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Characterization of a Longicyclic (2,2,2,2) Conjugated π System in 1,4-Difluorobenzene–Naphthalene Biplanemer

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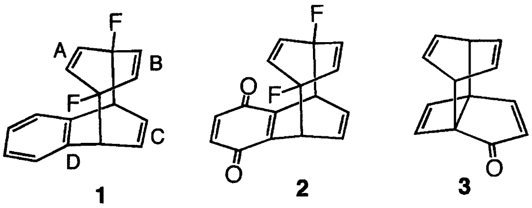
The electronic absorption spectrum of a 1,4-difluorobenzene–naphthalene biplanemer **1** exhibited a characteristic absorption band around 290 nm. This was attributable to intramolecular charge transfer interaction between the longicyclic conjugated π system and the benzene chromophore. The oxidation potential of **1** was 1.70 V (vs. Ag/AgCl), which was lower than those of the related compounds in which one of the double bonds of **1** was hydrogenated. Thermally, the biplanemer **1** underwent facile Cope rearrangement, followed by dehydrofluorination, to give 1-(4-fluorophenyl)naphthalene and 2-(3-fluorophenyl)naphthalene.

Recently we reported successful synthesis of a 1,4-difluorobenzene–naphthalene biplanemer **1**.[1] The four double bonds A—D, shown in **1** (Chart 1), one of which is incorporated in the benzene moiety, are arranged in a typical longicyclic (2,2,2,2) topology and interactions among them are expected.[2] The longicyclic conjugation was predicted to be the least stable interaction among four-ribbon longicycles.[3] Although characteristics of the conjugation are of considerable interest, only a few model compounds have been reported so far. Tsuji et al. examined the electronic absorption spectrum of 2,5-etheno[4.3.2]propella-3,8,10-triene-7-one (**3**). They compared the result with the spectra of its partly hydrogenated derivatives, in which particular effects caused by the conjugation were not appreciable.[4] Kimura observed an extremely red-shifted charge-transfer absorption band for 1,4-difluorobenzene–naphthoquinone biplanemer **2**, indicating a longicyclic (2,2,2,2) destabilization effect.[5] However, **2** was too thermally unstable to examine additional properties. We found that the thermal stability of **1** was sufficient to handle even at room temperature.[1a] Therefore, we attempted to characterize the longicyclic conjugation in **1** by comparing with related compounds **4**, **5**, and **6**, in which one of the double bonds of **1** was saturated systematically to block the longicyclic conjugation. We report results of diimide reduction of **1** to give **4**—**7**, and electronic absorption spectrum and oxidation potential of **1**.



1 2 3

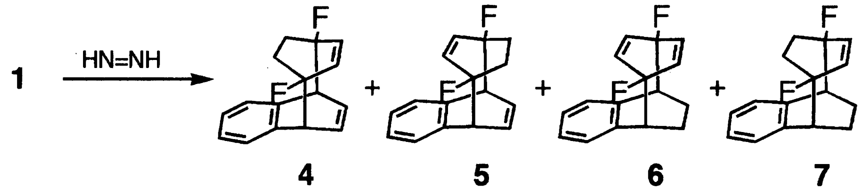
Chart 1.

Biplanemer **1** was reduced with diimide which was generated in situ by acid hydrolysis of potassium azodicarboxylate (PADC)[6] (Scheme 1). The yields of products are summarized in Table 1. When an equimolar amount of PADC was used, products **4**, **5**, and **6** were obtained in the yield of 16, 17, and 10%, respectively. The order of reactivity of double bond in **1** toward the diimide reduction was A≈B>C. Generally, the selectivity of diimide reduction is known to be affected mainly by steric factors but not by electronic effects.[7] In the case of **1**, examination of an HGS molecular model[8] suggests that steric hindrance around each double bond is similar and the three double bonds may be indistinguishable by steric factors. Atomic charge densities on the olefinic carbons of **1**, calculated by MNDO method,[9] are −0.0995, −0.1015, and −0.0881 for double bonds A, B, and C, respectively, and the order of the densities is parallel with the selectivity of the diimide reduction. Therefore, in the present case, the charge densities on the olefinic carbons may control the selectivity of the diimide reduction. When two or more molar amounts of PADC were used, both **4** and **6** underwent additional hydrogenation to give **7**, whereas **5**

