adamantanecarboxylate in phosphate buffer (pH 9.18) solution at 25 °C. The reciprocal of the difference absorbance around 260–280 nm was plotted against the reciprocal of the guest concentration. From the slope and the intercept, the association constant was obtained. The 1-adamantanecarboxylate concentration ranges from 1.27×10^{-4} M to 4.97×10^{-4} M. The association constants between β-cyclodextrin derivatives and *p*-nitrophenol (5×10^{-5} M) were also estimated by the difference spectra at 25 °C and pH 9.18, where β-cyclodextrin derivatives concentration range from 3.13×10^{-4} M to 1.51×10^{-3} M. The association constants in the presence of nucleobases were obtained in the same manner, where nucleobases concentration was same as the host concentration. The association constant between **6** (or **11**) and 1-adamantanecarboxylate was also estimated by means of CD spectra, where the concentrations of **6** (or **11**) and the carboxylate were 1.5×10^{-4} and 1.52×10^{-4} to 5.02×10^{-4} M (or 1.0×10^{-4} and 1.23×10^{-4} to 4.28×10^{-4} M), respectively. These spectral data were treated by the Benesi–Hildebrand method.

Acknowledgment. We thank Mr. H. Kondo and Mr. N. Tsuruzoe for the contribution to the early stage of this research. We are grateful to Professor T. Koga, Daiichi College of Pharmaceutical Sciences, for the measurement of CD spectra and also thank Mr. K. Tanaka (JEOL LTD.) for FAB mass spectral measurements.

Improved Synthesis and Electrophilic Bromination of Benzo[1,2-*c*:3,4-*c*']dithiophene. Charge-Transfer and Cycloaddition Reaction with Tetracyanoethylene

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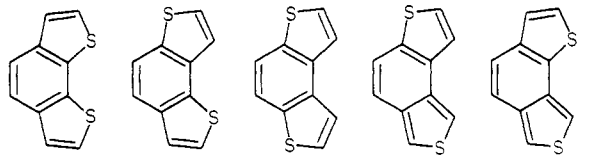
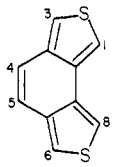
Benzo[1,2-*c*:3,4-*c*']dithiophene (**6**) is prepared in two steps and 47% overall yield from its tetrahydro precursor **7**. Bromination of **6** (NBS, AcOH) occurs in the thiophene moieties; preparation of the 1-Br, 3-Br, 1,3-Br_2, 1,3,6-Br_3, 1,3,6,8-Br_4, and 1,3,4,5,6-Br_5 derivatives of **6** is described. With tetracyanoethylene, **6** first forms a blue charge-transfer complex, which, on reflux in chloroform, is converted to the Diels–Alder type bis-adduct **16**.

All six isomeric benzodithiophenes **1–6** are known.[1]



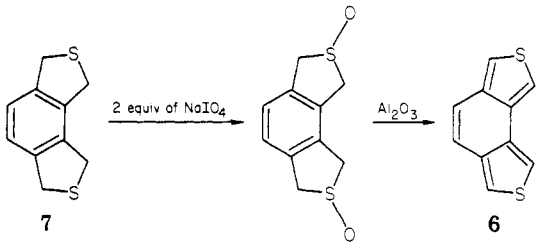
1 **2** **3** **4** **5**



6

Compounds **1–3**, with only benzo[*b*]thiophene moieties, are readily obtained in 50–70% yield. Compounds **4** and **5**, which each contain one benzo[*c*]thiophene moiety, are stable only in solution;[1] attempts to isolate them result in polymerization, presumably due to intermolecular Diels–Alder reactions analogous to those observed with other benzo[*c*]thiophenes.[2] Compound **6**, with two benzo[*c*]-thiophene moieties, on the other hand, is stable in pure form.[1,3,4] Previous syntheses gave relatively poor yields of **6**.[5] We describe here an improved synthesis of **6**. We also report on its bromination, as a typical electrophilic substitution reaction, and on its novel reaction with tetracyanoethylene.

Oxidation of tetrahydrobenzo[1,2-*c*:3,4-*c*']dithiophene (**7**)[6] with sodium periodate gave the disulfoxide **8** in 75% yield. Subsequent dehydration with neutral alumina[2] gave crystalline, pure **6**, mp 108–110 °C, in 63% yield. This



7 **8** **6**

route to **6** involves fewer steps than methods based on construction of the central, benzenoid ring.[1,3] Although it requires one more step than the direct dehydrogenation of **7**,[4] the overall yield is considerably better.

