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Synthesis of 1,1′-, 2,2′-, 1,2′-, and 2,6′-Biazulenes and Their Derivatives by Ullmann Reaction[1)]

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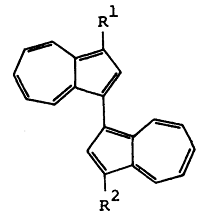
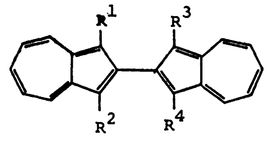
Four kinds of biazulenes, 1,1′- (**1a**), 2,2′- (**2a**), 1,2′- (**3a**), and 2,6′-biazulenes (**4a**), and their derivatives were synthesized by utilizing Ullmann-type coupling of haloazulene derivatives. Ullmann reaction of ethyl 3-iodo- (**5a**) and 2-iodoazulene-1-carboxylates (**6b**) gave diethyl 1,1′-biazulene-3,3′-dicarboxylate (**1b**) and diethyl 2,2′-biazulene-1,1′-dicarboxylate (**2b**), respectively, in excellent yields. The reaction of 2-iodoazulene gave **2a** directly. Diethyl 2-chloroazulene-1,3-dicarboxylate (**7a**) and its 5-alkyl derivatives also reacted to give tetraethyl 2,2′-biazulene-1,1′,3,3′-tetracarboxylate (**2d**) and its 5,5′-dialkyl derivatives, respectively. A mixed Ullmann reaction of **5a** and **6b** afforded a mixture of **1b**, **2b**, and diethyl 1,2′-biazulene-1′,3-dicarboxylate (**3b**). Similarly, a mixed Ullmann reaction of **7a** and diethyl 6-iodoazulene-1,3-dicarboxylate gave a mixture of **2d** and tetraethyl 2,6′-biazulene-1,1′,3,3′-tetracarboxylate (**4b**). The parent hydrocarbons of biazulenes, **1a**, **2a**, **3a**, and **4a**, could be derived from the corresponding ethoxycarbonyl derivatives, **1b**, **2b**, **2d**, **3b**, and **4b**, respectively, by decarboxylation. The planarity of biazulenes and their ester derivatives is also discussed on the basis of the spectral data.

Although benzenoid biaryls, such as biphenyls and binaphthalenes, have been known for a long time and studied extensively from the chemical and physical points of view, no biazulene, one of the non-benzenoid biaryls, had been known until Hagen *et al.*[2)] reported the photochemical synthesis of 2,2′- and 3,3′-biguaiazulenes. A number of positional isomers are possible for biazulenes. Recently, 4,4′-,[3)] 5,5′-,[4)] and 6,6′-biazulenes[5)] have been synthesized. The Ullmann-type biaryl coupling of aryl halides using copper at elevated temperature has been utilized for the synthesis of benzenoid biaryls. This reaction was applied on some haloazulene derivatives for synthesis of 1,1′- (**1a**), 2,2′- (**2a**), 1,2′- (**3a**), and 2,6′-biazulenes (**4a**), and their derivatives.



1a: $R^1=R^2=H$
1b: $R^1=R^2=CO_2C_2H_5$
1c: $R^1=R^2=CO_2H$
1d: $R^1=CO_2C_2H_5$; $R^2=H$
1e: $R^1=R^2=CO_2CH_3$
1f: $R^1=R^2=D$
1g: $R^1=R^2=Br$



2a: $R^1=R^2=R^3=R^4=H$
2b: $R^1=R^3=CO_2C_2H_5$; $R^2=R^4=H$
2c: $R^1=R^3=CHO$; $R^2=R^4=H$
2d: $R^1=R^2=R^3=R^4=CO_2C_2H_5$
2e: $R^1=R^3=CO_2H$; $R^2=R^4=H$
2f: $R^1=R^2=R^3=R^4=CO_2H$
2g: $R^1=R^3=CO_2C_2H_5$; $R^2=R^4=Br$
2h: $R^1=R^3=CO_2C_2H_5$; $R^2=R^4=I$
2i: $R^1=R^3=CO_2CH_3$; $R^2=R^4=Br$
2j: $R^1,R^3=R^2,R^4=$ -COOCO-
2k: $R^1=CO_2C_2H_5$; $R^2=R^3=R^4=H$
2m: $R^1=R^2=CO_2C_2H_5$; $R^3=R^4=H$

Chart 1.

Results and Discussion

A mixture of haloazulene and activated copper[6)] was heated at about 200—220 °C in an evacuated sealed tube and then the products were isolated. The results are listed in Table 1.

1,1′-Biazulene. Ethyl 3-chloro- and 3-bromoazulene-1-carboxylates[7a)] did not react at 220 °C, but changed into an unidentified black resinous substance at 250 °C. On the other hand, ethyl 3-iodoazulene-1-carboxylate (**5a**)[7a)] easily reacted at 220 °C to give diethyl 1,1′-biazulene-3,3′-dicarboxylate (**1b**), accompanied by a small amount of dehalogenated[8)] ethyl azulene-1-carboxylate (**5b**).[9)]

The complete hydrolysis of **1b** with alkali, and the subsequent decarboxylation of the resulting dicarboxylic acid (**1c**) upon heating gave the parent hydrocarbon, **1a**, in 55% yield. The mass spectrum of **1a** shows a molecular ion peak at m/e 254. A partial hydrolysis of **1b** with alkali, followed by decarboxylation afforded ethyl 1,1′-biazulene-3-carboxylate (**1d**) as a major product. Methylation of **1c** with diazomethane yielded a dimethyl ester (**1e**). Deuteration[10)] of **1a** with D_3PO_4 gave 1,1′-biazulene-3,3′-d_2 (**1f**) and bromination of **1a** with NBS gave an expected 3,3′-dibromo derivative (**1g**).

2, 2′-Biazulene. 2-Iodoazulene (**6a**)[7c)] and ethyl 2-iodoazulene-1-carboxylate (**6b**)[7b)] when heated with activated copper, reacted to give 2,2′-biazulene (**2a**) and diethyl 2,2′-biazulene-1,1′-dicarboxylate (**2b**), accompanied by small amounts of azulene and **5b**, respectively. 2-Iodoazulene-1-carboxaldehyde (**6c**), derived from **6a**, also reacted to give 2,2′-biazulene-1,1′-dicarboxaldehyde (**2c**). 2-Chloroazulene and ethyl 2-chloroazulene-1-carboxylate[7c)] did not react at 220—240 °C. However, diethyl 2-chloroazulene-1,3-dicarboxylate (**7a**),[7b,7c)] in which two electron-withdrawing ethoxycarbonyl substituents will activate the halogen, easily reacted to give tetraethyl 2,2′-biazulene-1,1′,3,3′-tetracarboxylate (**2d**) in an excellent yield, accompanied by a small amount of dehalogenated diethyl azulene-1,3-dicarboxylate (**7d**).[9)] Similarly, 5-methyl (**7b**)[7b)] and 5-isopropyl derivatives (**7c**)[7b)] also yielded tetraethyl 5,5′-dimethyl- (**8a**) and 5,5′-diisopropyl-2,2′-biazulene-1,1′,3,3′-tetracarboxylate (**8b**), respectively, along with the dehalogenated azulenes (**7e** and **7f**), although some of the starting haloazulenes were recovered unchanged. Besides the direct formation from **6a**, the parant hydrocarbon, **2a**, was derived from **2b** and **2d** by deethoxy-

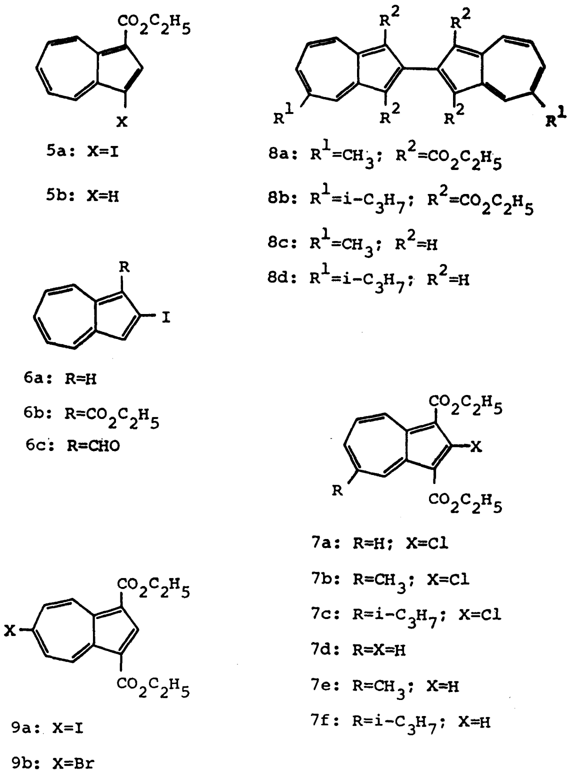


Chart 2.