Table 1. Yields of Hydrogenated Products in Diimide Reduction of **1**[a)]

PADC[b)] (mol. amt.)	Yield %				
	1	**4**	**5**	**6**	**7**
1	57	16	17	10	0
2	11	19	44	16	9
3	0	25	42	14	20

a) Yields were determined by the ratios of ^{1}H NMR integrals. b) PADC: potassium azodicarboxylate.



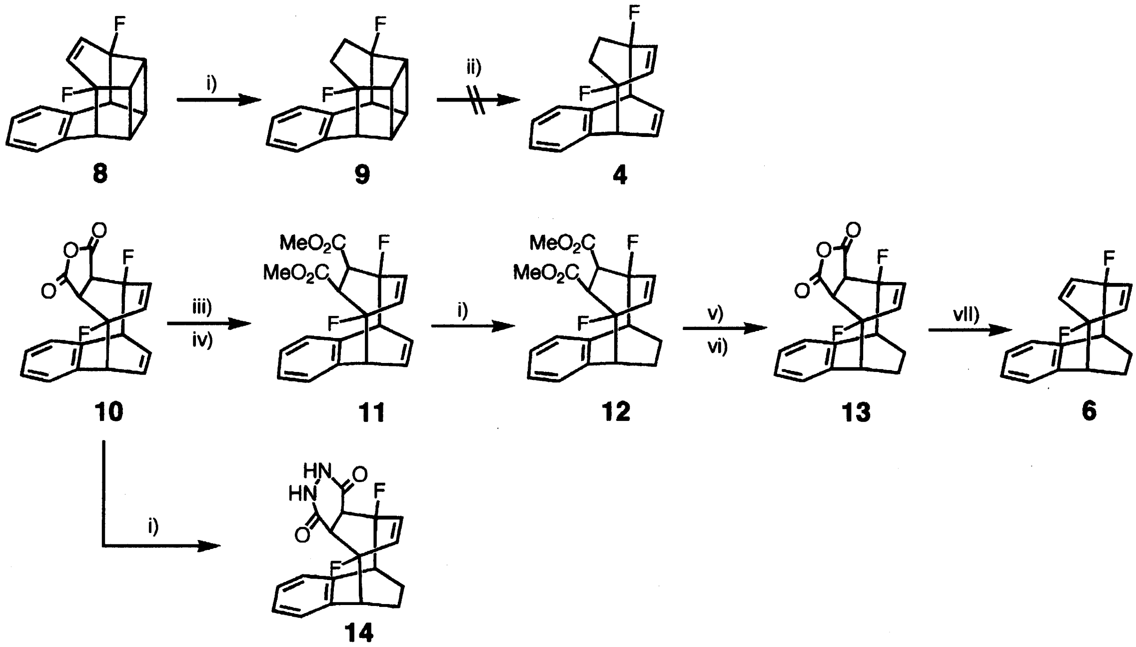
Scheme 1.

was not reduced further, because methylene protons of **5** sterically prevent diimide from approaching the double bonds A and C.[10)]