There are no previous studies on electrophilic substitution reactions of **6**. Bromination was selected as a typical example. Treatment of **6** at room temperature with 1 equiv of *N*-bromosuccinimide (NBS) in acetic acid gave two monobromo derivatives **9** and **10** and the dibromo derivative **11**. Compounds **9** and **10** were obtained as an approximately 1:1 mixture in 70% yield. They were separated from **11** (6%) by column chromatography, and **9** could be obtained pure by trituration of the **9**, **10** mixture with hexane.

The structures of **9–11** are based primarily on their NMR spectra, summarized in Table I. Several features identify **9** and **10**. First, both spectra show two strongly coupled "vinyl" protons (H_4, H_5), showing that bromination occurred in the thiophene moieties and not at the central double bond (contrast with phenanthrene). In **9**, both

(1) Gronowitz, S.; Dahlgren, T. *Chem. Scr.* **1977**, *12*, 57.
(2) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932 and references cited therein.
(3) MacDowell, D. W. H.; Maxwell, M. H. *J. Org. Chem.* **1970**, *35*, 799.
(4) Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326.
(5) The procedures in ref 1 and 3 are multistep, the starting materials are not readily available, and the yield in the final step is only 20%. The yield of **6** from **7** as reported in ref 4 was 35%.
(6) Giovannini, E.; Vuilleumier, H. *Helv. Chim. Acta* **1977**, *60*, 1452.

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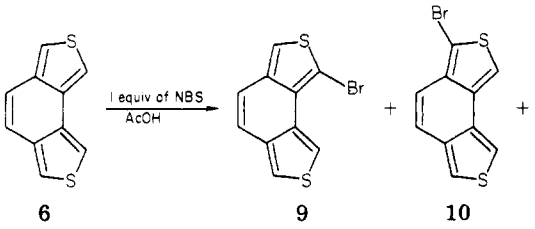
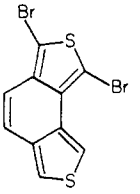


6 9 10

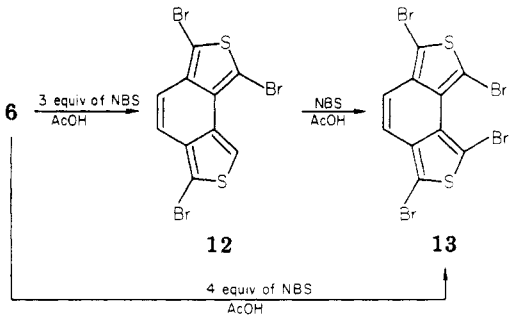


11

"vinyl" type protons are doublets of doublets, due to mutual coupling and much smaller coupling with a nearby thiophene-type proton ($J_{3,4}$ and $J_{5,6}$). In **10**, however, the higher field "vinyl" proton is a simple doublet (coupling only with H_5). This result puts the bromine at C1 in **9** and at C3 in **10**. Consistent with this conclusion, H_3 is a doublet in **9** (δ 7.71; $J_{3,4}$ = 0.6 Hz), whereas H_1 is a singlet in **10** (δ 7.39). Finally, H_6 appears at much lower field in **10** (and in **11**) than in **9** due to conjugative electron withdrawal by the bromo substituent.

The NMR spectrum of **11** also showed two strongly coupled "vinyl" type protons (H_4, H_5), showing that both bromines were in the thiophene moieties. The splitting pattern of these protons was similar to that of **10**, not **9**; hence one of the bromines must be at H3 and H6 must be unsubstituted. Thus, the only possibilities for **11** were the 1,3- or 3,8-dibromo derivatives. Since the remaining proton (δ 7.48) was a doublet, this proton had to be H8 (if it were H1, it would have been a singlet), and the structure of **11** is fixed as the 1,3-isomer.

