The Benzannelated Annulenes. Dibenzo[*d,j*]-6,8-bisdehydrothia[13]-, [15]-, and Dibenzo[*f,l*]-8,10-bisdehydrothia[17]annulene

Jūro Ojima,* Kiyomi Kusaki, Kazuyo Wada, and Yukiko Nakagawa
Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

(Received October 18, 1979)

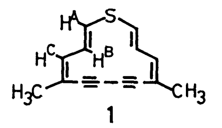
The title compounds have been synthesized by the double Wittig reaction of bis[(triphenylphosphonio)-methyl] sulfide dibromide with *o*-ethynylbenzaldehyde and/or *o*-ethynylcinnamaldehyde, followed by the oxidative coupling. The ^{1}H-NMR spectra of these compounds gave no evidence for a ring current.

Replacement of one of the double bonds of $(4n+2)$ or $(4n)\pi$ electron annulene with a sulfur atom which possesses a lone pair of electrons will lead to the potentially diatropic or paratropic system, respectively.

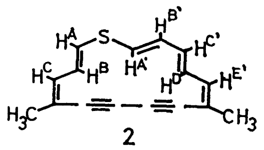
In connection with the studies to confirm the prediction Sondheimer *et al.* have synthesized dimethylbisdehydrothia[13]- **1**,[1a] [15]- **2**,[1b] and [17]annulene **3**[1c] as well as their bis(cyclohexene)-annelated ones[1a,b,d] in which the sulfur atom is flanked by ethylenic bond on both sides.

The method consists in employing a double Wittig condensation of bis[(triphenylphosphonio)methyl] sulfide dibromide **4**[2] with an appropriate aldehyde containing terminal acetylene group, followed an intramolecular oxidative coupling of the resulting acyclic compound.

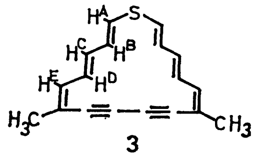
As an extension of our works on benzannelated annulenes,[3] we have now applied with advantage the method to the synthesis of benzannelated bisdehydrothiaannulenes by using *o*-ethynylbenzaldehyde **5**[3a] and/or *o*-ethynylcinnamaldehyde **10**[4] as the starting material and by the essentially same approach as that of Sondheimer *et al.*[1] We now describe the syntheses of the title compounds, *i.e.*, dibenzo[*d,j*]-6,8-bisdehydrothia[13]- **9**, -[15]annulene **14**, and dibenzo[*f,l*]-8,10-bisdehydrothia[17]annulene **12**.