The reduction products **5** and **7** were isolated from the product mixture by preparative thin-layer chromatography (TLC), whereas **4** and **6** were inseparable from each other even by use of $AgNO_3$-doped TLC. For characterization, preparation of **4** and **6** was attempted by alternative routes, as shown in Scheme 2. Cage olefin **8**, which was derived from **1** on sensitized irradiation,[1a,1b)] was reduced by diimide to give **9**. Rhodium(I)-catalyzed cleavage of a cyclobutane ring[11)] of **9** to **4** was not successful. This is presumably because strongly electron-withdrawing fluorine atoms on the bridgeheads prevented Rh(I) from oxidative insertion to a cyclobutane moiety of **9**, since unsubstituted pentacyclo[6.4.0.$0^{2,7}$.$0^{3,12}$.$0^{6,9}$]dodecane framework underwent Rh(I)-catalyzed cleavage of a cyclobutane.[12)] Compound **6** was prepared from **10** in four steps as follows. As the reaction of **10** with diimide (two molar amounts) gave a carbohydrazide **14** instead of **13**, which was a desirable precursor to **6**,[13)] the acid anhydride moiety of **10** was protected as dimethyl ester **11**. One of the double bonds of **11** was hydrogenated selectively by diimide to give **12**.[10)] The dimethyl ester **12** was deprotected to **13**, which was decarboxylated by electrolysis to give **6**.

In Fig. 1(a), electronic absorption spectra of **1** and the related compounds **5**, **6**, **7**, and **10** are shown. An *o*-xylene like absorption band was observed at 260—280 nm for the series of compounds. In the case of **1**, i) an evident bathochromic shift of the band and ii) a tailing of the band over 300 nm were observed, and iii) additional absorption band(s) appeared around 250 nm. The bathochromic shift suggests the existence of the longicyclic (2,2,2,2) conjugation among the four π system in **1**. Characteristics of the longicyclic conjugation may be also reflected in the experimental oxidation potential (E_{ox}) and chemical reactivity[14)] of **1**. As listed in Table 2, E_{ox} of **1** is 1.70 V (vs. Ag/AgCl), which is the lowest value among the series of compounds, though the four π systems are formally isolated. The calculated ionization potentials (I_p) show the same tendency as E_{ox}.

As shown in Fig. 1(b), the electronic absorption spectrum of **1** was affected by solvent polarity. A small shoulder around 290 nm observed in hexane shifted bathochromically (at ca. 300 nm) by change of sol-



Scheme 2. Reagents and conditions; i) PADC, AcOH, MeCN, −20 °C; ii) $[Rh(I)NBDCl]_2$, CH_2Cl_2, r.t.; iii) MeOH, KOH, r.t.; iv) MeOH, TFAA, r.t.; v) 10% KOH aq, r.t.; vi) TFAA, benzene, r.t.; iiv) electrolysis, Pt electrodes, 80% pyridine aq, silica gel, 4-*t*-butylcatechol, 0 °C. NBD : norbornadiene, TFAA : trifluoroacetic anhydride.