Table 1. The Ullmann-type coupling of haloazulenes into biazulenes

Haloazulene	Temp °C	Time h	Products (yield/%) Biazulenes	Others
5a	200	5	**1b** (83)	**5b**(8)
6a	180	6	**2a** (54)	Azulene(trace)
6b	220	6.5	**2b** (82)	**5b**(trace)
6c	220	4.5	**2c** (40)	
7a	220	9	**2d** (83)	**7d**(6)
7b	220	6.5	**8a** (53)	**7e** (7)
7c	235	6	**8b** (11)	**7f** (trace)
5a+**6b**	200	5.5	**1b** (28) **2b** (27) **3b** (22)	**5b**(18)
7a+**9a**	245	6	**2d** (21) **4b** (7)	**7d**(28)

carbonylation. Thus, alkaline hydrolysis of **2b** and **2d** and the subsequent decarboxylation of the resulting di- (**2e**) and tetracarboxylic acids (**2f**) upon heating gave **2a**. Conveniently, **2a** could be obtained directly from **2b** and **2d** by deethoxycarbonylation upon heating with 100% phosphoric acid[7a,7b,11] in excellent yields. Similar treatment of **8a** and **8b** gave 5,5′-dimethyl (**8c**) and 5,5′-diisopropyl-2,2′-biazulenes (**8d**), respectively. The mass spectrum of **2a** shows a molecular ion peak at *m/e* 254.

Vilsmeier reaction of **2a** gave a diformyl derivative which is identical with **2c**. Halogenation of the diester, **2b**, with **NBS** or **NIS** gave diethyl 3,3′-dibromo- (**2g**) or 3,3′-diiodo-2,2′-biazulene-1,1′-dicarboxylates (**2h**). Dimethyl 3,3′-dibromo-2,2′-biazulene-1,1′-dicarboxylate (**2i**) was derived from **2g** by alkaline hydrolysis, followed by methylation. When treated with acetic anhydride, the tetracarboxylic acid, **2f**, yielded a dianhydride (**2j**), whose ethanolysis with sodium ethoxide followed by decarboxylation upon heating afforded a mixture of **2a**, **2b**, ethyl 2,2′-biazulene-1-carboxylate (**2k**), and diethyl 2,2′-biazulene-1,3-dicarboxylate (**2m**).

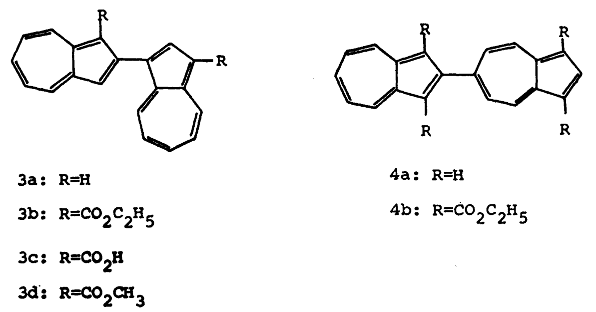


Chart 3.

1,2′-Biazulene. A mixed Ullmann reaction of **5a** and **6b** afforded a mixture of **1b**, **2b**, and diethyl 1,2′-biazulene-1′,3-dicarboxylate (**3b**). The parent hydrocarbon, **3a**, was obtained from **3b** upon alkaline hydrolysis followed by decarboxylation of the resulting dicarboxylic acid (**3c**). Its mass spectrum shows a molecular ion peak at *m/e* 254. Dimethyl 1,2′-biazulene-1′,3-dicarboxylate (**3d**) was derived from **3c** by methylation.

2,6′-Biazulene. A mixed Ullmann reaction of **7a** and diethyl 6-iodoazulene-1,3-dicarboxylate (**9a**) prepared from 6-bromo compound (**9b**)[12] gave a mixture of **2d** and tetraethyl 2,6′-biazulene-1,1′,3,3′-tetracarboxylate (**4b**). The expected 6,6′-biazulene could not be obtained. The parent hydrocarbon, **4a**, was obtained by deethoxycarbonylation of **4b** upon heating with 100% phosphoric acid.

The structures of biazulenes and their derivatives obtained here were confirmed on the basis of the spectral data described below, as well as the above-mentioned chemical evidence.

Infrared Spectra of Biazulenes. The C=O stretching vibrations in the ester derivatives of biazulenes are listed in Table 2. Even for the sterically crowded biazulene derivatives, **2b**, **2d**, **4b**, **8a**, and **8b**, these bands appear in the region comparable to those of the

Table 2. Carbonyl stretching vibration of ethoxycarbonyl group of azulene and biazulenes

Compound	ν/cm^{-1} $CHCl_3$[a)]	KBr
1b	1684sh 1680	1684
2b	1682sh 1678	1684
2d	1684sh 1678	1684
3b	1684sh 1678	1689 1684
4b		1684
8a	1683sh 1672	1685
8b	1684sh 1673	1684
5b	1683sh 1678	
7d	1686sh 1681	1684

a) sh: Shoulder.

TABLE 3. LONG-WAVE ABSORPTION (BAND A) OF BIAZULENES AND RELATED AZULENES λ/nm (log ε)

Compound	Solvent$^{a)}$	Band A$^{b)}$		
1a	iso	612(2.80)		
1d	cyc	589(2.50)		
1b	iso	575(2.33)		
2a	chl	694(2.43) 554(2.97)	635(2.91)	592(3.06)
8c	chl	650(2.61)	608(2.75)	564(2.67)
8d	iso	712(2.50) 565(2.95)	640(2.95)	603(3.04)
2k	cyc	644(2.91)	593(3.14)	554(3.10)
2b	iso	640(2.59)	586(2.99)	552(3.01)
2m	chl	627(2.66)$^{\text{sh}}$	545(2.95)	510(2.89)$^{\text{sh}}$
2d	cyc	597(2.53)	547(2.97)	513(3.02)
8a	iso	610(2.51)	550(2.98)	521(3.03)
8b	iso	600(2.67)	548(3.10)	518(3.12)
3a	iso	614(2.94)	579(2.96)	
3b	iso	564(2.89)	540(2.89)	
4a	chl	595(2.95)		
4b	chl	585(2.56)	530(3.04)	504(3.08)
Azulene	cyc	693(2.24)	663(2.22)	633(2.54)
		604(2.51)	580(2.56)	557(2.40)
		540(2.37)	522(2.23)	
5b	iso	644(2.23)	587(2.60)	545(2.65)
7d	cyc	601(2.21)	551(2.68)	514(2.74)

a) iso: Isooctane; cyc: cyclohexane; chl: chloroform. b) sh: Shoulder.

conjugated esters in azulene derivatives. This suggests that, in these compounds, the ester groups are favorably in the same plane with the azulene ring and, consequently, the two azulene rings in **2b**, **2d**, **4b**, **8a**, and **8b** are not coplanar.

Electronic Spectra of Biazulenes. Biazulenes show four main electronic absorption bands (A, B, C, and D) in analogy with azulene (shown in Tables 3 and 4). As shown in Figs. 1 and 2, in the spectra of the parent biazulenes, **1a**, **2a**, **3a**, and **4a**, the bands (B, C, and D) in the ultraviolet region show large red shifts with increasing intensities compared with those of azulene, while the visible absorptions (A) exhibit increases in intensities accompanied by loss of the fine structures that appeared in the spectrum of azulene. It is known[13] that the substitution of alkoxycarbonyl groups at C-1 and/or C-3 of azulenes results in blue shift of the band (A) and in red shift of the bands (B and C). The substitution of ethoxycarbonyl groups at C-3 (and C-3′) of 1,1′-biazulene causes blue shifts while decreasing the intensity of band (A), but no appreciable effect on band (B). The substitution of ethoxycarbonyl groups at C-1′, 3 of 1,2′-biazulene results in blue shifts of the bands (A and B).