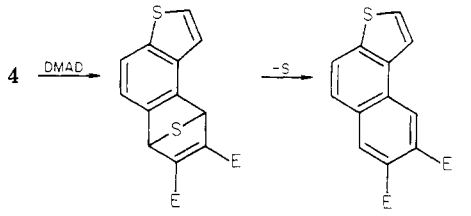
Bromination of **6** with 2 equiv of NBS gave a mixture of products that could not be easily separated. However, with 3 equiv of NBS the tribromo derivative **12** was obtained (48%), and with 4 equiv of NBS the tetrabromo derivative **13** was isolated (30%). The structures were



12 13

clear from the NMR spectra (Table I); bromination occurs only in the thiophene moieties, even when a large excess of NBS is used. Attempts to prepare hexabromo **6** starting with 4,5-dibromo derivative also failed (see Experimental Section).

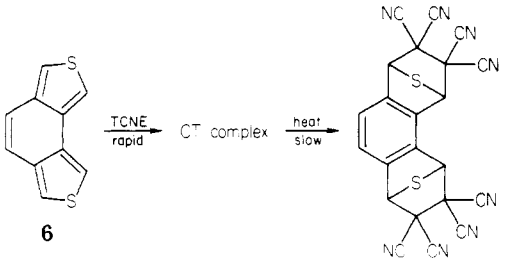
Benzo[*c*]thiophene and various derivatives such as **4** and **5**[1] react rapidly with dienophiles (for example, **4** → **15**, DMAD = dimethyl acetylenedicarboxylate, E = CO_2CH_3). The driving force is the aromatization of the benzenoid ring (though the aromaticity of the thiophene moiety is in fact lost). Compound **6**, on the other hand, though a *c*-fused thiophene, is not expected to be reactive toward dienophiles because the six-membered ring does not become aromatic until two cycloadditions have occurred (and of course, in the process, the aromaticity of two thiophene



14 15

moieties would be lost). Hence it is not surprising that **6** does not form cycloadducts with DMAD or *N*-phenylmaleimide.

On the other hand, **6** is an electron-rich aromatic compound and should be a strong electron donor. We found that benzene solutions of **6** produce a deep blue color when treated with 2 equiv of tetracyanoethylene (TCNE). Evaporation of the solvent under reduced pressure gave a dark blue crystalline solid, mp 187–189 °C dec, which showed a CT band at 607 nm (ϵ 45). When a suspension of this complex in chloroform was heated at reflux overnight, the blue color disappeared and a white solid precipitated. This solid is the Diels–Alder bis-adduct **16**. The



6 16

structure of **16** follows from its NMR spectrum, which consists of a singlet for the aromatic protons (δ 7.79) and two doublets at δ 6.30 and 6.62, J = 1.9 Hz, for the bridgehead protons. Although two stereoisomers of **16** are possible, only one appears to have formed (anti?).

Although **16** is formally a Diels–Alder adduct, it clearly is formed in a stepwise manner. Dienophiles that do not form CT complexes with **6** do not form adducts. On the other hand, tetracyanoquinodimethane (TCNQ) forms a CT complex with **6** (CT band at 627 nm, ϵ 52), which, however, does not lead to a cycloadduct.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Varian T-60 or Bruker WM-250 spectrometer in $CDCl_3$ solutions containing Me_4Si as an internal standard, unless otherwise noted. Chemical shifts are reported in δ units (J values are in hertz). ^{13}C NMR spectra were determined on a Varian CFT-20 or Bruker WM-250 spectrometer. Infrared and UV–vis spectra were recorded on a Perkin-Elmer 167 and Varian Cary-219 spectrometer, respectively. Mass spectra were obtained with a Finnigan 4000 spectrometer or, for high resolution, a Varian CHS spectrometer. Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Analyses are by Spang Microanalytical Laboratory.

1,3,6,8-Tetrahydrobenzo[1,2-*c*:3,4-*c*']dithiophene 2,7-Dioxide (8). Sodium periodate (860 mg, 4 mmol) in 50 mL of water was added to a methanol (200 mL) solution of 1,3,6,8-tetrahydrobenzo[1,2-*c*:3,4-*c*']dithiophene[6] (400 mg, 2 mmol). The solution was stirred for 12 h at room temperature and then filtered to remove inorganic salts. The filtrate was evaporated to dryness (vacuum) and the residue was recrystallized from methanol/ethyl acetate to give 340 mg (75%) of **8**: mp 202–204 °C; ^1H NMR (250 MHz, acetone-d_6) δ 7.40 (s, 2 H), 4.20 (m, 8 H); ^{13}C NMR (20 MHz, MeOD) δ 137.7, 135.4, 127.6, 60.1, 58.8; IR (KBr) 3000 (w), 2950 (w), 1450 (m), 1380 (m), 1020 cm^{-1} (s); mass spectrum, *m/e* (relative intensity) 226 (100), 208 (2), 178 (8); high-resolution mass