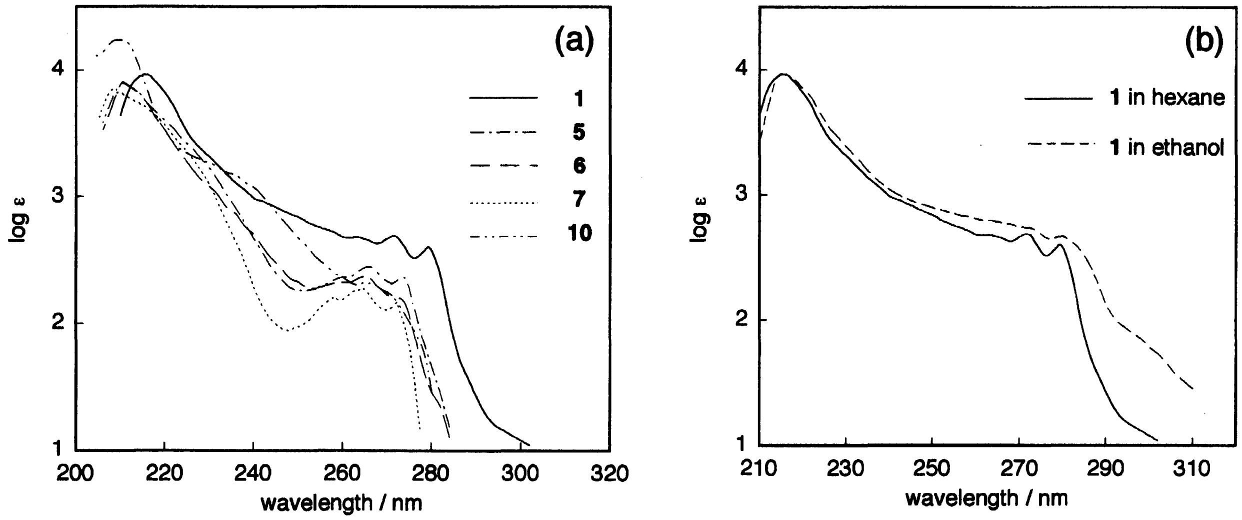


Fig. 1. Electronic absorption spectra of **1** and the related compounds. (a) **1**, **5**, **6**, and **7** in hexane, **10** in ether. (b) Solvent effects on absorption of **1**.

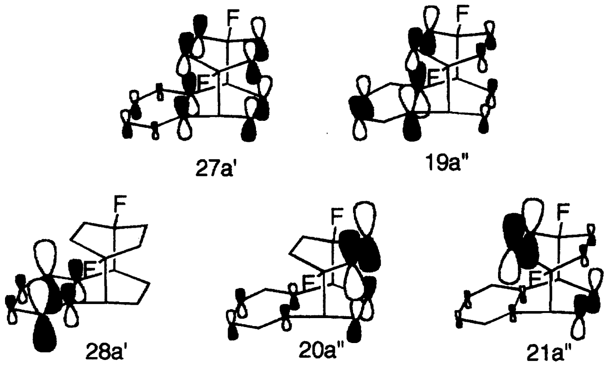
Table 2. Oxidation Potentials and Calculated Ionization Potentials of **1** and the Related Compounds

Compd	**1**	**5**	**6**	**7**	**10**
E_{ox}/V vs. Ag/AgCl	1.70	1.94	1.95	2.19	2.05
I_{p}/eV[a)]	9.449	9.471	9.487	9.524	9.941

a) Calculated by MNDO method.

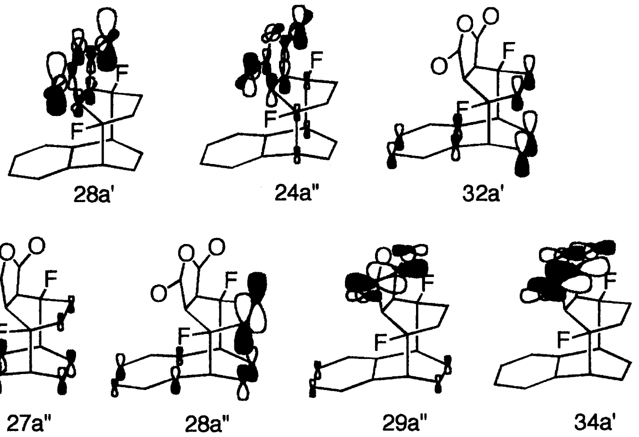
vent to ethanol. This absorption band was attributable to intramolecular charge transfer (CT) from the longicyclic π system to the benzene chromophore. CNDO/S calculation[15)] of **1** suggests that such a CT transition will appear at 289 nm (27a′→28a′, Table 3). The calculation also predicts that there are absorption bands ascribable to ππ* transition of the longicyclic chromophore at 249 nm (27a′→20a″) and 262 nm (27a′→21a″). Therefore we deduced that ππ* absorption bands of the longicyclic part appeared around 250 nm, although neither peak nor shoulder of the transitions was appreciable. In the case of **10**, in which the three π chromophores are arrayed in laticyclic manner, a shoulder appears around 240 nm [Fig. 1(a)] and the position of the shoulder was little affected by solvent polarity. As shown in Table 4, CNDO/S calculation of **10** suggests that the shoulder is constituted by nπ* transitions of the carbonyl groups (24a″→29a″, 24a″→34a′,