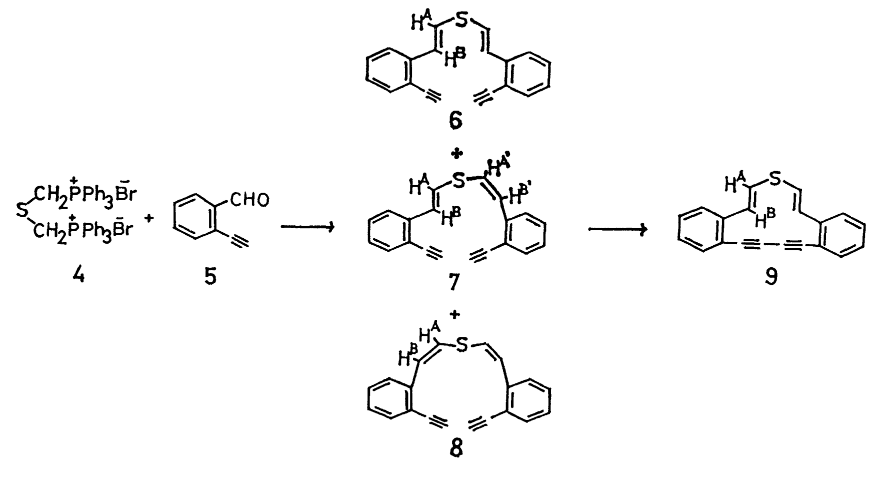
1

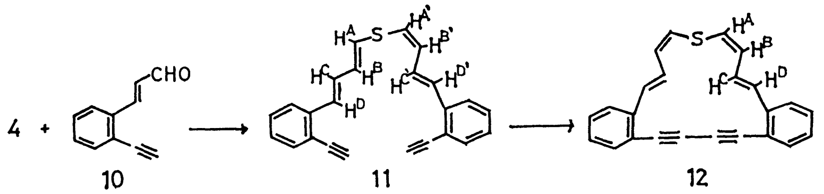


2



3





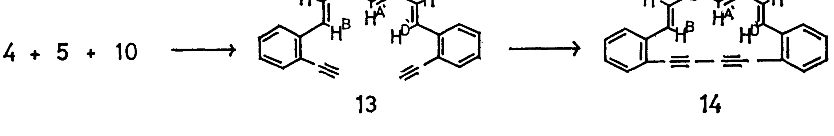


Table 1. The ^{1}H-NMR data of thiaannulenes **1**—**3** at 100 MHz and

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$
1	4.49 d (15)		5.40 dd(15, 9)		2.80 d (9)	
9	3.43 d (16)		3.20 d (16)			
2	(3.55—4.2)	1.09 d (14)	0.79 dd(15, 11)	←—3.55—4.2—→		
14	3.12[a)] d (16)	(2.5—3.0)[a)]	2.28 d (16)	3.35[b)] dd(16, 9)		(2.5—3.0)[b)]
3	4.42 d (15)		4.85 dd(15, 9)		3.09 dd(15, 9)	
12	3.40 d (9)		3.62 dd(9, 9)		(2.3—2.8)	

a, b) These assignments may be reversed in each group.

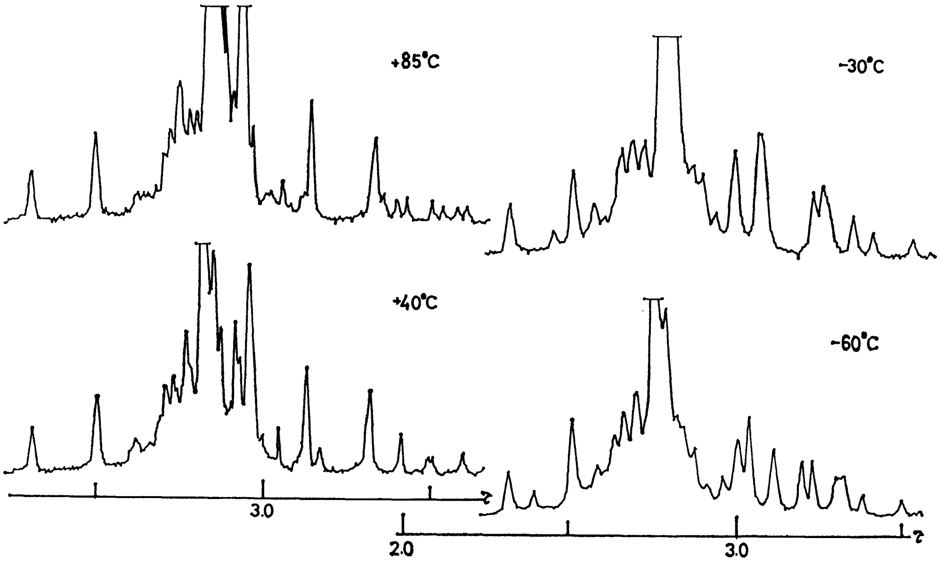


Fig. 1. ^{1}H-NMR FT spectra of **14** in $CDCl_3$ at 80 MHz (Internal Standard, TMS).