In the case of 2,2′-biazulene, the substitution of ethoxycarbonyl groups at C-1, 1′ (and C-3, 3′) results in blue shifts of the bands (A and B). Especially the spectra of tetraesters, **2d**, **8a**, and **8b**, are similar to those of diethyl azulene-1,3-dicarboxylates, **7d**, **7e**, and

TABLE 4. THE ULTRAVIOLET ABSORPTION SPECTRA OF BIAZULENES AND RELATED AZULENES λ/nm (log ε)

Compound	Solvent$^{a)}$	Band B		Band C$^{b)}$		Band D$^{b)}$
1a	meth	384(4.19)		308(4.58)	300(4.54)$^{\text{sh}}$	263(4 73) 245(4.51)
1d	meth	375(4.07)		300(4.68)	287(4.72)	260(4.55) 238(4.53)
1b	meth	382(4.14)		304(4.71)	279(4.82)	239(4.60)
2a	chl	436(4.76)	410(4.45) 390(4.22)$^{\text{sh}}$	328(4.82)	316(4.84)	250(4.30)
8c	meth	438(4.82)	414(4.63)	332(4.95)	324(4.91)	256(4.38)
8d	meth	434(4.82)	409(4.61)	329(4.99)	317(4.98)	248(4.40)
2k	chl	433(4.45)	411(4.43)	317(4.96)	276(4.14)$^{\text{e}}$	246(4.47)
2b	meth	410(4.08)		320(5.00)		245(4.65)$^{\text{sh}}$
2m	chl	435(3.80)$^{\text{sh}}$	396(4.28)	305(5.13)	270(4.64)$^{\text{e}}$	237(4 82)
2d	meth	377(4.18)	348(4.37)	315(5.10)	303(4.85) 275(4.66)$^{\text{e}}$	238(4.80)
8a	meth	379(4.30)	345(4.41)	317(5.09)	279(4.66)$^{\text{e}}$	242(4.78)
8b	meth	380(4.25)	350(4.35)	319(5.02)	282(4.57)$^{\text{e}}$	245(4.67)
3a	meth	461(4.27)	441(4.26)	311(4.64)	264(4.54)	232(4.37)
3b	meth	425(4.09)		343(4.40)$^{\text{sh}}$ 289(4.71)	307(4.69)	235(4.55)
4a	chl	448(4.01)$^{\text{sh}}$ 410(4.55)	418(4.55)	338(4.60)	317(5.01)	258(4.27)$^{\text{sh}}$
4b	meth	377(4.44)		348(4.54)	317(4.95) 273(4.62)$^{\text{e}}$	236(4.78)
Azulene	cyc	353(3.14) 337(3.63) 322(3.47)	341(3.71) 326(3.54)	280(4.72) 271(4.73)	275(4.74)	238(4.24)
5b	cyc	370(3.88)	354(3.78)	299(4.60)	290(4.55)$^{\text{sh}}$	234(4.26)
7d	cyc	371(4.14)		302(4.69)	291(4.60)$^{\text{sh}}$ 272(4.53)$^{\text{e}}$	234(4.63)

a) meth: Methanol; iso: isooctane; chl: chloroform; cyc: cyclohexane. b) e: A characteritic band in 1,3-bis(ethoxycarbonyl)azulenes and their derivatives; sh: shoulder.

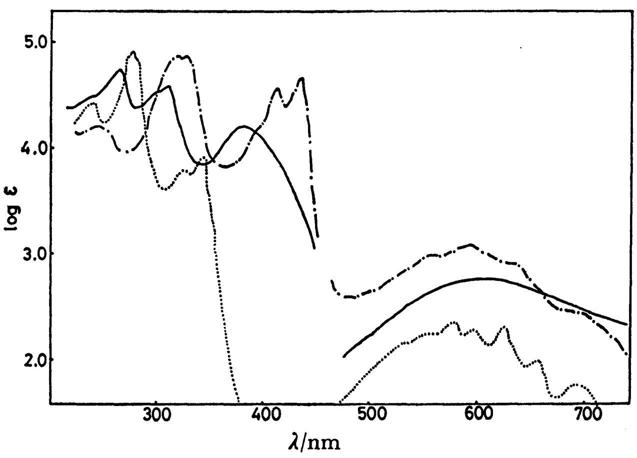


Fig. 1. Electronic Spevtra of **1a** (—— in methanol for UV, isooctane for visible region), **2a** (—•— in chloroform), and azulene (…… in cyclohexane).

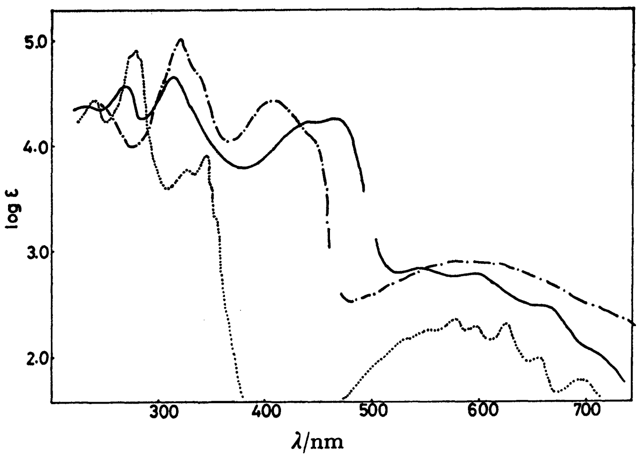


Fig. 2. Electronic Spectra of **3a** (—— in methanol for UV, isooctane for visible region), **4a** (—•— in chloroform), and azulene (…… in cyclohexane).

7f, but the molar absorption coefficients being approximately doubled. This observation suggests that the two azulene rings in **2d**, **8a**, and **8b** are twisted around the 2,2′-bond.

The NMR Spectra of Biazulenes. The NMR spectra data of biazulenes and chemical shift differences (Δδ) between biazulenes and the reference compounds are listed in Tables 5 and 6. A study using a Dreiding model of 1,1′-biazulene shows that the steric interactions for H-2···H-8′, H-2′···H-8, and H-8···H-8′ are significant and sugests that the two azulene ring are not coplanar with each other. In fact, in the NMR spectral data of 1,1′-biazulenes, **1a**, **1b**, and **1d**, it is observed that there is no large chemical shift deference (Δδ) between the ring protons in **1a** and those in azulene, and between the ethyl protons in esters, **1b** and **1d**, and

TABLE 5. NMR SPECTRAL DATA OF BIAZULENES (AT 60 MHz, IN $CDCl_3$, CHEMICAL SHIFTS[a,b] IN δ FROM TMS, COUPLING CONSTANTS IN J/Hz)[g]