Table 3. S_{j} from S_0 Transitions of **1** after Configuration Interaction Calculated by CNDO/S



CI state	Wavelength/nm	Oscillator strength	Main transition	Assignment
1	289.3	0.0324	27a′→28a′	CT
2	287.6	0.0033	27a′→19a″	ππ*
3	262.2	0.0037	27a′→20a″	ππ* (longicycle)
4	249.6	0.0023	27a′→21a″	ππ* (longicycle)
5	222.4	0.0441		
6	221.4	0.2138		
7	220.4	0.0047		
8	212.3	0.0004		

Table 4. Selected S_j from S_0 Transitions of **10** after Configuration Interaction Calculated by CNDO/S



CI state	Wavelength/nm	Oscillator strength	Main transition	Assignment
2	259.3	0.0094	32a′→27a″	ππ* (laticycle)
3	244.7	0.0011	32a′→28a″	ππ* (laticycle)
4	242.1	0.0073	24a″→29a″	nπ*
5	234.8	0.0001	24a″→34a′ 28a′→29a″	nπ*

and 28a′→29a″) and a ππ* transition of the laticyclic chromophore (32a′→28a″). Compounds **5** and **6** show similar absorption bands and neither intramolecular CT band nor characteristic absorption of the laticyclic chromophores is clear.

In summary, the CT absorption band in the long wavelength region and the low oxidation potential observed for biplanemer **1** may reflect the destabilization effects of the longicyclic (2,2,2,2) conjugation predicted by Goldstein and Hoffmann.[3)]

Experimental

Apparatus and General Procedures. Melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a JEOL JNM PMX-60 (60 MHz) spectrometer. SC-NMR were recorded on a Varian VXR-500 (500 MHz) equipment at the SC-NMR Laboratory of Okayama University. IR spectra were recorded on a JASCO FT-IR 5000 spectrometer. UV spectra were recorded on a Hitachi 228 spectrophotometer. Cyclic voltammetric measurements were carried out with a Yanagimoto P-1100 polarographic analyzer. Elemental analyses were performed on a Yanaco MT-2 CHN-corder.

Materials. Compounds **1**, **8**, and **10** were prepared by our methods.[1,5)] Potassium azodicarboxylate (PADC) was prepared by the method of Berson et al.[6)]

Reduction of Biplanemer 1 with Diimide. General Procedure. To a mixture of **1** (30 mg, 0.12 mmol) and PADC in MeCN (1 ml) was added a solution of acetic acid (5 molar amounts of PADC) in MeCN (1 ml) dropwise at −22 °C under an atmosphere of nitrogen. The mixture was stirred at the temperature for 3.5 h. After filtration of the salts, the solvent was evaporated under reduced pressure. The residue was passed through a silica gel column using dichloromethane to give a product mixture of **4**, **5**, **6**, and **7**. The yield of each product was determined by ^{1}H NMR analysis. Values are listed in Table 1.

4: ^{1}H NMR (500 MHz) $\delta=7.19$ (2H, m), 7.13 (2H, m), 6.55 (2H, AA′XX′), 5.19 (2H, AA′XX′), 3.83 (2H, m), 1.65 (2H, m), and 1.52 (2H, m).

5: Colorless crystals; mp 124—125 °C; ^{1}H NMR (500 MHz) $\delta=7.17$ (4H, m), 6.66 (2H, AA′XX′), 5.38 (2H, AA′XX′), 3.91 (2H, m), 2.37 (2H, d, $J=9$ Hz), and 1.91 (2H, m); IR (KBr), 2944, 1477, 1458, 1375, 1048, 978, 873, 745, and 665 cm^{-1}; UV (hexane) $\lambda_{\max}$ 258 nm ($\log\varepsilon=2.28$), 266 (2.32), and 272 (2.21). Found: C, 77.22; H, 5.67%. Calcd for $C_{16}H_{14}F_2$: C, 78.67; H, 5.78%.