The double Wittig reaction of 2 molar equivalents of *o*-ethynylbenzaldehyde **5**[3a)] and 1 molar equivalent of bis[(triphenylphosphonio)methyl] sulfide dibromide **4**[2)] in *N*,*N*-dimethylformamide with ethanolic lithium ethoxide at 80 °C yielded an acyclic stereoisomeric mixture in a good yield, from which *trans-trans* isomer **6** (1%), *cis-trans* isomer **7** (21%), and *cis-cis* isomer **8** (25%) were isolated; only **8** was obtained as crystals. Configuration of each isomer was confirmed by IR and NMR spectra. Oxidative coupling of the mixture of **6**—**8** was carried out with anhydrous copper(II) acetate in pyridine and dry ether at 50 °C as reported by Darby *et al.*[5)] Column chromatography of the product on alumina gave the cyclic compounds, from which we could isolate *trans-trans* isomer **9** as crystals in a 17% yield. Similarly, the reaction of the salt **4** with *o*-ethynylcinnamaldehyde **10**[4)] gave a very unstable stereoisomeric mixture in a 35% yield, from which only mono-*cis* isomer **11** was isolated as bright yellow crystals. Coupling of the unstable mixture as before gave only di-*cis* isomer **12** in a 20% yield, although several isomers were obtained for both dimethyl-**1**[c)] and bis(cyclohexene)-annelated [17]annulene.[1d)] The double Wittig reaction between the salt **4** and each 1 molar equivalent of **5** and **10** was carried out at 70 °C in *N*,*N*-dimethylformamide. Column chromatography of the product afforded the desired acyclic compound of [15]annulene in an 18% yield along with analogues of [13]- and [17]annulenes. We isolated all-*trans* isomer **13** as yellow crystals by further purification. Oxidative coupling of the acyclic mixture containing **13** gave the mixture of the cyclic compounds, from which we could isolate all-*trans* isomer **14** in a 15% yield. The assignment of the structure of these compounds was made on the basis of their spectral properties as well as elemental analyses for the crystalline compounds, and the assigned conformations were given to these compounds in analogy with the dimethylthiaannulenes **1**—**3**, which were shown to have the conformations based on ^{1}H-NMR spectroscopy of the corresponding dideuterio compounds.[1)] The dibenzo[*d,j*]-6,8-bisdehydrothia[13]annulene **9**, -[15]annulene **14**, and dibenzo[*f,l*]-8,10-bisdehydrothia-[17]annulene **12** formed light yellow needles (164 °C (dec)), yellow needles (141 °C (dec)), yellow needles (196 °C (dec)), respectively; all these compounds ap-

9, **12**, **14** AT 90 MHz IN CDCl$_3$ (τ-Values, TMS as an internal standard)

H^D	H$^{D'}$	H^E	H$^{E'}$	CH$_3$	Benzenoid H
				7.71 s	
					2.4—2.8 m
	1.07 dd(14, 14)		(3.55—4.2)	8.39, 8.43 s s	
	(2.5—3.0)[a)]				2.5—3.0 m
5.63 dd(15, 12)		2.81 d (12)		7.78 s	
3.22 d (16)					2.3—2.8 m

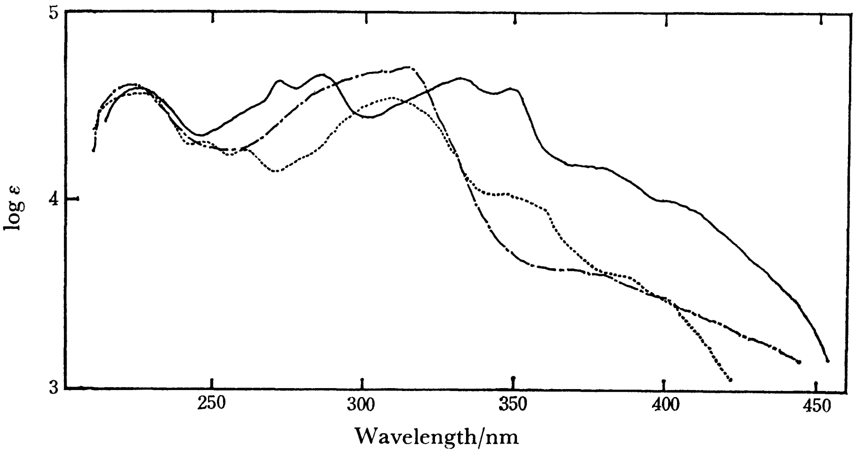


Fig. 2. Electronic spectra of dibenzothiaannulenes **9** (--------), **12**(———), and **14** (—·—·—) in THF.

pear to be considerably stable.