Compound	H-1 H-1′	H-2 H-2′	H-3 H-3′	H-4 H-4′	H-5 H-5′	H-6 H-6′	H-7 H-7′	H-8 H-8′	Coupling constants	OCH_2–CH_3 (J=7.0) Others
1a[c]		8.06^{d}	7.48^{d}	8.30^{d}	7.06^{t}	7.51^{t}	6.96^{t}	8.30^{d}	$J_{2,3}=3.9$ $J_{4,5}=J_{5,6}=J_{7,8}=9.5$	
1d		8.50^{s}		9.60^{d}	6.87	—	7.87^{m}	8.38^{d}	$J_{4,5}=J_{7,8}=9.5$ $J_{4',5'}=J_{7',8'}=9.5$ $J_{2',3'}=4.0$	4.41^{q} 1.43^{t}
		8.01^{d}	7.53^{d}	8.32^{d}				8.24^{d}		
1b		8.52^{s}		9.73^{d}	7.10	—	7.95^{m}	8.40^{d}	$J_{4,5}=J_{7,8}=9.5$	4.46^{q} 1.45^{t}
2a[d]	7.86^{s}		7.86^{s}	8.28^{d}	7.13^{t}	7.50^{t}	7.13^{t}	8.28^{d}	$J_{4,5}=J_{5,6}=9.5$	
8c	7.68^{s}		7.68^{s}	$8.17^{br\ s}$		7.37^{d}	6.97^{t}	8.13^{d}	$J_{4,6}<1$ $J_{6,7}=J_{7,8}=10$	$2.63^{s}(CH_3)$
8d[e]	7.60^{s}		7.60^{s}	8.09^{d}		7.28^{d}	6.93^{t}	8.03^{dd}	$J_{4,6}=J_{6,8}=1.2$ $J_{6,7}=J_{7,8}=10$	3.05^{sept} $C\underline{H}(CH_3)_2$ 1.40^{d} $CH(C\underline{H}_3)_2$
2b			7.40^{s}	8.39^{d}	7.13	—	7.92^{m}	9.68^{d}	$J_{4,5}=J_{7,8}=9.5$	4.08^{q} 0.85^{t}
2d				9.83^{d}	7.52	—	8.02^{m}	9.83^{d}	$J_{4,5}=J_{7,8}=9.5$	3.92^{q} 0.56^{t}
8a				9.81^{d}		7.86^{d}	7.58^{dd}	9.69^{dd}	$J_{4,6}=1.5$ $J_{6,7}=9.7$ $J_{6,8}=2.0$ $J_{7,8}=9.5$	3.90^{q} 0.53^{t} 2.81^{s} (CH_3)
8b				9.85^{d}		7.88^{d}	7.63^{dd}	9.68^{dd}	$J_{4,6}=1.5$ $J_{6,8}=9.7$ $J_{6,8}=2.0$ $J_{7,8}=9.7$	3.95^{q} 0.58^{t} 3.16^{sept} $C\underline{H}(CH_3)_2$ 1.45^{d} $CH(C\underline{H}_3)_2$
3a		8.25^{d}	7.40^{d}	8.16^{d}	6.90	—	7.92^{m}	8.96^{d}	$J_{2,3}=3.9$ $J_{4,5}=J_{7,8}=9.5$ $J_{4',5'}=J_{7',8'}=9.5$	
	7.68^{s}		7.68^{s}	8.20^{d}				8.20^{d}		
3b		8.56^{s}		9.66^{d}	7.18	—	7.92^{m}	8.50^{d}	$J_{4,5}=J_{7,8}=9.5$	4.43^{q} 1.43^{t}(C-3)
			7.38^{s}	8.33^{d}				9.51^{d}	$J_{4',5'}=J_{7',8'}=9.5$	4.06^{q} 0.82^{t}(C-1′)
4a[f]	7.81^{s}		7.81^{s}	8.38^{d}	7.23^{t}	7.60^{t}	7.23^{t}	8.38^{d}	$J_{4,5}=J_{5,6}=10$	
	7.43^{d}	7.90^{t}	7.43^{d}	8.48^{d}	7.93^{d}		7.93^{t}	8.48^{d}	$J_{1',2'}=3.5$ $J_{4',5'}=10.5$	
4b				9.83^{d}	7.7	—	8.1^{m}	9.83^{d}	$J_{4,5}=J_{4',5'}=11$	4.00^{t} 0.65^{t}(C-1,3)
		8.90^{s}		9.80^{d}	7.73^{d}		7.73^{d}	9.80^{d}		4.45^{q} 1.46^{t}(C-1′,3′)

a) In symmetrical biazulenes (**1a**, **1b**, **2a**, **2b**, and **8a—d**), the chemical shifts for two identical protons are listed on upper line. b) In asymmetrical biazulenes, the chemical shifts for protons numbered with prime are listed on lower line. c) 100 MHz. d) 100 MHz, FT-mode. e) In CCl_4. f) 200 MHz. g) s: Singlet; d: doublet; t: triplet; q: quartet; sept: septet; m: multiplet.

TABLE 6. CHEMICAL SHIFT DIFFERENCE ($\Delta\delta = \delta_{\text{biazulene}} - \delta_{\text{azulene}}$)[a,b] BETWEEN BIAZULENES AND REFERENCE AZULENES

Compound	H-1 H-1′	H-2 H-2′	H-3 H-3′	H-4 H-4′	H-5 H-5′	H-6 H-6′	H-7 H-7′	H-8 H-8′	OCH$_2$–CH$_3$		Others
1a		0.11	0.06	−0.01	−0.09	−0.04	−0.19	−0.01			
1b		0.07		0.01				0.09	−0.09	0.02	
2a	0.44		0.44	−0.03	−0.02	−0.05	−0.02	−0.03			
8c	0.35		0.35	−0.29		−0.20	−0.09	−0.15			0.00(CH$_3$)
8d	0.39		0.39	−0.10		−0.13	−0.03	−0.09			0.06C$\underline{\text{H}}$(CH$_3$)$_2$ 0.08CH(C$\underline{\text{H}}_3$)$_2$
2b			0.09	−0.10				−0.04	−0.40	−0.85	
2d				−0.09				0.09	−0.51	−0.56	
8a				−0.03		−0.06	−0.34	0.01	−0.56	−0.93	0.01(CH$_3$)
8b				−0.03		−0.02	0.00	−0.05	−0.48	−0.87	0.08C$\underline{\text{H}}$(CH$_3$)$_2$ 0.03CH(C$\underline{\text{H}}_3$)$_2$
3a		0.30	−0.02	−0.15	0.25			0.65			
	0.26		0.26	−0.11				−0.11			
3b		0.11		−0.06				0.01	0.05	0.00	
			0.07	−0.16				−0.21	−0.42	−0.61	
4a	0.39		0.39	0.07	0.08	0.05	0.08	0.07			
	0.01	−0.05	0.01	0.17	0.78		0.78	0.17			
4b				0.09				0.09	−0.43	−0.79	
		0.09		−0.01				0.06	0.02	0.02	

a) In symmetrical biazulenes (**1a**, **1b**, **2a**, **2b**, and **8a**—**d**), the chemical shift differences for two identical protons are listed on upper line. b) In asymmetrical biazulenes (**3a**, **b** and **4a**, **b**), the chemical shift difference for the protons numbered with prime are listed on lower line.

those in **5b**. So, it seems that the two azulene rings in 1,1′-biazulenes, **1a**, **1b**, and **1d**, are not coplanar. In contrast with this, in the NMR spectra of 2,2′-biazulenes, **2a**, **8c**, and **8d**, it is shown that the ring protons (H-1, 1′, 3, and 3′) at the 1 and 3-positions of azulene rings are shifted markedly downfield by 0.35—0.43 ppm and the other ring protons slightly upfield. The downfield shifts of H-1, 1′, 3, and 3′ in 2,2′-biazulenes suggest that these protons are located in the peripheral zone of another azulene ring and consequently, 2,2′-biazulenes, **2a**, **8c**, and **8d**, exist in such a conformation that the two azulene rings are coplanar or nearly coplanar. This result is consistent with the conclusion from the ESR study on 2,2′-biazulene anion radical in which the two azulene rings were found to be coplanar.[14] The NMR spectrum of 2,6′-biazulene, **4a**, also shows downfield shifts of H-1, 3 and H-5′, 7′ by δ 0.39 and 0.78 ppm, respectively, compared with the corresponding protons of azulene. This fact suggests that **4a** also exists in a coplanar conformation.

On the other hand, in the NMR spectra of sterically crowded ester derivatives of 2,2′-biazulenes, **2b**, **2d**, **8a**, and **8b**, the ethyl proton signals of the ethoxycarbonyl groups appear at higher field than of **5b** and **7b**. Such a large upfield shift of ethyl proton signals presumably arises from long-range shielding by another azulene ring. This fact suggests that ethoxyl groups are located above the plane of another azulene ring and consequently, that the two azulene rings in ester derivatives, **2b**, **2d**, **8a**, and **8b**, are twisted to avoid the large steric interactions between the ethoxycarbonyl groups at C-1, 3 and C-1′, 3′.

Experimental

All mp's were uncorrected. Electronic spectra were measured on a Hitachi EPS-3 Spectrometer and IR Spectra on a Shimadzu IR-27 infracord. NMR spectra were obtained by a Varian A-60 D Spectrometer and in some cases on a JNM-100 instrument in Fourier transform mode. Mass spectra were recorded on a Hitachi RMU-6 mass spectrometer at 25 eV.

General Procedure for Ullmann Reaction of Haloazulenes. A mixture of haloazulenes and activated copper[6] was heated in an evacuated, sealed glass tube (see Table 1). After cooling, the reaction mixture was extracted with chloroform. The solvent was evaporated *in vacuo* and the resulting residue was chromatographed.