7: Colorless prisms; mp 114—115 °C; ^{1}H NMR (500 MHz) $\delta=7.21$ (2H, m), 7.13 (2H, m), 6.27 (2H, AA′XX′), 3.44 (2H, m), 2.44 (2H, m), and 1.46—1.58 (4H, m); IR (KBr) 2924, 1458, 1381, 1064, 1013, 975, 888, 857, 806, 756, 723, and 652 cm^{-1}; UV (hexane) $\lambda_{\max}$ 258 nm ($\log\varepsilon=2.20$), 264 (2.27), and 272 (2.16). Found: C, 77.50; H, 6.45%. Calcd for $C_{16}H_{16}F_2$: C, 78.03; H, 6.55%.

Reduction of 8 with Diimide. Cage olefin **8** (27 mg, 0.11 mmol) was reduced to **9** with diimide generated from 22 molar amounts of PADC, as described above at 0 °C. The solvents were evaporated under reduced pressure and the residue was extracted with 50 ml of a mixed solvent of hexane : ether (1 : 1 v/v). The extract was washed with aqueous $NaHCO_3$ and water. After the usual workup, the crude product was chromatographed on silica gel using CH_2Cl_2 to give **9** (25 mg, 92%).

9: Colorless plates; mp 98—101 °C; ^{1}H NMR (60 MHz) $\delta=7.23$ (4H, bs), 4.04 (2H, m), 2.83—3.90 (4H, m), and 1.20—1.73 (4H, m); IR (KBr) 2980, 2930, 1454, 1062, and 891 cm^{-1}; UV (hexane) $\lambda_{\max}$ 213 nm ($\log\varepsilon=3.95$), 258 (2.20, sh), 264 (2.28), and 270 (2.19, sh). Found: C, 78.54; H, 5.70%. Calcd for $C_{10}H_{14}F_2$: C, 78.67; H, 5.78%.

Preparation of 6. Acid anhydride **10** (270 mg, 0.86 mmol) was hydrolyzed with 5 ml of 10% KOH in MeOH at room temperature. The mixture was diluted with 3 ml of water, acidified with dilute hydrochloric acid, and extracted with ether 3×20 ml. The combined extracts were dried over anhyd. $MgSO_4$. After the usual workup, ether was evaporated under reduced pressure. The residue was treated with 3 ml of trifluoroacetic anhydride in benzene (5 ml) at room temperature for 5 min.[16] To the mixture was added 2 ml of MeOH and the mixture was stirred at room temperature for 30 min. The solvents were evaporated under reduced pressure and trifluoroacetic acid was removed by azeotropic distillation with carbon tetrachloride to give **11** (293 mg, 95%).

The diester **11** (293 mg, 0.93 mmol) was reduced to **12** by diimide, which was generated from 2 molar amounts of PADC as described above. Compound **12** was hydrolyzed with 10% KOH in MeOH to the corresponding dicarboxylic acid, which was converted to the acid anhydride **13** by treatment with 3 ml of trifluoroacetic anhydride in 5 ml of dry benzene for 5 min at room temperature (193 mg, 66% from **11**).

11: Colorless prisms; mp 142—144 °C; ^{1}H NMR (60 MHz) $\delta=7.16$ (4H, bs), 6.53 (2H, AA′XX′), 6.03 (2H, AA′XX′), 3.80 (2H, m), 3.55 (6H, s), and 3.09 (2H, bs); IR (KBr) 1763 and 1216 cm^{-1}; UV (ether) $\lambda_{\max}$ 210 nm ($\log\varepsilon=4.17$), 267 (2.46), and 272 (2.44).