The ^{1}H-NMR spectral data of the protons of **9**, **12**, and **14**, altogether with those of **1**—**3** reported by Sondheimer *et al.*[1] are summarized in Table 1. The individual assignments were made on the basis of the multiplicity, coupling constants, and the data of the closely related compounds.[1] The signals of all olefinic protons could not be located precisely, because the signals due to benzenoid protons were also observed in almost the same region as those of olefinic protons. Comparison of the chemical shifts of the olefinic protons of the dibenzannelated annulene with those of the corresponding dimethylthiaannulene **1**—**3** shows that the dibenzothiaannulenes **9**, **12**, **14** are atropic, reflecting that annelation of two benzene rings eliminate the ring current observed for **1**—**3**. The NMR spectra of [13]- **9** and [17]annulene **12** proved to be temperature-independent in the range of −60 to 60 °C, in contrast to the cases for dimethylthia-[13]- **1** and [17]annulene **3**.[1a,c] On the other hand, the spectra of [15]annulene **14** which are illustrated in Fig. 1, are temperature-dependent, though the dimethylthia[15]annulene **2** being a rigid molecule. As seen from Fig. 1, the signals become more complex from +85 °C to −60 °C, especially in the τ 3.0—3.5 region. The change of the band is not understandable by taking for a rotation about a *trans* double bond. Thus, although this behavior is not understood, similar type of NMR temperature dependence has been observed in the case of the spectra of monodehydro-[14]annulene.[6] However, a possible explanation is the increase of the anisotropic effect of the fused benzene rings on cooling, reflecting that the macrocyclic ring becomes more planar.[7]

The electronic spectra of **9**, **12**, **14** are illustrated in Fig. 2. It is recognized that the electronic spectra of carbocyclic annulenes and dehydroannulenes have been shown to alternate, the main maxima of $(4n+2)\pi$-electron systems being at higher wavelength than those of $4n$ systems.[8] However, this trend is not exhibited for the electronic spectra of these benzothiaannulene series, reflecting that the compounds **9**, **12**, **14** are atropic.

Experimental

All melting points are uncorrected. Brockmann Alumina (Act. II—III) wasused for column chromatography. The IR spectra were measured on a Hitachi EPI-S2 spectrophotometer. The UV spectra were taken on a Hitachi 124 spectrophotometer and refer to tetrahydrofuran solution. Shoulders in UV spectra are indicated by sh. The NMR measurements were made with a Varian EM-390, a Hitachi R-900 at 90 MHz or a Varian FT-80A spectrometer at 80 MHz in $CDCl_3$ using tetramethylsilane as an internal standard and recorded in τ-values. The mass spectra were obtained on a JEOL JMS-OI-SG-2 or JEOL JMS-D 100 spectrometer at 75 eV using direct insertion technique. Evaporation of solvents was carried out at water aspirator pressure.