Reaction of ***5a****.* A mixture of **5a**[7a] (500 mg) and copper (500 mg) was treated according to the general procedure. A green residue from the extract was chromatographed on a silica-gel column with benzene as an eluent to give two fractions. The first fraction gave 23 mg of **5b**.[9] The second fraction gave 254 mg of **1b** as bluish green needles (from cyclohexane–benzene): mp 211—212 °C; IR (KBr) 1684, 1449, 1414, 1285, 1205, 1044, 781, and 741 cm^{-1}. Found: C, 78.62; H, 5.84%. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57%.

Reaction of ***6a****.* A mixture of **6a**[7c] (300 mg) and copper (600 mg) was treated according to the general procedure. The products were chromatographed on an alumina column with benzene. The first fraction gave a small amount of azulene. The second fraction gave 81 mg of **2a** as green scales (from chloroform): mp 320 °C.

Reaction of ***6b****.* A mixture of **6b**[7b] (100 mg) and copper (200 mg) was treated in the usual way. The products were chromatographed on an alumina column with benzene to give three fractions. The first fraction gave a small amount of a mixture of **5b** and **6b**. The second fraction gave 50 mg of **2b** as bluish needles (from ethanol); mp 151.5—152 °C. Found: C, 78.63; H, 5.53%. Calcd for $C_{24}H_{18}O_4$: C, 78.37; H, 5.57%. The third fraction eluted with chloroform gave 4 mg of brown needles[15] (from benzene); mp 245—246 °C. [MS, *m/e*: 352 (M$^+$, 100%); calcd for $C_{24}H_{16}O_3$, 352 (M)].

Reaction of ***6c****.* A mixture of **6c** (363 mg) and copper

(700 mg) was treated according to the general procedure. The products were chromatographed on an alumina column with chloroform to give 160 mg of **2c** as dark violet scales (from chloroform); mp 284—285 °C (dec); IR (KBr) 1635 cm^{-1}; NMR (CDCl$_3$) δ=7.45 (2H, s, H-3,3′), 7.6—8.1 (6H, m, H-5,5′,-6,6′ and -7,7′), 8.55 (dm, J=10 Hz, H-4,4′), 9.90 (2H, dm, J=10 Hz, H-8,8′), and 10.37 (s, 2 CHO). Found: C, 85.10; H, 4.34%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%.

Reaction of 7a. A mixture of **7a**[7c] (100 mg) and copper (200 mg) was treated in the usual way. The products were chromatographed on a silica-gel column with benzene to give three fractions. The first fraction gave 5 mg of **7d.**[9] The second fraction gave 8 mg of **7a**. The third fraction eluted with chloroform gave 73 mg of **2d** as red prisms (from ethanol); mp 181—182 °C. Found: C, 71.01; H, 5.72%. Calcd for $C_{32}H_{30}O_8$: C, 70.83; H, 5.57%.

Reaction of Diethyl 2-Chloro-5-methylazulene-1,3-dicarboxylate (7b). A mixture of **7b**[7b] (1.09 g) and copper (2.18 g) was treated in the usual way. Chromatography of the products on a silica-gel column with benzene gave two fractions. The first fraction gave 140 mg of a mixture of **7b** and diethyl 5-methylazulene-1,3-dicarboxylate (**7e**)[16] (1 : 1 ratio by NMR). The second fraction gave 515 mg of **8a** as red prisms (from benzene–cyclohexane); mp 179—180 °C. Found: C, 71.69; H, 6.25%. Calcd for $C_{34}H_{34}O_8$: C, 71.56; H, 6.01%.

Reaction of Diethyl 2-Chloro-5-isopropylazulene-1,3-dicarboxylate (7c). A mixture of **7c**[7b] (500 mg) and copper (1.0 g) was treated in the manner described above. The chromatography of the products on a silica-gel column with benzene gave two fractions. The first fraction gave a small amount of a mixture of **7c** and diethyl 5-isopropylazulene-1,3-dicarboxylate (**7f**).[17] The second fraction gave 50 mg of **8b** as red prisms (from ethanol); mp 174—175 °C. Found: C, 72.93; H, 6.90%. Calcd for $C_{38}H_{42}O_8$: C, 72.82; H, 6.76%.

Reaction of a mixture of 5a and 6b. A mixture of **5a** (200 mg), **6b** (200 mg), and copper (400 mg) was treated in the usual way. The chromatography of the product on a silica-gel column with benzene gave fractions, a, b, c, and d. The fraction a, b, and d gave **5b** (45 mg), **1b** (68 mg), and **2b** (65 mg), respectively. The yellow fraction c gave 53 mg of **3b** as dark green needles (from cyclohexane); mp 119—120 °C. Found: C, 78.12; H, 5.74%. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57%. TNB-complex: brown needles (from ethanol); mp 130—131 °C. Found: C, 63.04; H, 4.42; N, 6.73%. Calcd for $C_{32}H_{25}O_{10}N_3$: C, 62.80; H, 4.12; N, 6.87%.

Reaction of a Mixture of 7a and 9a. A mixture of diethyl 6-bromoazulene-1,3-dicarboxylate (**9b**)[12] (900 mg), potassium iodide (17 g), water (10 cm^3), and acetic acid (80 cm^3) was treated under reflux for 50 h. The reaction mixture was diluted with water and the resulting precipitate was collected by filtration and dried *in vacuo*. Chromatography on a silica-gel column with benzene gave a mixture of diethyl 6-iodoazulene-1,3-dicarboxylate (**9a**) and **9b** (1 : 5 ratio by NMR), which could not be separated by thin layer chromatography. NMR of **9a**: δ=1.45 (t, J=7.0 Hz, 2 $OCH_2C\underline{H}_3$), 4.45 (q, J=7.0 Hz, 2 $OC\underline{H}_2CH_3$), 7.81 (d, J=11.5 Hz, H-5,7), 8.80 (s, H-2), 9.61 (d, J=11.5 Hz, H-4,8). This mixture of 6-haloazulenes (680 mg) was mixed with **7a** (1.0 g) and copper (2.0 g) and the mixture was treated in the manner described above. The chromatography of the crude products on a silica-gel column with benzene gave six bands. The fifth band afforded 61 mg of **4b** as red needles (from ethanol); mp 257—258 °C. Found: C, 70.50; H, 5.31%. Calcd for $C_{32}H_{30}O_4$: C, 70.83; H, 5.51%. From the sixth band 276 mg of **2d** was obtained.

1,1′-Biazulene-3,3′-dicarboxylic Acid (1c). A solution of **1b** (256 mg) dissolved in a solution of potassium hydroxide (100 mg) in ethanol (25 cm^3) containing water (0.5 cm^3) was heated under reflux for 5 h. After cooling the solution was diluted with water (30 cm^3) and acidified with 2 mol dm^{-3} HCl. Greenish crystals separated out were collected by filtration and washed repeated with water, to afforded 224 mg (98%) of **1c** as microcrystals, mp 290—293 °C (dec). IR (KBr): 3000—2570, 1647, 1456, 1287, 1236, 1029, 755, and 732 cm^{-1}. Found: C, 77.02; H, 4.24%. Calcd for $C_{22}H_{14}O_4$: C, 77.18 ; H, 4.12%.

1,1′-Biazulene (1a): Heating of **1c** (280 mg) at 250 °C/15 Torr† in a sublimation apparatus afforded 120 mg of blue crystals which were chromatographed on an alumina column (benzene) to give a single bluish green fraction, yielding 115 mg (55%) of **1a** as bluish green scales (from hexane): mp 104—105 °C; MS, *m/e*, 255 (M$^+$ +1, 21.4%), 254 (M$^+$, 100), 253 (M$^+$ −1, 18.5), 252 (41.4), and 251 (22.8); IR (KBr) 2990 (w), 1567 (s), 1488 (m), 1453 (m), 1406 (w), 1389 (vs), 1304 (m), 1290 (m), 1269 (w), 1212 (m), 1142 (w), 1130 (w), 1043 (w), 967 (w), 961 (w), 943 (m), 900 (m), 877 (w), 855 (w), 827 (m), 787 (vs), 747 (m), 735 (m), and 727 (s) cm^{-1}. Found: C, 94.35; H, 5.83%. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55%.