Table I. Proton NMR Spectral Data of Bromo Derivatives of 6[a]

compd	H_1	H_3	H_4	H_5	H_6	H_8
9		7.71 (d)	7.04 (dd)	7.18 (dd)	7.75 (dd)	7.50 (d)
		0.6	10.0, 0.6	10.0, 0.9	3.1, 0.9	3.1
10	7.39 (s)		6.99 (d)	7.08 (dd)	8.59 (dd)	7.46 (d)
			9.5	9.5, 0.9	2.8, 0.9	2.8
11			6.95 (d)	7.13 (dd)	8.55 (dd)	7.48 (d)
			10.0	10.0, 0.9	3.0, 0.9	3.0
12			7.03 (d)	7.10 (d)		8.51 (s)
			9.5	9.5		
13			7.00 (s)	7.00 (s)		

[a] δ (J, hertz).

spectrum, calcd for $C_{10}H_{10}O_2S_2$ m/e 226.01223, found 226.01092.

Benzo[1,2-c:3,4-c']dithiophene (6). The disulfoxide 8 (226 mg, 1 mmol) and neutral alumina (400 mg, activity I, 70–230 mesh) were thoroughly mixed and heated at 140–150 °C (25 torr) in a cold-finger sublimer to give 120 mg (63%) of 6: mp 108–110 °C (lit.[3] mp 111–112 °C); ^1H NMR (60 MHz) δ 7.70 (d, J = 2.7 Hz, 2 H), 7.46 (d, J = 2.7 Hz, 2 H), 7.11 (s, 2 H); mass spectrum, m/e (relative intensity) 190 (100), 158 (4), 145 (13).

Bromination of 6. One Equivalent of NBS. To a solution of 6 (380 mg, 2 mmol) in acetic acid (20 mL) was added over 30 min a solution of NBS (360 mg, 2 mmol) in acetic acid (60 mL). The mixture was stirred at room temperature for an additional 30 min. Water (200 mL) was added and the mixture was extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). Vacuum removal of the solvent left a brown residue, which was chromatographed (silica gel, hexane eluent) to give 42 mg (6%) of 1,3-dibromobenzo[1,2-c:3,4-c']dithiophene (11): mp 120–122 °C; ^1H NMR (250 MHz), see Table I; ^{13}C NMR (62.9 MHz) δ 136.70, 130.64, 130.41, 122.29, 121.00, 119.53, 119.18, 118.35, 105.77, 104.00; IR (KBr) 3100 (w), 1430 (w), 1390 (w), 1195 (w), 1020 (m), 860 (w), 800 cm^{-1} (s); mass spectrum, m/e (relative intensity) 350 (60), 348 (100), 346 (50), 269 (35), 267 (28); high-resolution mass spectrum, calcd for $C_{10}H_4Br_2S_2$ m/e 347.81026, found 347.80645.

The second chromatography fraction gave 380 mg (70%) of 1:1 mixture (NMR) of 9 and 10. Pure 9, mp 70–71 °C, was obtained as the residue after triturating the mixture with hexane. For the ^1H NMR spectra of 9 and 10 at 250 MHz, see Table I; mass spectrum (mixture), m/e (relative intensity) 270 (100), 268 (84), 189 (31); high-resolution mass spectrum (mixture) calcd for $C_{10}H_5BrS_2$ m/e 269.89969, found 269.89941.

Bromination of 6. Three Equivalents of NBS. A suspension of 6 (190 mg, 1 mmol) and NBS (540 mg, 3 mmol) in acetic acid (20 mL) was stirred at room temperature for 30 min. Water (200 mL) was added, and the resulting yellow precipitate was collected and recrystallized from chloroform to give 210 mg (48%) of 12: mp 157–158 °C; ^1H NMR (250 MHz), see Table I; IR (KBr) 3100 (w), 1350 (w), 1200 (m), 1120 (w), 1030 (w), 980 (w), 790 cm^{-1} (s); mass spectrum, m/e (relative intensity) 430 (12), 428 (30), 426 (26), 424 (9), 348 (6), 346 (13), 344 (5), 40 (100); high-resolution mass spectrum, calcd for $C_{10}H_3Br_3S_2$ m/e 427.71885, found 427.71961.