*Bis[2-(*o*-ethynylphenyl)vinyl] Sulfides **6**, **7**, and **8**.* Lithium ethoxide prepared from lithium (0.33 g, 0.047 gatm) in ethanol (112 ml) was added dropwise with stirring under nitrogen atmosphere at 80—86 °C over a period of 1.5 h to a mixture of *o*-ethynylbenzaldehyde **5**[3a] (5.8 g, 0.045 mol) and bis[(triphenylphosphonio)methyl] sulfide dibromide **4**[2] (13.2 g, 0.0177 mol) in *N*,*N*-dimethylformamide (446 ml). After further 2 h of stirring at the same temperature, the mixture was then poured into water (500 ml) and extracted thoroughly with benzene. The extracts were washed with dilute hydrochloric acid, aq sodium hydrogencarbonate and saturated sodium chloride solution successively, dried over sodium sulfate, and evaporated to give a dark brown semisolid. Chromatography over a column of alumina (160 g) with hexane-ether (95:5—85:15) as eluent gave a mixture of acyclic compound. The mixture was again taken up in ether and absorbed on alumina (120 g). Careful elution with hexane-ether (98:2) resulted in separation of three isomers. Early eluents gave *trans-trans* isomer **6** (0.05 g, 1.0%) as a light yellow liquid, MS: *m/e* 286 (M^+, 100); mol wt, 286.3; IR (neat): 3300 (-C≡CH), 2100 (-C≡C-), 1585 (C=C), 960, 950 cm^{-1} (*trans* C=C); UV: λ_{max}225 (35100), 252 (25400), 337 nm (27300); NMR: *ca.* 2.4—2.9 (m, 10H, H^B and benzenoid H), 3.00 (d, $J=16$, 2H, H^A), 6.65 (s, 2H, -C≡CH). The following eluents gave *cis-trans* isomer **7** (1.05 g, 21%) as a light yellow liquid, MS: *m/e* 286 (M^+, 100); mol wt, 286.3; IR (neat): 3300 (-C≡CH), 2100 (-C≡C-), 1597 (C=C), 960, 945 (*trans* C=C), 712, 704 cm^{-1} (*cis* C=C); UV: λ_{max} 226 (37200), 250 (26200), 332 nm (31700); NMR: *ca.* 2.2—3.0 (m, 10H, H^B, $H^{B'}$, and benzenoid H), 3.10 (d, $J=16$, 1H, H^A), 3.42 (d, $J=11$, 1H, $H^{A'}$), 6.66 (s, 1H, -C≡CH), 6.67 (s, 1H, -C≡CH). The last eluents gave *cis-cis* isomer **8** (1.27 g, 25%) as solid, which was recrystallized from hexane-benzene to give colorless needles, mp 86—88 °C, MS: *m/e* 286 (M^+, 100); mol wt, 286.3; IR (KBr): 3300 (-C≡CH), 2100 (-C≡C-), 1590 (C=C), 706 cm^{-1} (*cis* C=C); UV: λ_{max}227 (27500), 248 sh (19600), 326 nm (21300); NMR: 2.2—2.9 (m, 8H, benzenoid H), 2.93 (d, $J=11$, 2H, H^B), 3.47 (d, $J=11$, 2H, H^A), 6.65 (s, 2H, -C≡CH).

Found: C, 84.01; H, 4.95%. Calcd for $C_{20}H_{14}S$: C, 83.88; H, 4.93%.

Dibenzo[d, j]*-6,8-bisdehydrothia*[*13*]*annulene* ***9***. A solution of a mixture of **6**, **7**, and **8** (2.37 g, 8.3 mmol) in pyridine (141 ml) and dry ether (47 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (10.6 g) in pyridine (303 ml) and dry ether (101 ml) during 2 h at 45—50 °C and the reaction mixture was stirred for further 1.5 h at the same temperature. After cooling, the mixture was diluted with benzene (500 ml) and filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (50 ml × 2). The filtrate was then poured into 7% hydrochloric acid (1000 ml), and the aq layer was further extracted with benzene. The combined organic layer was washed with 7% hydrochloric acid, water, aq sodium hydrogencarbonate, saturated sodium chloride solution successively, and dried over sodium sulfate. A dark brown liquid obtained by solvent removal was chromatographed on alumina (120 g) with hexane as eluent. Early fractions gave a very unstable liquid which was turned to brownish amorphous on dryness and exposed to air. The following fractions gave *trans-trans* isomer **9** (0.045 g, 17%) as relatively stable crystals. Recrystallization from hexane-benzene afforded light yellow needles, mp 164 °C (dec); MS: *m/e* 284 (M^+, 100); mol wt, 284.3; IR (KBr): 2200 (-C≡C-), 1595 (C=C), 940 cm^{-1} (*trans* C=C); UV: λ_{max} 218 (40900), 227 sh (38300), 247 (19400), 261 (17900), 308 (34500), 346 (10600), 360 sh (8700), 388 sh nm (3100); NMR: see Table 1.

Found: C, 84.60; H, 4.26%. Calcd for $C_{20}H_{12}S$: C, 84.47; H, 4.25%.

