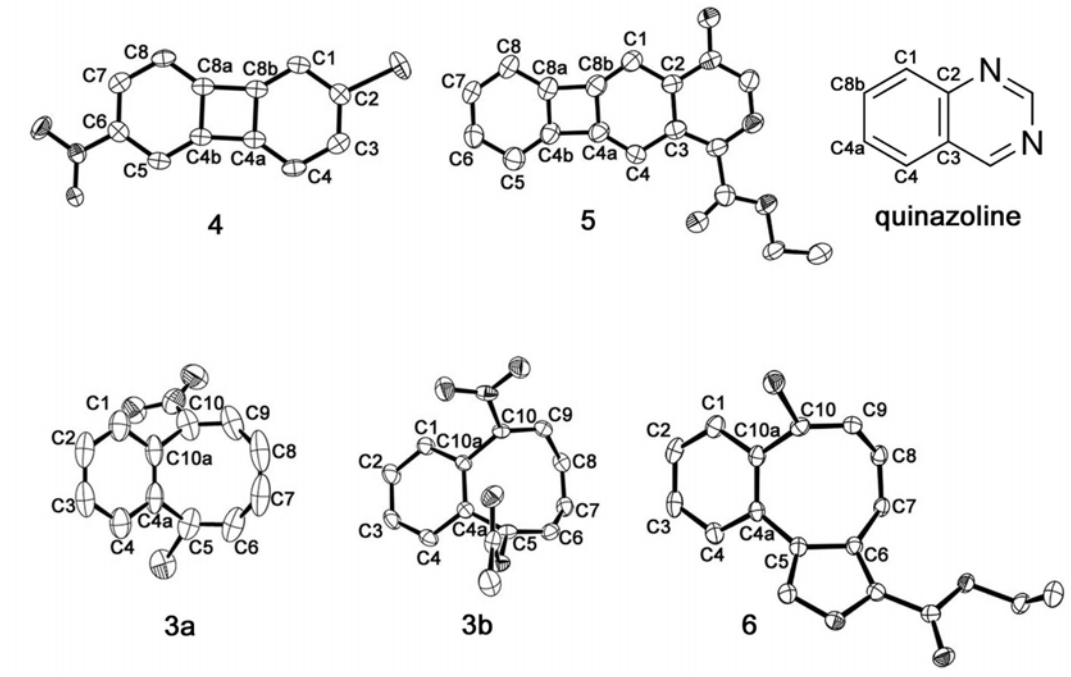


Figure 1. Ortep or chemical structure drawings of benzocyclooctenes, biphenylenes and quinazoline with carbon numbering for Tables 2 and 3. In the Ortep drawings, hydrogen atoms are omitted for clarity.

Table 2. Bond lengths of biphenylenes and quinazoline[a]

	C1-C2 C3-C4 C5-C6 C7-C8	C2-C3 C6-C7	C4-C4a C4b-C5 C8-C8a C8b-C1	C4a-C8b C8a-C4b	C4a-C4b C8a-C8b
1[b]	1.423(4)	1.385(4)	1.372(4)	1.426(4)	1.514(4)
4[c]	1.414(5) 1.415(5) 1.414(5) 1.415(5)	1.373(5) 1.373(5)	1.368(5) 1.359(5) 1.368(5) 1.359(5)	1.413(4) 1.413(4)	1.502(5) 1.502(5)
6	1.429(7) 1.458(7) 1.421(8) 1.384(7)	1.423(6) 1.374(7)	1.341(7) 1.381(7) 1.370(7) 1.340(7)	1.449(7) 1.410(7)	1.513(7) 1.490(7)
quinazoline	1.414 1.411	1.399	1.354 1.358	1.399	

[a] The carbon numbering is shown in Figure 1. [b] Mean measured bond lengths of crystallographically independent molecules, see Ref. 7. [c] The molecule occupies the special position (-1 symmetry) with a disordered structure. Therefore, C5, C6, C7, C8, C8a, and C8b are generated from C1, C2, C3, C4, C4a, and C4b by the symmetric operation, respectively. [d] Mean measured bond lengths of crystallographically independent molecules, see Ref. 8.