TNB Complex of 1a: Dark blue neeldes (from ethanol): mp 200—201 °C. Found: C, 56.23; H, 3.17; N, 12.06%. Calcd for $C_{32}H_{20}O_{12}N_6$: C, 56.52; H, 2.96; N, 12.13%. IR (KBr) 2990, 1972, 1569, 1488, 1453, 1389, 1304, 1290, 1269, 1212, 1147, 1130, 1043, 967, 961, 943, 936, 900, 877, 855, 827, 787, 747, 735, and ,727 cm^{-1}.

Ethyl 1,1′-Biazulene-3-carboxylate (1d). To a warmed ethanol solution (25 cm^3) of **1b** (76 mg, 0.19 mmol) was added 1 cm^3 of aqueous KOH (11 mg, 0.19 mmol) . The solution was heated under reflux for 15 min and then diluted with water (50 cm^3). The precipitated **1b** (3 mg) was colloected by filtration. The filtrate was acidified with diluted HCl to give a mixture of di- and monocarboxylic acids which was collected by filtration and dried. The mixture, without further purification, was heated at 270—280 °C/10 Torr in a sublimation apparatus to give a mixture of the decarboxylated products, which was chromatographed on an alumina column with benzene. The first elution with benzene afforded 4 mg of **1a**. The second elution with benzene yielded 18 mg of **1d**, blue needles (from ethanol), mp 137—138 °C. Found: C, 84.89; H, 5.72%. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

Dimethyl 1,1′-Biazulene-3,3′-dicarboxylate (1e). Treatment of **1c** (51 mg) with ethereal diazomethane gave 39 mg of **1e** as bluish green needles (from benzene–cyclohexane): mp 232—233 °C; UV$_{max}$ (MeOH), nm (log ε), 240 (4.64), 279 (4.83), 304 (4.71), and 405 (4.14), [575 (2.30) in isooctane]; IR (KBr) 1701, 1200, 1029 cm^{-1}. Found: C, 77.76; H, 4.66%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

1,1′-Biazulene-3,3′-d$_2$ (1f). This compound was prepared by a modification of the method reported.[10] To a solution of **1a** (50 mg) in cyclohexane (5 cm^3) was added 85% D_3PO_4 (3 cm^3) under a nitrogen atmosphere. The solution was shaken until **1a** in the organic layer had transferred completely into the D_3PO_4 phase and then the upper layer was removed by using a small pipette. To the brown phosphoric acid layer obtained was added 3 cm^3 of deuterium oxide. The resulting solution was extracted with cyclohexane. The organic layer was passed through anhydrous sodium sulfate and evaporated under a reduced pressure. The crude product was recrystallized from pentane to give 39 mg of **1f** as bluish green scales: mp 103—104 °C; MS, *m/e*, 256 (M$^+$,

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† 1 Torr≈133.322 Pa.

100%); NMR ($CDCl_3$) δ=6.97 (t, J=9.5 Hz, H-7,7′), 7.05 (t, J=9.5 Hz, H-5,5′), 7.50 (t, J=9.5 Hz, H-6,6′), 8.04 (s, H-2,2′), 8.25 (d, J=9.5 Hz, H-4,4′ or H-8,8′), and 8.29 (d, J=9.5 Hz, H-8,8′ or H-4,4′).

3,3′-Dibromo-1,1′-biazulene (1g). To a solution of **1a** (50.8 mg) in benzene (2 cm^3) was added NBS (72 mg) with stirring at room temp. After stirring for a day, the reaction mixture was chromatographed on an alumina column with benzene to give 52.8 mg of **1g** as blue needles (from cyclohexane–benzene 9 : 1 mixture): mp 173—175 °C; IR (KBr) 1579, 1381, 862, and 737 cm^{-1}; NMR ($CDCl_3$) δ= 7.20 (t, J=10 Hz, H-5,5′ and H-7,7′), 7.78 (t, J=10 Hz, H-6,6′), 7.96 (s, H-2,2′), and 8.20 and 8.35 (d, J=9.5 Hz, H-4,4′ and H-8,8′). Found: C, 58.00; H, 3.07%. Calcd for $C_{20}H_{12}Br_2$: C, 58.29; H, 2.94%.

2,2′-Biazulene-1,1′-dicarboxylic Acid (2e). A solution of **2b** (180 mg) and potassium hydroxide (60 mg) in 0.5 cm^3 of water and 5 cm^3 of ethanol was heated under reflux for 3 h, and diluted water (10 cm^3). After cooling, the solution was acidified by 1 mol dm^{-3} HCl to give 150 mg (97%) of **2e** as red crystals (from ethanol): mp 160—165 °C (dec); IR (KBr) 3030, 1650, 1395, 1239, 950, and 814 cm^{-1}. Found: C, 77.08; H, 4.30%. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12%.

Dimethyl 2,2′-Biazulene-1,1′-dicarboxylate was obtained by treatment of **2e** with ethereal diazomethane as blue-violet needles (from methanol): mp 183—184 °C; IR (KBr) 1689 cm^{-1}; NMR ($CDCl_3$) δ=3.63 (s, 2 CO_2CH_3), 7.40 (s, H-3,3′), 7.3—7.9 (m, H-5—7 and H-5′—7′), 8.38 (d, J=9 Hz, H-4,4′), and 9.56 (d, J=9 Hz, H-8,8′). Found: C, 77.73; H, 4.81%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

2,2′-Biazulene-1,1′,3,3′-tetracarboxylic Acid (2f). A solution of **2d** (300 mg) and potassium hydroxide (320 mg) in 0.5 cm^3 of water and 8 cm^3 of ethanol was refluxed for 10 h. The solution was diluted with 20 cm^3 of water and filtreted through a glass-filter to remove an insoluble material. The filtrate was acidified with 2 mol dm^{-3} HCl and then red crystals separated out were collected by filtration and repeatedly washed with water to give 231 mg of **2f** as red crystalline powder, mp 210—215 °C, which is sparingly soluble in organic solvents. IR (KBr) 3030, 1701 sh, 1658, 1449, and 1229 cm^{-1}. Found: C, 67.03; H, 3.41%. Calcd for $C_{24}H_{14}O_8$: C, 66.98; H, 3.28%.

Treatment of **2f** with diazomethane afforded the tetramethyl ether as red prisms (from chloroform): mp—320 °C; NMR ($CDCl_3$) δ=3.45 (s, OCH_3), 7.5—8.0 (m, H-5—7 and H-5′—7′), 9.75 (br d, J=9 Hz, H-4,4′ and H-8,8′); IR (KBr) 1695, 1451, 1391, 1193, and 1151 cm^{-1}. Found: C, 68.81; H, 4.54%. Calcd for $C_{28}H_{22}O_8$: C, 69.13; H, 4.56%.

2,2′-Biazulene (2a). *Decarboxylation of* **2e**: Heating of **2e** (100 mg) at 250 °C/0.5 Torr in a sublimation apparatus afforded green solid which was dissolved in chloroform and the solution was passed through an alumina column. The solvent of the eluent was removed *in vacuo*. The residue was recrystallized from chloroform to give 43 mg of **2a** as green scales with metallic luster: mp>320 °C; IR (KBr) 3030 (w), 1567 (m), 1534 (m), 1451 (m), 1408 (s), 1389 (m), 1359 (m), 1299 (w), 1248 (w), (1096 w), 1012 (w), 989 (w), 971 (w), 899 (w), and 720 (s) cm^{-1}; NMR (DMSO-d_6, at 150 °C) δ= 7.15 (br t, J=9 Hz, H-5,5′,7,7′), 7.40 (br t, J=9 Hz, H-6,6′), 7.85 (s, H-1,1′, 3,3′), 8.31 (br d, J=9 Hz, H-4,4′,8,8′); MS, *m/e*, 255 (M^+ +1, 20.6%), 254 (M^+, 100), and 252 (27.4). Found: C, 94.47; H, 5.41%. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55%.

Decarboxylation of **2f**: The treatment of **2f** in a manner similar to that described above gave 23 mg of **2a**.

Deethoxycarbonylation of **2b** *with 100% Phosphoric Acid*: A mixture of **2b** (300 mg) and 100% phosphoric acid (3 cm^3) was heated at 95 °C for 1 h. The reaction mixture was diluted with ice–water (10 g). Green crystals were collected by filtration, washed repeatedly with water and dried, yielding 19 mg (99%) of **2a**.

Deethoxycarbonylation of **2d** *with 100% Phosphoric Acid*: A mixture of **2d** (50 mg) and 100% phosphoric acid (3 cm^3) was heated at 95 °C for 2 h. The reaction mixture was treated in a manner to the above, yielding 20 mg (95%) of **2a**.