Bromination of 6. Four Equivalents of NBS. The procedure was analogous to that described for the preparation of 12, except that 4 equiv of NBS was used. From 190 mg (1 mmol) of 6 there was obtained 150 mg (30%) of 13, mp 208–210 °C, from chloroform: ^1H NMR (250 MHz), see Table I; IR (KBr) 3100 (w), 1370 (m), 1280 (m), 1120 (m), 1010 (m), 920 (m), 860 (m), 790 cm^{-1} (s); mass spectrum, m/e (relative intensity) 510 (17), 508 (73), 506 (99), 504 (65), 502 (16), 428 (65), 426 (100), 424 (72), 422 (19), 348 (38), 346 (66), 344 (35); high-resolution mass spectrum, calcd for $C_{10}H_2Br_4S_2$ m/e 505.62942, found 505.63018.

Compound 13 was similarly obtained from 12 (210 mg, 0.5 mmol), NBS (90 mg, 0.5 mmol), and acetic acid (30 mL). The yield was 150 mg (59%).

3,4,5,6-Tetrakis(bromomethyl)-1,2-dibromobenzene. A solution of dibromoprehnitene[8] (2.92 g, 10 mmol) and bromine (6.4 g, 40 mmol) in carbon tetrachloride (150 mL) was irradiated at reflux with a 200-W lamp for 1 day. The solution was washed successively with aqueous sodium bisulfite, sodium bicarbonate, and water and dried ($MgSO_4$). Removal of the solvent (vacuum) left a solid that was recrystallized from hexane to give 5.0 g (82%) of 3,4,5,6-tetrakis(bromomethyl)-1,2-dibromobenzene: mp 187–188 °C; ^1H NMR (60 MHz) δ 4.70 (s, 4 H), 4.52 (s, 4 H); ^{13}C NMR (20 MHz) δ 139.46, 137.23, 113.23, 30.96, 24.71; IR (CCl_4) 2960 (w), 1500 cm^{-1} (s); mass spectrum, m/e (relative intensity) 610 (0.5), 608 (0.8), 606 (0.5), 533 (1.4), 531 (9.5), 529 (19.1), 527 (18), 525 (9), 523 (1.5), 128 (100); high-resolution mass spectrum, calcd for $C_{10}H_8Br_6$ m/e 607.56703, found 607.56811.

4,5-Dibromobenzo[1,2-c:3,4-c']dithiophene. To a solution of $Na_2S·9H_2O$ (4.8 g, 20 mmol) in ethanol (250 mL) and water (50 mL) was added 6.1 g (10 mmol) of 3,4,5,6-tetrakis(bromomethyl)-1,2-dibromobenzene over 1 h. The mixture was stirred at reflux overnight and then diluted with water (300 mL). The resulting yellow precipitate was collected and air-dried to give 1.5 g (43%) of crude 1,3,6,8-tetrahydro-4,5-dibromobenzo[1,2-c:3,4-c']dithiophene: ^1H NMR (60 MHz) δ 4.68 (s, 4 H), 4.60 (s, 4 H); mass spectrum, m/e (relative intensity) 354 (12), 352 (25), 350 (13), 272 (13), 270 (13), 84 (100).

A suspension of the crude disulfide (1 g, 3 mmol) and dichlorodicyanoquinone (DDQ; 1.43 g, 6 mmol) in chlorobenzene (150 mL) was heated at reflux for 3 h. Removal of the solvent (vacuum) left a brown residue that was chromatographed (basic alumina, benzene eluent) to give 110 mg (11% overall) of 4,5-dibromobenzo[1,2-c:3,4-c']dithiophene: mp 167–169 °C; ^1H NMR (250 MHz) δ 7.85 (d, J = 3.2 Hz, 2 H), 7.75 (d, J = 3.2 Hz, 2 H); ^{13}C NMR (62.9 MHz) δ 136.34, 130.46, 123.28, 118.34, 117.75; IR (KBr) 3100 cm^{-1} (s); mass spectrum, m/e (relative intensity) 350 (65), 348 (100), 346 (50); high-resolution mass spectrum, calcd for $C_{10}H_4Br_2S_2$ m/e 347.81026, found 347.80645.