Biphenylene (**1**) can be regarded as a weekly coupled benzenoid system rather than a dibenzo derivative of cyclobutadiene. Biphenylene (**1**) has a planar rectangular cyclobutadiene skeleton and shows a [4]radialene-like bond alteration in order to minimize the unfavorable contribution of the center anti-aromatic 4nπ-electron circuits. Thus, the radial bonds of C4-C4a, C4b-C5, C8-C8a, and C8b-C1 are the shortest [1.372(4) Å] and phenylene-connecting bonds of C4a-C4b and C8a-C8b are the longest [1.514(4) Å] (Table 2).[7] In 2-chloro-6-nitrobiphenylene (**4**), essentially the same bond alteration was found and all bonds were about 0.01-Å shorter than those of biphenylene probably due to the electron-withdrawing effect of the substituents. Similarly, no obvious enhancement or cancellation of the bond alteration was observed in pyrimidine-fused biphenylene **5** and the bond lengths in the biphenylene part are roughly intermediate between **1** and **4**. Interestingly, the pyrimidine-fused benzene ring is slightly expanded compared to that of quinazoline.[8] This is probably due to the anti-aromatic effect of the biphenylene moiety.

Contrary to the biphenylene, cyclooctene (cyclooctatetraene) is known as a non planar molecule in order to avoid the unfavorable 4nπ-electron circuit. Therefore, the double bonds are found at the certain positions in a crystal. In the case of benzocyclooctene, the double bonds are fixed by the fusion of benzene ring[9] and a clear bond alteration is found at the cyclooctene ring in crystals (see Table 3). On the other hand, no obvious effect from the cyclooctene ring to the benzene ring is observed in any cases.

Table 3. Bond lengths of benzocyclooctenes[a]

	C1-C2 C3-C4	C2-C3	C4-C4a C10a-C1	C4a-C10a	C4a-C5 C10-C10a	C5-C6 C9-C10	C6-C7 C8-C9	C7-C8
Benzocy- clooctene[b]	1.379 1.374	1.376	1.396 1.389	1.399	1.481 1.475	1.330 1.321	1.445 1.453	1.316
3a[c]	1.378(7)	1.356(11)	1.395(7)	1.375(11)	1.475(7)	1.321(7)	1.459(8)	1.264(14)
3b[d]	1.385(4) 1.377(5)	1.380(4)	1.396(5) 1.403(3)	1.391(3)	1.474(3) 1.480(3)	1.329(4) 1.323(4)	1.466(4) 1.474(4)	1.359(4)
6	1.378(3) 1.386(3)	1.389(3)	1.405(3) 1.402(3)	1.401(3)	1.478(3) 1.481(3)	1.423(3) 1.328(3)	1.473(3) 1.468(3)	1.324(3)

[a] The carbon numbering is shown in Figure 1. [b] Ref. 9. [c] The molecule occupies the special position (*m* symmetry) with a disordered structure. Therefore, C3, C4, C4a, C5, C6, and C7 are generated from C2, C1, C10a, C10, C9, and C8 by the symmetric operation, respectively. [d] Bond lengths of the major molecule.

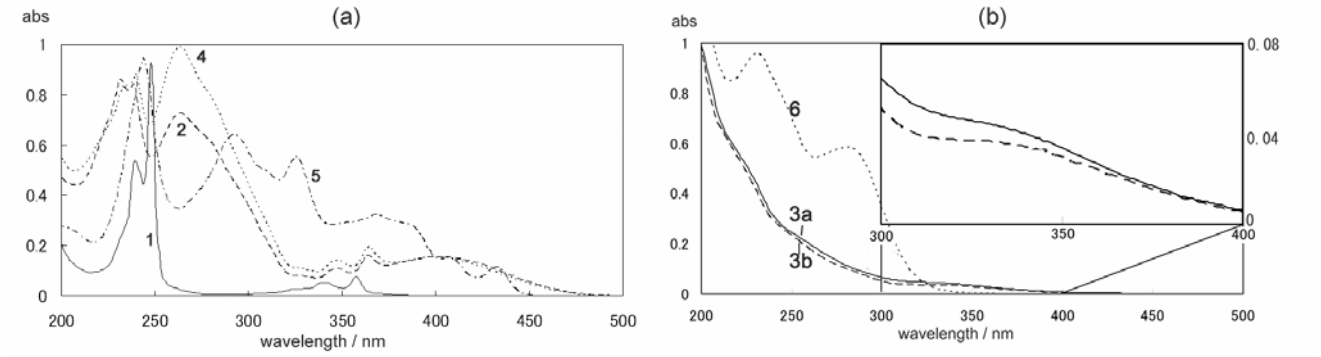


Figure 2. UV-vis spectra. (a) Biphenylene (**1**, solid line), 2-nitrobiphenylene (**2**, broken line), 2-chloro-6-nitrobiphenylene (**4,** dotted line), and 4-(ethoxycarbonyl)benzocyclobutadieno-[5,6-*g*]quinazoline 1-oxide (**5**, dotted broken line); (b) 5-chloro-8-nitrobenzocyclooctene (**3a,** solid line), 5-acetoxy-8-nitrobenzocyclooctene (**3b**, broken line), and 7-chlorobenzocyclooctено-[5,6-*c*]pyrrole-3-carboxylate (**6**, dotted line).