5,5′-Dimethyl-2,2′-biazulene (8c). A mixture of **8a** (55 mg) and 100% phosphoric acid (3 cm^3) was treated in a manner similar to the above, yielding 28 mg (99%) of **8c** as green needles (from chloroform): mp 244—245 °C; MS, *m/e*, 282 (M^+, 100%), 265 (14), 141 (M^{2+}, 11); IR (KBr) 2985 (w), 2890 (w), 1572 (m), 1522 (m), 1464 (m), 1418 (m), 1391 (s), 1376 (m), 1302 (w), 1250 (w), 1218 (m), 1157 (w), 1057 (w), 979 (m), 936 (m), 910 (m), 837 (m), 804 (s), 794 (m), 763 (w), and 733 (m) cm^{-1}; NMR (DMSO-d_6) δ=2.58 (s, 2 CH_3), 7.05 (t, J=10 Hz, H-7,7′), 7.47 (d, J=10 Hz, H-6,6′), 7.72 (s, H-1,1′,3,3′), 8.18 (d, J=10 Hz, H-8,8′), and 8.27 (br s, H-4,4′). Found: C, 93.13; H, 6.48%. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

5,5′-Diisopropyl-2,2′-biazulene (8d). *Deethoxycarbonylation of* **8b** *with 100% Phosphoric Acid*: A mixture of **8b** (40 mg) and 100% phosphoric acid (3 cm^3) was treated in a manner similar to the above, afforded 20 mg of **8d** (from pentane): mp 150—151 °C; MS, *m/e*, (M^+ +2, 40%), 339 (M^+ +1, 30), 338 (M^+, 100), 323 (M^+ −15, 40), 308 (M^+ −30, 6), 265 (12), and 169 (M^{2+}, 9); IR (KBr) 2985 (m), 2959 (m), 1572 (m), 1520 (m), 1460 (m), 1445 (m), 1403 (vs), 1381 sh (m), 1333 (w), 1299 (w), 1250 (w), 1220 (w), 1182 (w), 1136 (w), 1101 (w), 1012 (w), 941 (w), 928 (m), 882 (w), 815 (vs), and 770 (m) cm^{-1}. Found: C, 91.86; H, 7.63%. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74%.

With Alkaline Hydrolysis: A solution of **8b** (100 mg) and potassium hydroxide (80 mg) in a mixture of water (0.3 cm^3) and ethanol (5 cm^3) was heated under reflux for 3 h. After cooling, the solution was diluted with water (10 cm^3) and acidified with 1 mol dm^{-3} HCl to give 72 mg of a tetracarboxylic acid. Decarboxylation of the acid (60 mg) by heating at 260 °C/0.5 Torr in sublimation apparatus afforded 37 mg of **8d** as green needles, mp 150—151 °C (from pentane).

2-Iodoazulene-1-carboxaldehyde (6c). To a solution of **6a**[7c] (100 mg) in DMF (0.5 cm^3) was added phosphoryl chloride (0.1 cm^3) at room temp with stirring. After being stirred for another 1 h, the reaction mixture was poured into sat. aq $NaHCO_3$ and extracted with ether. The organic extract was washed with water, dried over Na_2SO_4, and evaporated. The residue was chromatographed on an alumina column with benzene to give 110 mg (99%) of **6c** as red prisms (from ethanol); mp 140—141 °C; IR (KBr) 1639 cm^{-1}; NMR ($CDCl_3$) δ=7.43 (s, H-3), 7.3—8.0 (m, H-5—7), 8.33 (d, J=10 Hz, H-4), 9.70 (d, J=10 Hz, H-8), and 10.12 (s, CHO). Found: C, 47.18; H, 2.70%. Calcd for $C_{11}H_7OI$: C, 46.85; H, 2.52%.

Formylation of **2a**. To a suspension of **2a** (20 mg) in DMF (3 cm^3) was added $POCl_3$ at room temp with stirring. The mixture was heated at 60 °C for 1 h and then quenched with water to give green crystals, which were collected by filtration, dried over $CaCl_2$, in a desiccator. The chromatography of the crude products on an alumina column with chloroform gave 24 mg (98%) of **2c**, dark violet scales, mp 284—285 °C (dec).

Diethyl 3,3′-Dibromo-2,2′-biazulene-1,1′-dicarboxylate (2g). To a solution of **2b** (580 mg) in dry benzene (50 cm^3) was added NBS (636 mg). The mixture was stirred overnight at room temp. The color of the solution turned bluish violet from reddish violet. The solvent was evaporated and the residue was chromatographed on a silica-gel column with benzene to give 569 mg of **2g** as blue needles (from ethanol): mp 178—179 °C. λ_{max} (MeOH), nm (log ε), 239 (4.37), 315 (4.78), 364 sh, and 380 (3.93) [560 (3.00), 598 (2.97), 656 (2.62) in benzene]; IR (KBr) 1686 cm^{-1}; NMR (CDCl$_3$) δ=0.65 (t, J=7.0 Hz, 2 OCH$_2$C$\underline{H}_3$), 4.00 (q, J=7.0 Hz, 2 OC$\underline{H}_2$CH$_3$), 7.35—8.10 (m, H-5—7 and H-5′—7′), 8.58 (d, J=9 Hz, H-4,4′), and 9.73 (br d, J=9 Hz, H-8,8′). Found: C, 56.30; H, 3.72%. Calcd for $C_{26}H_{20}O_4Br_2$: C, 56.16; H, 3.63%.

Diethyl 3,3′-Diiodo-2,2′-biazulene-1,1′-dicarboxylate (2h). To a solution of **2b** (292 mg, 0.73 mmol) in CH$_2$Cl$_2$ (3 cm^3) was added *N*-iodosuccinimide (352 mg) with stirring at room temp. After stirring for 1.5 h, the reaction mixture was chromatographed on an alumina column with benzene to give violet crystals (496 mg) of 2 h. Recrystallization from EtOH-CH$_2$Cl$_2$ (9 : 1) afforded blue prisms: mp 207—208 °C; IR (KBr) 1675, 1195, and 1031 cm^{-1}; NMR (CDCl$_3$) δ= 0.60 (t, J=7.0 Hz, 2 OCH$_2$C$\underline{H}_3$), 3.90 (q, J=7.0 Hz, 2 OC$\underline{H}_2$CH$_3$), 7.36—7.96 (m, H-5—7 and 5′—7′), 8.65 (br d, J=9.5 Hz, H-4,4′), and 9.75 (br d, J=9.5 Hz, H-8,8′). Found: C, 48.26; H, 3.13%. Calcd for $C_{26}H_{20}O_4I_2$: C, 48.04; H, 3.10%.

Dimethyl 3,3′-Dibromo-2,2′-biazulene-1,1′-dicarboxylate (2i). A solution of **2g** (988 mg) and potassium hydroxide (1.5 g) in a mixture of water (5 cm^3) and ethanol (10 cm^3) was heated under reflux for 15 h. The solution was diluted with water and acidified with dilute HCl. The precipitates were collected by filtration, washed with water, dried over CaCl$_2$, and recrystallized from ethanol to give a dicarboxylic acid as black prisms; mp near 300 °C (dec); IR (KBr) 2940 and 1630 cm^{-1}. Found: C, 53.17; H, 2.73%. Calcd for $C_{22}H_{12}O_4Br_2$: C, 52.84; H, 2.24%. This acid was treated with ethereal diazomethane to give **2i** as violet needles (from ethanol): mp 285—286 °C; IR (KBr) 1684 cm^{-1}; NMR (CDCl$_3$) δ= 3.55 (OCH$_3$). Found: 54.28; H, 3.20%. Calcd for $C_{24}H_{16}O_4Br_2$: C, 54.27; H, 3.04%.

2,2′-Biazulene-1,1′ : 3,3′-tetracarboxylic Dianhydride (2j). A mixture of **2f** (1.89 g) in acetic anhydride (15 cm^3) was heated under gentle boiling for 2 h to give 1.6 g of **2j** as red crystals: mp>300 °C; IR (KBr) 1706, 1133, 1016, and 762 cm^{-1}. Found: C, 72.81; H, 2.65%. Calcd for $C_{24}H_{10}O_6$: C, 73.10; H, 2.56%.