Bromination of 4,5-Dibromobenzo[1,2-c:3,4-c']dithiophene. With use of the same procedure for the preparation of 13 from 6, the 4,5-dibromo derivative of 6 (20 mg, 0.06 mmol) and NBS (45 mg, 0.24 mmol) in acetic acid (20 mL) gave, after recrystallization from chloroform, 25 mg (71%) of a pentabromo derivative, mp 210–211 °C, considered to be 1,3,4,5,6-pentabromo 6 (the only other possibility, the 1,3,4,5,8-isomer, is considered less likely because of crowding between the C1 and C8 bromines): ^1H NMR (250 MHz) δ 8.72 (s, 1 H); IR (KBr) 3100 cm^{-1} (w); mass spectrum, m/e (relative intensity) 590 (0.2), 588 (12), 586 (22), 584 (22), 582 (12), 580 (0.2), 93 (100); high-resolution mass spectrum, calcd for $C_{10}HBr_5S_2$ m/e 583.53998, found 583.53613.

Charge-Transfer Complexes of 6. To a solution of 6 (19 mg, 0.1 mmol) in benzene (10 mL) was added a solution of TCNE (25.6 mg, 0.2 mmol) in benzene (10 mL). The resulting blue solution was evaporated (vacuum) to give a dark blue solid, mp 187–189 °C dec. The IR and mass spectra of this solid were a composite of the spectra of 6 and TCNE. The visible spectrum ($CHCl_3$) showed λ_{max} 607 nm (ε 45).

The TCNQ complex, similarly prepared, melted at 175–180 °C dec; λ_{max} ($CHCl_3$) 627 nm (ε 52).

Cycloadduct 16. To a solution of 6 (190 mg, 1 mmol) in benzene (100 mL) was added a solution of TCNE (256 mg, 2 mmol) in benzene (100 mL). The blue solution was evaporated to dryness (vacuum), and the resulting blue solid was suspended in chloroform (50 mL) and heated at reflux overnight, whereupon

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the blue color changed to yellow. The yellow solid that remained after solvent removal was recrystallized from chloroform–acetone to give 300 mg (67%) of the bis-TCNE adduct **16**: mp 160 °C dec; ^{1}H NMR (250 MHz, acetone-d_6) δ 7.79 (s, 2 H), 6.62 (d, J = 1.9 Hz, 2 H), 6.30 (d, J = 1.9 Hz, 2 H); ^{13}C NMR (20 MHz, acetone-d_6) δ 151.09, 144.90, 133.95, 121.38, 120.30, 120.11, 73.17, 71.20, 61.94, 61.80; IR (KBr) 3010 (m), 2940 (w), 2260 (w), 1500 (w), 810 cm^{-1} (s); mass spectrum, m/e (relative intensity) 190 (100), 158 (4), 145 (14), 128 (57). Anal. Calcd for $C_{22}H_6N_8S_2$: C, 59.18; H, 1.36; N, 25.10; S, 14.36. Found: C, 59.52; H, 1.48; N, 24.82; S, 14.14.

Acknowledgment. We are indebted to the National Institutes of Health (GM 15997) for financial support of this research.

Registry No. **6**, 23062-31-9; **6**·2TCNE, 88703-12-2; **6**·2TCNQ, 88687-09-6; **7**, 63458-32-2; **8**, 88686-98-0; **9**, 88686-99-1; **10**, 88687-00-7; **11**, 88687-01-8; **12**, 88687-02-9; **13**, 88687-03-0; **16**, 88687-04-1; NBS, 128-08-5; TCNE, 670-54-2; TCNQ, 1518-16-7; 4,5-dibromobenzo[1,2-*c*:3,4-*c*']dithiophene, 88687-07-4; dibromoprehnitrene, 36321-73-0; 1,2-dibromo-3,4,5,6-tetrakis(bromomethyl)benzene, 88687-05-2; 1,3,4,5,6-pentabromobenzo[1,2-*c*:3,4-*c*']dithiophene, 88687-08-5; 1,3,6,8-tetrahydro-4,5-dibromobenzo[1,2-*c*:3,4-*c*']dithiophene, 88687-06-3; sodium disulfide, 1313-82-2.