*Bis[4-(*o*-ethynylphenyl)-1,3-butadienyl] Sulfide **11**.* Lithium ethoxide prepared from lithium (0.32 g, 0.046 gatm) in ethanol (106 ml) was added dropwise with stirring under nitrogen atmosphere at 70—75 °C during 2 h to a mixture of *o*-ethynylcinnamaldehyde **10**[4] (6.3 g, 0.040 mol) and the salt **4** (13.5 g, 0.018 mol) in *N*,*N*-dimethylformamide (422 ml). The reaction mixture was stirred for further 1.5 h under an atmosphere of nitrogen at the same temperature. After work up as described for the isolation of **8**, a dark red semisolid obtained was chromatographed on alumina (160 g). The fractions eluted with hexane-ether (98:2—96:4) gave the stereoisomeric mixture of acyclic compound as very unstable liquid (2.14 g, 35%). After the liquid was passed through a short column of alumina (30 g) with hexane-ether, the crystals (1.50 g, 25%) obtained was recrystallized from hexane-ether, giving mono-*cis* isomer **11** as light yellow needles, mp 134—136 °C, MS: *m/e* 338 (M^+, 100); mol wt, 338.4; IR (KBr): 3280 (-C≡CH), 2150 (-C≡C-), 1680, 1623 (C=C), 970 (*trans* C=C), 710, 700 cm^{-1} (*cis* C=C); UV: λ_{max} 233 (27500), 258 sh (20200), 267 (21500), 283 (19400), 365 nm (31100); NMR: 2.2—2.8 (m, 12H, H^C, $H^{C'}$, H^D, $H^{D'}$, and benzenoid H), 3.40—3.78 (m, 4H, H^A, $H^{A'}$, H^B, and $H^{B'}$), 6.60 (s, 2H, -C≡CH).

Found: C, 85.39; H, 5.08%. Calcd for $C_{24}H_{18}S$: C, 85.17; H, 5.36%.

Dibenzo[f,l]*-8,10-bisdehydrothia*[*17*]*annulene* ***12***. A solution of the isomeric mixture containing **11** (0.57 g, 16.8 mmol) in pyridine (30 ml) and dry ether (10 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (2.17 g) in pyridine (64 ml) and dry ether (21 ml) for 1.5 h at 50—55 °C and the reaction mixture was stirred for further 1 h at the same temperature. After work up as described for the isolation of **9**, a dark red brown liquid obtained was chromatographed on alumina (130 g). The fractions eluted with hexane-ether (97:3) gave di-*cis* isomer **12** (111 mg, 20%) as solid. Recrystallization from hexane-ether afforded pure **12** as yellow needles, mp 196 °C (dec), MS: *m/e* 336 (M^+, 100); mol wt, 336.4; IR (KBr): 2235, 2185 (-C≡C-), 1620 (C=C), 965 (*trans* C=C), 700, 680 cm^{-1} (*cis* C=C); UV: λ_{max} 226 (38300), 272 (41200), 286 (46300), 332 (44200), 348 (39400), 375 sh (16100), 404 sh nm (9720); NMR: see Table 1.

Found: C, 85.50; H, 4.51%. Calcd for $C_{24}H_{16}S$: C, 85.68; H, 4.79%.

*2-(*o*-Ethynylphenyl)vinyl 4-(*o*-Ethynylphenyl)-1,3-butadienyl Sulfide **13**.* Lithium ethoxide prepared from lithium (0.19 g, 0.027 gatm) in ethanol (46 ml) was added dropwise with stirring under nitrogen atmosphere at 69—71 °C over a period of 1 h to a mixture of *o*-ethynylbenzaldehyde **5** (1.39 g, 0.011 mol), *o*-ethynylcinnamaldehyde **10** (1.67 g, 0.011 mol), and the salt **4** (7.93 g, 0.011 mol) in *N*,*N*-dimethylformamide (249 ml). After further 2 h of stirring at the same temperature under nitrogen atmosphere, the mixture was poured into water (500 ml). After work up as described for the isolation of **8**, a dark brown semisolid was passed through a short column of alumina (40 g) with hexane-ether to remove polymeric products. A dark red liquid obtained by evaporation of solvents was cautiously chromatographed on alumina (140 g) with hexane-ether (96:4). The early eluents gave a mixture of acyclic compound of [13]annulene (0.941 g). The following eluents afforded an unstable red liquid of a mixture of acyclic compound of the desired [15]annulene (0.609 g, 18%). The last fractions gave a mixture of acyclic compound of [17]annulene (0.171 g). The unstable red liquid of the acyclic mixture of [15]-annulene was passed through a short column of alumina (30 g). The eluents with hexane gave solid (0.203 g, 6.0%) which was recrystallized from hexane–ether to afford all-*trans* isomer **13** as light yellow needles, mp 117—118 °C, MS: *m/e* 312 (M^+, 100); mol wt, 312.4; IR (KBr): 3300 (-C≡CH), 2180 (-C≡C-), 1620, 1590, 1585 (C=C), 965 cm^{-1} (*trans* C=C); UV: λ_{max} 227 (33900), 237 sh (29300), 255 (25300), 290 (14100), 349 nm (33100); NMR: 2.17—3.03 (m, 11H, H^B, $H^{B'}$ or $H^{C'}$, $H^{D'}$, and benzenoid H), 3.49 (d, $J=14$, 1H, H^A or $H^{A'}$), 3.60 (d, $J=14$, H^A or $H^{A'}$), 3.65 (dd, $J=14$, 10, 1H, $H^{B'}$ or $H^{C'}$), 6.65 (s, 2H, -C≡CH).