Ethanolysis of 2j. To an ethanol solution of sodium ethoxide, prepared from 207 mg of sodium, was added 1.3 g of **2j** and the mixture was heated for 1 h. After cooling, the solution was diluted with water (50 cm^3) and acidified with dilute HCl to give precipitates which were collected by filtration, washed with water and dried over CaCl$_2$ in a desiccator. Decarboxylation of the mixture of carboxylic acids by heating at 260—280 °C/10 Torr gave a brown violet substance. Chromatography over a silica-gel column using benzene as an eluent gave four fractions, a, b, c, and d. The fraction a gave 7 mg of **2a**. The fraction b gave 183 mg (15%) of ethyl 2,2′-biazulene-1-carboxylate (**2k**) as blue sacles (from cyclohexane): mp 145—146 °C; IR (KBr) 1682 cm^{-1}; NMR (CDCl$_3$) δ=1.26 (t, J=7.0 Hz, OCH$_2$C$\underline{H}_3$), 4.41 (q, J=7.0 Hz, OC$\underline{H}_2$CH$_3$), 6.78—7.83 (9H, m, H-1′,3,3′, H-5—7, and H-5′—7′). 8.26 (3H, br d, J=9.5 Hz, H-4,4′,8′), and 9.28 (br d, J=9.5 Hz, H-8). Found: C, 84.35; H, 5.70%. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%. The fraction c gave 323 mg (22.4%) of diethyl 2,2′-biazulene-1,3-dicarboxylate (**2m**) as blue scales (from ethanol): mp 151—152 °C; IR (KBr) 1677 cm^{-1}; NMR (CDCl$_3$) δ=0.80 (t, J=7.0 Hz, 2 OCH$_2$C$\underline{H}_3$), 4.08 (q, J=7.0 Hz, 2 OC$\underline{H}_2$CH$_3$), 7.46 (s, H-1′,3′), 7.0—8.0 (m, H-5—7 and H-5′—7′), 8.30 (br d, J=9.5 Hz, H-4′,8′), and 9.58 (br d, J=9.5 Hz, H-4,8). Found: C, 78.64; H, 5.79%. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57%. The fraction d afforded 528 mg (36.6%) of **2b**.

1,2′-Biazulene-1,3-dicarboxylic Acid (3c). A mixture of **3b** (123 mg) and potassium hydroxide (166 mg) in a mixture of water (0.5 cm^3) and ethanol (3 cm^3) was heated under reflux for 5 h. The solution was diluted with water (10 cm^3) and acidified with 2 mol dm^{-3} HCl. The brown precipitates separated out were collected by filtration, repeatedly washed with water and dried over CaCl$_2$ in a desiccator to give 97 mg of **3c** as brown crystals (from ethanol): mp 240—243 °C (dec); IR (KBr) 2915, 1650, and 1645 cm^{-1}. Found: C, 77.31; H, 4.20%. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12%.

Dimethyl 1,2′-Biazulene-1′,3-dicarboxylate (3d). Treatment of **3c** with diazomethane gave **3d** as dark brown-blue needles (from ethanol): mp 124—125 °C; IR (KBr) 1686 and 1684 cm^{-1}; UV$_{max}$ (MeOH), nm (log ε), 237 (4.58), 288 (4.71), 306 (4.70), 344 sh (4.45), and 426 (4.14). Found: C, 77.76; H, 4.66%. Calcd for $C_{24}H_{18}O_4$: C, 77.83; H, 4.86%.

1,2′-Biazulene (3a). Heating of **3c** (64 mg) at 215—220 °C/15 Torr afforded 43 mg of crude crystals which were chromatographed on an alumina column with benzene as an eluent to give 34 mg of **3a** as green scales with metallic luster (from pentane): mp 144—145 °C; MS, *m/e*, 255 (M$^+$ +1, 20.7%), 254 (M$^+$, 100), 253 (M$^+$ −1, 65.1), 252 (M$^+$ −2, 81.7), 226 (12), 148 (33), 127 (M^{2+}, 15), and 126 (37); IR (KBr) 3030 (w), 1590 (w), 1565 (s), 1513 (vs), 1468 (w), 1412 (s), 1391 (vs), 1337 (m), 1297 (m), 1261 (w), 1215 (w), 1193 (w), 1110 (w), 1017 (w), 988 (w), 971 (w), 965 (w), 943 (m), 908 (w), 898 (m), 885 (w), 852 (w), 827 (m), 810 (s), 780 (s), and 722 (s) cm^{-1}. Found: C, 94.29; H, 5.55%. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55%.

TNB-complex: Brown scales (ethanol); mp 189—190 °C. Found: C, 67.20; H, 3.51; N, 8.74%. Calcd for $C_{26}H_{17}O_6N_3$: C, 66.81; H, 3.67; N, 8.99%.

2,6′-Biazulene (4a). A mixture of **4b** (13 cm^3) in 5 cm^3 of 100% phosphoric acid was heated at 95 °C for 2 h. The reaction mixture was treated similarly to the cases of **2a** from **2b**, giving 5 mg (90%) of **4a** as green scales (from chloroform): mp 300 °C; MS, *m/e*, 255 (M$^+$ +1, 21.0%), 254 (M$^+$, 100), and 252 (35.2); IR (KBr) 3070 (w), 1570 (w), 1445 (w), 1399 (m), 1370 (m), 1227 (w), 1196 (w), 1186 (w), 1110 (w), 1014 (w), 990 (w), 971 (w), 909 (w), 899 (w), 876 (m), 810 (vs), 885 (w), and 727 (m) cm^{-1}. Found: C, 94.70; H, 5.52%. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55%.

References

1) This work was presented in part at the 20th National Meeting of the Chemical Society of Japan, Tokyo, April 1967, *cf.* Abstr., p. 437.

2) R. Hagen, E. Heilbronner, and P. A. Staub, *Helv. Chim. Acta*, **51**, 45 (1968).

3) H. Maus, Ph. D. Thesis, University Marburg (1962).

4) M. Hanke and C. Jutz, *Angew. Chem.*, **91**, 227 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 214 (1979).

5) M. Hanke and C. Jutz, *Synthesis*, **1980**, 31.

6) E. C. Kleinder and R. Adams, *J. Am. Chem. Soc.*, **55**, 4225 (1933); H. W. Gibson and F. C. Bailey, *J. Org. Chem.*, **34**, 557 (1976).

7) a) T. Morita and K. Takase, *Sci. Repts, Ser. 1. Tohoku University*, **62**, 83 (1980); b) T. Morita, T. Fujita, T. Nakadate, and K. Takase, *ibid.*, **62**, 91 (1980); c) T. Nozoe, S. Seto, and S. Matsumura, *Bull. Chem. Soc. Jpn.*, **35**, 1990 (1962).

8) J. Forrest, *J. Chem. Soc.*, **1960**, 566; **1960**, 581; A. H. Lewin, and T. Cohen, *Tetrahedron Lett.*, **1965**, 4531.

9) T. Nozoe, S. Seto, S. Matsumura, and Y. Murase,

Bull. Chem. Soc. Jpn., **35**, 1179 (1962).

10) A. Bauder and H. H. Guthard, *Helv. Chim. Acta*, **41**, 889 (1958).

11) T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, *Tetrahedron*, **27**, 3357 (1971).

12) T. Nozoe, K. Takase, and M. Tada, *Bull. Chem. Soc. Jpn.*, **38**, 247 (1965); R. N. McDonald and J. M. Richmond, *J. Chem. Soc., Chem. Commun.*, **1973**, 605; R. N. McDonald, J. M. Richmnod, J. R. Curtis, H. E. Petty, and T. L. Hoskins, *J. Org. Chem.*, **41**, 1811 (1976).

13) A. G. Anderson, Jr., and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4979 (1953).

14) Y. Ikegami and S. Seto, *Mol. Phys.*, **16**, 101 (1969); *Bull. Chem. Soc. Jpn.*, **43**, 2409 (1970).

15) Details of the structure will be published elsewhere in near future.

16) H. Akino, *Sci. Repts. Hirosaki University*, **11**, 18 (1964); *Chem. Abstr.*, **63**, 1754 (1965).

17) T. Nozoe, S. Seto, S. Matsumura, and T. Asano, *Proc. Jpn. Acad.*, **32**, 339 (1956).