UV-vis analysis

UV-vis spectra of the biphenylene and benzocyclooctenes in acetonitrile are shown in Figure 2 and the data are summarized in Table 4. Biphenylene (**1**) has two strong (248 and 240 nm) and three weak (358, 339, and 331 nm) absorption bands. From Figure 2a, nitrobiphenylenes **2** and **4** showed broad absorption bands at 400 and 264 nm in addition to the similar absorption bands to biphenylene. The longer-wavelength broad band is probably due to intramolecular charge transfer. A complicated absorption pattern was observed in byphenylene-fused pyrimidine **5**. In the cases of benzocyclooctenes **3a** and **3b** (Figure 2b), a weak absorption band due to n-π* transition of the nitro-olefinic moiety was observed at 325 nm as a shoulder. Only two absorption bands (282 and 232 nm) were recorded in **6**.

Table 4. Absorption maxima of biphenylenes and benzocyclooctenes in acetonitrile

	λ / nm (logε)[a]						
1:	358 (3.94),	339 (3.78),	331 (3.52),	248 (5.03),	240 (4.79)		
2:	403 (3.63),	364 (3.65),	348 (3.48),	328 (3.35),	241 (4.79),	239 (4.43),	232 (4.47)
3a:	325sh [0.09],	269sh [0.37],	223sh [1.00]				
3b:	324sh (3.10),	255sh (3.86),	221sh (4.26)				
4:	400 [0.16],	364 [0.20],	347 [0.14],	327 [0.11],	264 [1.00],	240 [0.89],	234 [0.85]
5:	433 (3.67),	407 (3.78),	382sh (4.05),	370 (4.11),	352sh (4.05),	326 (4.34),	310sh (4.30),
	292 (4.40),	244 (4.57)					
6:	282 (4.14),	232 (4.35)					

[a]Values in brackets are relative intensity.

In conclusion, the selective preparation method for 2-nitrobiphenylene with bismuth subnitrate and thionyl chloride reported by Muathen[5] could not be reproduced by us and the reaction gave a mixture of 2-nitrobiphenylene and 2-chloro-6-nitrobiphenylene as well as 5-chloro-10-nitrobenzocyclobutene. This result was very similar to that reported by McOmie and his co-workers even in the by-product formation,[3] although the reagent system was different (HNO_3, AcOH, and Ac_2O) and therefore acetoxylation occurred instead of chlorination. The reaction of 2-nitrobiphenylene and 5-chloro-10-nitrobenzocyclooctene with ethyl isocyanoacetate in the presence of *t*-BuOK gave the corresponding pyrimidine *N*-oxide and pyrrole, respectively. In both cases, the ring fusion was observed at the localized double bonds established by the X-ray analysis. From the X-ray analysis of the biphenylenes, the distinct bond alteration was not affected by the fusion of a pyrimidine ring, although slight ring expansion of the pyrimidine-fused benzene ring was observed.

EXPERIMENTAL

General

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using $CDCl_3$ as a solvent, and tetramethylsilane as an internal standard for ^1H and ^{13}C. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. Mass spectra (EI, 70 eV) were measured with a JEOL JMS-700. Elemental analyses were performed with a Yanaco MT-5 elemental analyzer.

X-ray measurements of the single crystals were done with Rigaku AFC7R Mercury CCD (10 kW) or Rigaku AFC8S Mercury CCD (1.5 kW). UV-vis spectra were measured in acetonitrile with a HITACHI U-2810 spectrophotometer. Dehydrated tetrahydrofuran was purchased from Kanto Chemical Co. and used without further purification. Potassium *tert*-butoxide was sublimed at 200 °C under a reduced pressure (*ca.* 0.1 mmHg) and dissolved in dry THF (1.0 mol L^{-1}). Biphenylene was prepared according to the literature procedure.[10] Ethyl isocyanoacetate was prepared according to the literature procedure.[11] Other commercially available materials were used without further purification.