13: Colorless needles; mp 292—293 °C; ^{1}H NMR (60 MHz) $\delta=7.10$ (4H, m), 6.43 (2H, AA′XX′), 3.67 (2H, m), 3.10 (2H, m), 2.50 (2H, m), and 1.50—1.93 (2H, m); IR (KBr) 1866 and 1792 cm^{-1}; UV (CH_2Cl_2) $\lambda_{\max}$ 257 nm ($\log\varepsilon=2.19$), 263 (2.23), and 268 (2.12). Found: C, 68.32; H, 4.28%. Calcd for $C_{18}H_{14}F_2O_3$: C, 68.35; H, 4.46%.

Electrooxidative Bisdecarboxylation of 13. An ice-cooled solution of **13** (172 mg, 0.54 mmol) and triethylamine (0.15 ml, 0.8 mmol) in 25 ml of 80% aqueous pyridine was electrolyzed with a current of 200 mA for 13 h using a pair of platinum plate electrodes. The solution was acidified with 17 ml of diluted nitric acid (2 M, M=mol dm^{-3}) and extracted with 20 ml of CH_2Cl_2. After the usual workup, the products were chromatographed on silica gel using a mixed solvent of hexane : CH_2Cl_2 (2 : 1 v/v) to give **6** (44 mg, 33%).

6: Colorless plates; mp 123—124.5 °C; ^{1}H NMR (500 MHz) $\delta=7.14$ (2H, m), 7.02 (2H, m), 6.47 (2H, AA′XX′), 5.69 (2H, AA′XX′), 3.63 (2H, m), 2.46 (2H, m), and 1.67 (2H, m); IR (KBr) 2920, 1456, 1367, 1110, 1089, 1053, 980, 839, 754, 733, and 656 cm^{-1}; UV (hexane) $\lambda_{\max}$ 259 nm ($\log\varepsilon=2.48$), 266 (2.52), and 273 (2.42). Found: C, 78.59; H, 5.70%. Calcd for $C_{16}H_{14}F_2$: C, 78.67; H, 5.78%.

Reduction of 10 with Diimide. To a mixture of **10** (50 mg, 0.16 mmol) and PADC (78 mg, 0.4 mmol) in 4 ml of MeCN was added a solution of acetic acid (73 ml, 1.28 mmol) in 2 ml of MeCN dropwise at 0 °C. The mixture was stirred at 0 °C for 3 h. After filtration of the salts, followed by evaporation of the solvents under reduced pressure, the crude product was chromatographed on silica gel using a mixed solvent of chloroform : ether (1 : 2 v/v) to give a carbohydrazide **14** (40 mg, 75%).

14: Colorless needles, mp 263 °C (decomp); ^{1}H NMR (500 MHz) $\delta=7.29$ (2H, m), 7.22 (2H, m), 6.31 (2H, AA′XX′), 4.25 (2H, bs, D_2O exchangeable), 3.64 (2H, m), 2.47 (2H, m), and 1.72 (2H, m); IR (KBr) 3314, 3246, 1693, 1680, 1584, and 1435 cm^{-1}. Found: C, 65.42; H, 4.75%; N, 8.34. Calcd for $C_{18}H_{16}F_2N_2O_2$: C, 65.45; H, 4.88; N, 8.48%.

Thermal Cope Rearrangement of 1. A solution of **1** (32 mg, 0.13 mmol) in 15 ml of hexane was heated at reflux for 30 min. Hexane was evaporated under reduced pressure and the residue was chromatographed on silica gel using preparative TLC (pentane) to give **16** (22 mg, 76%) and **17** (5 mg, 16%).