Found: C, 84.31; H, 4.92%. Calcd for $C_{22}H_{16}S$: C, 84.57; H, 5.16%.

Dibenzo[d, j]*-6,8-bisdehydrothia*[*15*]*annulene 14.* A solution of the acyclic mixture containing **13** (1.92 g, 6.15 mmol) in pyridine (106 ml) and dry ether (35 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (7.84 g) in pyridine (231 ml) and dry ether (77 ml) during 2 h at 46—50 °C. The mixture was stirred at the same temperature for further 2 h. After work up as in the isolation of **9**, the red liquid obtained was chromatographed on alumina (100 g). The all-*trans* isomer **14** (0.41 g, 21%) was obtained from fractions eluted with hexane–ether (98:2) as solid. Recrystallization from hexane–ether gave pure **14** as yellow needles, mp 141 °C (dec); MS: *m/e* 310 (M^+, 64%), 309 (100); mol wt, 310.4, IR (KBr): 2180 (-C≡C-), 1630, 1600, 1590 (C=C), 985 cm^{-1} (*trans* C=C); UV: λ_{max} 222 (40400), 283 sh (37000), 300 sh (46100), 313 (49800), 375 sh (4020); NMR: see Table 1.

Found: C, 84.83; H, 4.34%. Calcd for $C_{22}H_{14}S$: C, 85.12; H, 4.55%.

The authors wish to thank Professor F. Sondheimer and Dr. J. E. Anderson, University College London, for helpful suggestions and Dr. Akio Yasuhara, National Institute for Environmental Studies, for measurement of the mass spectra. One of the authors (J. O.) is grateful to the Ministry of Education for financial support of this investigation through a Grant-in-Aid (054103, 1975) for Scientific Research.

References

1) a) R. L. Wife and F. Sondheimer, *J. Am. Chem. Soc.*, **97**, 640 (1975); b) R. L. Wife, P. J. Beeby, and F. Sondheimer, *ibid.*, **97**, 641 (1975); c) R. L. Wife and F. Sondheimer, *Tetrahedron Lett.*, **1975**, 195; d) R. H. McGirk and F. Sondheimer, *Angew. Chem.*, **84**, 897 (1972).

2) K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

3) a) J. Ojima, T. Yokomachi, and A. Kimura, *Bull. Chem. Soc. Jpn.*, **49**, 2840 (1976); b) J. Ojima, A. Kimura, and M. Ikeguchi, *ibid.*, **49**, 3709 (1976); c) J. Ojima, M. Enkaku, and C. Uwai, *ibid.*, **50**, 933 (1977).

4) J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, *Bull. Chem. Soc. Jpn.*, **48**, 367 (1975).

5) a) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, **42**, 1960 (1977); b) J. Ojima, Y. Shiroishi, and M. Fujiyoshi, *Bull. Chem. Soc. Jpn.*, **51**, 2112 (1978).

6) F. Sondheimer *et al.*, Special Publications No. 21, The Chemical Society, **1967**, p. 83.

7) The authors are deeply indebted to Prof. Sondheimer for this suggestions and pointing out Ref. 6.

8) P. J. Garratt and K. Grohmann, "Houben-Weyl, Methoden der Organischen Chemie," Geog Thieme Verlag, Stuttgart (1972), Vol. V, Part 1d, p. 533.