Nitration of biphenylene using bismuth subnitrate and thionyl chloride

Nitration of biphenylene (**1**) was performed according to the literature.[5] To a stirred solution of **1** (0.760 g, 5.00 mmol) and thionyl chloride (0.729 mL, 10.0 mmol) in CH_2Cl_2 (50 mL) was added bismuth subnitrate (80% purity; 2.20 g, 1.25 mmol). After vigorous stirring for 1 h at rt, the mixture was filtered to remove the inorganic materials. The organic filtrate was washed successively with saturated 1.0-M aqueous HCl, water, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (10% EtOAc/hexane) to give **2** (0.170 g, 17%), **3a** (0.361 g, 31%), and **4** (0.046 g, 4%). **2**: yellow needles; mp 105-107 °C; R_f 0.4 (10% EtOAc/hexane); UV-vis λ_{max} (log ε) 403 (3.63), 364 (3.65), 348 (3.48), 328 (3.35), 241 (4.79), 239 (4.43), and 232 (4.47); ^{1}H NMR δ 6.70 (1H, d, J = 7.6 Hz), 6.80 (2H, m), 6.92 (2H, m), 7.36 (1H, s), and 7.78 (1H, dd, J = 7.6 and 1.2 Hz); ^{13}C NMR δ 111.7, 116.4, 119.0, 119.4, 126.4, 129.7, 130.6, 148.1, 148.2, 148.5, 152.3, and 158.1; IR (KBr disk) ν_{max} 1522, 1464, 1419, 1325, and 1163 cm^{-1}; MS *m/z* (rel. intensity) 197 (M^+ 100%); Anal. Calcd for $C_{12}H_7NO_2$: C, 73.09; H, 3.58; N, 7.10. Found: C, 72.97; H, 3.74; N, 7.03%. **3a**: yellow crystal, mp 108-110 °C; R_f 0.3 (10% EtOAc/hexane); UV-vis λ_{max} [relative intensity] 325 sh [0.09], 269 sh [0.37], and 223 sh [1.00]; ^{1}H NMR δ 6.05 (2H, m), 6.39 (1H, m), 7.11 (1H, m), 7.42 (3H, m), and 7.72 (1H, m); ^{13}C NMR δ 126.7, 128.0, 128.8, 129.4, 129.6, 129.8, 130.5, 132.4, 133.9, 134.7, 138.7, and 150.2; IR (KBr disk) ν_{max} 1635, 1517, 1437, 1331, and 1167 cm^{-1}; MS *m/z* (rel. intensity) 235 [M^+ (Cl^{37}), 2%] and 233 [M^+ (Cl^{35}), 7%]; Anal. Calcd for $C_{12}H_8NO_2Cl$ C, 61.69; H, 3.45; N, 5.99. Found: C, 61.56; H, 3.42; N, 5.92%. **4**: yellow needles, mp 196-198 °C; R_f 0.5 (10% EtOAc/hexane); UV-vis λ_{max} [relative intensity] 400 [0.16], 364 [0.20], 347 [0.14], 327 [0.11], 264 [1.00], 240 [0.89], and 234 [0.85]; ^{1}H NMR δ 6.75 (2H, m), 6.82 (1H, m), 6.93 (1H, dd, J = 7.6 and 1.5 Hz), 7.42 (1H, m), and 7.83 (1H, dd, J = 7.6 and 1.5 Hz); ^{13}C NMR δ 112.1, 117.2, 120.0, 120.5, 126.5, 130.0, 135.2, 146.1, 148.6, 149.6, 151.2, and 156.2; IR (KBr disk) ν_{max} 1599, 1522, 1458, 1333, 1265, 1109, and 1057 cm^{-1}; MS *m/z* (rel. intensity) 233 [M^+ (Cl^{37}), 33%] and 231 [M^+ (Cl^{35}), 100%].