Acid-Catalyzed Cyclization of 3,3',4,4'-Tetrahydro-1,1'-binaphthyl and Single-Crystal X-ray Structure Determination of a Polycyclic Stable Ozonide

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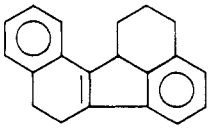
Amberlyst-15 (A-15) catalyzed cyclization of 3,3',4,4'-tetrahydro-1,1'-binaphthyl (**1**) in refluxing toluene during 12 h provided, as the major product, (±)-1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**). Ozonization of **2a** gave a stable ozonide (**3**), mp 159–161 °C. The structure of this ozonide was established by single-crystal X-ray analysis: monoclinic unit cell $P2_1/c$, a = 10.616 (1) Å, b = 9.607 (3) Å, c = 15.052 (4) Å, β = 105.06 (2)°, D_{calcd} 1.372 g cm^{-1}, Z = 4, final agreement factor 6.3%. Prolonged treatment (12–100 h) of **1** or **2a** with A-15 in refluxing toluene yielded a mixture of three 1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthenes (**4a**, **4b**, **4c**) and 1,2,3,12c-tetrahydrobenzo[*j*]fluoranthene (**5**). Hydrocarbon **2a** was readily dehydrogenated in the presence of hot Pd/C to benzo[*j*]fluoranthene (**6**).

Acid-catalyzed cyclization of 3,3',4,4'-tetrahydro-1,1'-binapthyl (**1**, Scheme I) for 12 h using Amberlyst-15 (A-15)[2] in refluxing toluene provided, as the major product, a $C_{20}H_{28}$ olefin which was thought to be 1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**) or 1,2,3,7,8,12c-hexahydrobenzo[*j*]fluoranthene (**2b**).



2b

Since ^{1}H and ^{13}C NMR failed to provide a distinction between **2a** and **2b**, an ozonization was carried out. This ozonolysis did not proceed as expected. Treatment of the olefin **2a** with ozone in dichloromethane until a blue color appeared, followed by addition of dimethyl sulfide[3a] to the reaction mixture, and removal of the solvent afforded a white crystalline solid which melted with decomposition at 150–160 °C. In a separate experiment, treatment of the ozonization reaction mixture with $NaBH_4$ in isopropyl alcohol also gave this unknown compound. Its IR spectrum showed that carbonyl and hydroxyl functions were absent, but, a weak C–O stretching absorbance[3b] was observed at 1250 cm^{-1}. An epoxide group seemed unlikely since the mass spectrum showed fragments at 32 and 306 amu. These data and a C,H elemental analysis are consistent with an ozonide structure. That a stable secondary ozonide had formed was established by single-crystal X-ray crystallographic analysis which showed the unknown compound to be the ozonide **3**.[3c] Therefore, 1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**) is the structure of the initial acid-catalyzed cyclization product.

Table I. Cyclization Products of 1 with A-15 in Refluxing Toluene[a]

	%				
h	4a	4b	4c	1	5
24	9	3	2	76	10
48	27	15	8	5	45
72	31	19	8	2	40
96	30	19	8	2	41

[a] These ratios were determined by GC analysis[5] with the order of emergence from the GC column found to be **4a**, **4b**, **4c**, **1**, and **5**.

Whereas **2a** readily formed from **1** by heating in the presence of A-15 during a 12 h reflux period in toluene, additional reflux caused slow disproportionation of **2a** to

(1) Dobbs, T. K., M.S. Thesis, Oklahoma State University, 1978.
(2) We thank Rohm and Haas Co., Philadelphia, Pennsylvania 19105, for a generous sample of A-15. Literature describing the use and properties of A-15 is available from Rohm and Haas Co.
(3) (a) Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett.* **1966**, 4273. (b) Bailey, P. S. "Ozonization in Organic Chemistry"; Academic Press: New York, 1978, Vol I, p 32. (c) The systematic name for structure **3** is (6a*S*,8a*S*,14a*S*)-5,6,14,14a-tetrahydro-4*H*,13*H*-6a,8a-epoxydinaphtho[1,8-*cd*:2',1'-*f*][1,2]dioxepin. We thank Dr. K. Loening, Chemical Abstracts Services, for kindly supplying this information.

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