16: Colorless plates, mp 71—72 °C (lit, 71—72 °C);[17] ^{1}H NMR (500 MHz) $\delta=7.91$ (1H, d, $J=9.0$ Hz), 7.87 (1H, d, $J=8.0$ Hz), 7.85 (1H, d, $J=9.0$ Hz), 7.52 (1H, dd, $J=9.0$, 7.5 Hz), 7.50 (1H, dd, $J=9.0$, 2.0 Hz), 7.48 (2H, dd, $J=8.5$, 2.0 Hz), 7.45 (1H, dd, $J=8.0$, 1.5 Hz), 7.39 (1H, dd, $J=7.5$, 1.5 Hz), and 7.19 (2H, t, $J=8.5$ Hz); IR (KBr) 1605, 1506, 1399, 1222, 839, 801, 793, and 781 cm^{-1}; UV (EtOH) $\lambda_{\max}$ 223 nm ($\log\varepsilon=4.60$) and 283 (3.88). HRMS (EI) Found: m/z 222.0824. Calcd for $C_{16}H_{11}F$: M, 222.0845.

17: Colorless plates, mp 103.5—104 °C; ^{1}H NMR (500 MHz) $\delta=7.99$ (1H, d, $J=2.0$ Hz), 7.91 (1H, d, $J=8.0$ Hz), 7.89 (1H, d, $J=6.0$ Hz), 7.87 (1H, d, $J=8.5$ Hz), 7.70 (1H, dd, $J=6.0$, 2.0 Hz), 7.68 (2H, m), 7.52 (1H, dd, $J=7.0$, 2.0 Hz), 7.49 (1H, dd, $J=7.0$, 2.0 Hz), 7.18 (1H, d, $J=8.5$ Hz), and 7.17 (1H, d, $J=8.5$ Hz); IR (KBr) 1603, 1514, 1502, 1224, 862, 826, and 748 cm^{-1}; UV (EtOH) $\lambda_{\max}$ 248 nm ($\log\varepsilon=4.69$) and 286 (4.01). HRMS (EI) Found: m/z 222.0847. Calcd for $C_{16}H_{11}F$: M, 222.0845.

CNDO/S Calculation of 1 and 10. CNDO/S calculation was carried out using a molecular model whose geometry was optimized by MNDO method. The lowest 60 configurations were included for CI calculation. The results are summarized in Tables 3 and 4.

Electrochemical Measurements. The working electrode was a platinum disk and the counter electrode was a platinum coil. A saturated calomel electrode was used as reference. Nitrogen purged solutions of substrates (10^{-3} M) in 0.5 M tetrabutylammonium perchlorate in MeCN were used for the measurements. The measurements were carried out at a sweep rate of 50 mV s^{-1}. The working electrode was polished for every scan.

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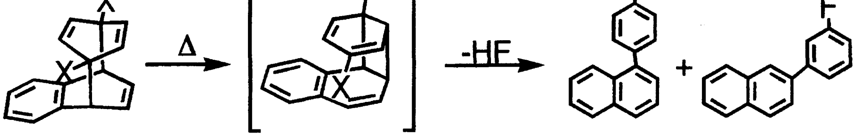

1 (X=F)
1′ (X=H)
15 (X=F)
15′ (X=H)
16
17

Scheme 3.

surements. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 06854034 from the Ministry of Education, Science and Culture.

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2) According to MNDO calculation, distances between double bonds in **1** are 2.44 Å for A–D and B–C, and 2.74—2.76 Å for A–B and C–D.

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13) Diimide have been known to reduce double bonds in many carboxylic acids and acid anhydrides without undergoing nucleophilic attack on their carbonyl groups.[7)] In the present case, hydrazine formed through disproportionation of diimide might react with the acid anhydride moiety of **10** simultaneously with the diimide reduction of a double bond of **10** to give **14**.

14) Upon heating at 70 °C, biplanemer **1** underwent Cope rearrangement followed by dehydrofluorination to give **16** and **17** within 30 min (Scheme 3), while **5**, **6**, and **10** were quite stable at the temperature. Yang reported that unsubstituted **1′** (X=H) gave rearranged product **15′** in quantitative yield.[12)]

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