Nitration of biphenylene using AcOH and HNO_3 in Ac_2O[3]

To a stirred solution of **1** (0.304 g, 2.0 mmol) in acetic anhydride (10 ml) was added a mixture of acetic acid (2.0 ml) and nitric acid (0.2 ml) at 0 °C. After 15 min at 0 °C, the mixture was stirred for 45 min at

rt. The mixture was added water, and extracted three times with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatography on silica gel (40% $CHCl_3$/hexane) to give **2** (0.075 g, 19%) and **3b** (0.129 g 25%). **3b**: yellow powder; mp 113-115 °C; R_f 0.05 (40% $CHCl_3$/hexane); UV-vis λ_{max} (log ε) 324 sh (3.10), 255 sh (3.86), and 221 sh (4.26); ^{1}H NMR δ 2.09 (3H, s), 5.91 (1H, m), 6.07 (2H, m), 7.17 (1H, m), 7.25 (1H, m), 7.39 (2H, m), and 7.77 (1H, m); ^{13}C NMR δ 20.8, 117.7, 126.7, 127.5, 128.4, 129.3, 130.6, 130.7, 130.8, 134.6, 136.4, 148.2, 150.2, and 168.6; IR (KBr disk) ν_{max} 1757, 1664, 1520, 1373, 1324, 1203, 1122, 1074, and 1038 cm^{-1}; MS *m/z* (rel. intensity) 257 (M^+ 2%); Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.49; H, 4.34; N, 5.46%.

4-(Ethoxycarbonyl)benzocyclobutadieno[5,6-*g*]quinazoline 1-oxide (5)

To a stirred solution of **2** (0.591 g, 3.00 mmol) and ethyl isocyanoacetate (0.393 mL, 3.60 mmol) in dry THF (30 mL) was added 1.0 M solution of potassium *tert*-butoxide in THF 3.6 ml by a syringe at 0 °C under N_2. The mixture was then stirred for 30 h at rt. The reaction was quenched by adding a 1.0 M aqueous HCl solution. The mixture was extracted three times with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel to give **5** (0.254 g, 29%) as yellow crystals: mp 206-208 °C; R_f 0.38 (20% EtOAc/$CHCl_3$); UV-vis λ_{max} (log ε) 433 (3.67), 407 (3.78), 382 sh (4.05), 370 (4.11), 352 sh (4.05), 326 (4.34), 310 sh (4.30), 292 (4.40), and 244 (4.57); ^{1}H NMR δ 1.48 (3H, t, J = 6.9 Hz), 4.52 (2H, q, J = 6.9 Hz), 7.14 (4H, m), 7.76 (1H, s), 7.99 (1H, s), and 8.91 (1H, s); ^{13}C NMR δ 14.3, 62.5, 105.7, 110.9, 121.2, 121.8, 127.9, 131.8, 132.4, 138.5, 143.7, 148.4, 148.5, 149.6, 152.4, 156.9, and 164.0; IR (KBr disk) ν_{max} 1707, 1510, 1417, 1315, 1259, and 1155 cm^{-1}; MS *m/z* (rel. intensity) 292 (M^+, 100%).

Ethyl 8-chlorobenzocycloocteno[5,6-c]pyrrole-3-carboxylate (6)

To a stirred solution of a **3b** (0.116 g, 0.500 mmol) and ethyl isocyanoacetate (0.066 ml, 0.60 mmol) in dry THF (20 ml) was added a 1.0-M solution of potassium *tert*-butoxide in THF (0.60 mL) by a syringe at 0 °C under N_2. The mixture was stirred for 24 h at rt. The reaction was quenched with a 1.0-M aqueous HCl solution. The mixture was extracted three times with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatography on silica gel (30% EtOAc/hexane) to give **6** (0.040 g, 27%) as colorless crystals: mp 165-167 °C; R_f 0.4 (30% EtOAc/hexane); UV-vis λ_{max} (log ε) 282 (4.14) and 232 (4.35); ^{1}H NMR δ 1.36 (3H, t, J = 6.8 Hz), 4.34 (2H, m), 5.95 (1H, dd, J = 11.7 and J 3.9 Hz), 6.32 (1H, d, J = 2.9 Hz), 6.75 (1H, m), 6.91 (1H, d, J = 2.9 Hz), 7.08 (1H, d, J = 6.4 Hz), 7.34 (2H, m), 7.49 (1H, m), and 9.30 (1H, brs); ^{13}C NMR δ 14.5, 60.5, 119.3, 120.2, 126.6, 127.3, 127.4, 127.5, 127.7, 128.6, 128.8, 130.0, 130.9, 131.9, 134.1, 138.7, and 160.7; IR (KBr disk) ν_{max} 3294, 1668, 1410, 1379, 1261, 1169, and 1130

cm^{-1}; MS *m/z* (rel. intensity) 301 [M^+ (Cl^{37}), 27%] and 299 [M^+ (Cl^{35}), 81%]; Anal. Calcd for $C_{17}H_{14}NO_2Cl$ C, 68.12; H, 4.71; N, 4.67. Found: C, 68.00; H, 4.78; N, 4.63%.

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