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Synthesis and Spectroscopic Studies of 1,1′-(1,8-Naphthylene)-di-1*H*-1,2,3-triazoles[1)]

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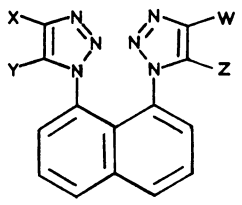
The first 1,8-diheteroaromatic naphthalenes, 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazoles (**1**), were synthesized by 1,3-dipolar cycloadditions of 1,8-diazidonaphthalene to acetylenic esters. The spectral properties of these compounds were studied and compared with those of the corresponding 1-(1-naphthyl)-1*H*-1,2,3-triazoles (**2**). The two triazole rings at the peri-positions in **1** are in a face-to-face arrangement according to the results of ^{1}H NMR spectra. The UV spectra of **1** are almost identical with each other and show a red shift from those of corresponding **2**. No significant spectral differences between **1** and **2** were observed in the IR spectra. The fragment ion with two azirine groups at the peri-position in the naphthalene ring was observed in the MS spectra of **1**.

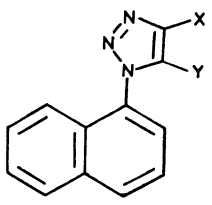
Naphthalenes with substituents in the 1 and 8 positions exhibit unique properties in both structure and reactivity, because the substituents exist in close proximity in these compounds.[2)] Recently, 1,8-diarylnaphthalenes have been synthesized and studied extensively in view of their geometry and inherent strain due to steric overcrowding.[3)] However, heteroaromatic analogues with heterocyclic rings in the peri-position have not yet been studied, presumably because of difficulties in synthesizing them.

Thus, we have attempted to synthesize the new 1,8-diheteroaromatic naphthalenes, 1,1′-(1,8-naphthylene)-di-1*H*-1,2,3-triazoles (**1a—k**), by the 1,3-dipolar cycloaddition of 1,8-diazidonaphthalene to several acetylenic esters. This paper deals with their syntheses and spectral properties comparing with corresponding 1-(1-naphthyl)-1*H*-1,2,3-triazoles (**2a—h**).

Results and Discussion

The thermal 1,3-dipolar cycloaddition of azides to alkynes is a well-known route to 1*H*-1,2,3-triazoles, and the reaction of various azides have been investigated.[4)]





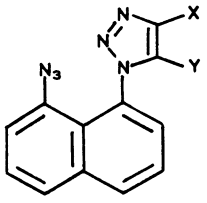
1a: W=X=Y=Z=CO_2Me
1b: W=X=Y=Z=CO_2Et
1c: W=X=Y=Z=CO_2Pr^i
1d: W=X=Y=Z=CO_2Bu^t
1e: W=X=CO_2Et, Y=Z=H
1f; W=X=H, Y=Z=CO_2Et
1g: W=Y=CO_2Et, X=Z=H
1h: W=X=Z=CO_2Et, Y=H
1i: W=Y=Z=CO_2Et, X=H
1j: W=X=COOH, Y=Z=H
1k: W=X=Y=Z=H

2a: X=Y=CO_2Me
2b: X=Y=CO_2Et
2c: X=Y=CO_2Pr^i
2d: X=Y=CO_2Bu^t
2e: X=CO_2Et, Y=H
2f: X=H, Y=CO_2Et
2g: X=COOH, Y=H
2h: X=Y=H

However, the reactions of 1,8-diazidonaphthalene, as well as 1-azidonaphthalene, have not yet been reported. The reactions of 1,8-diazidonaphthalene with a large excess of acetylenedicarboxylates, RO_2C-C≡CCO_2R (R=Me, Et, Pr^i, and Bu^t), afforded **1a—d** via the formation of dialkyl 1-(8-azido-1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate. In order to avoid the decomposition of 1,8-diazidonaphthalene, the reactions were carried out in the dark and at room temperature. The reaction with an unsymmetrical acetylene, ethyl propiolate, gave three isomeric triazoles, **1e—g**. The identification of **1e** and **1f** as shown in the figure was made by comparing the ^{1}H NMR chemical shifts of triazole ring protons in **1e** and **1f** with those in previously reported 1-phenyl-4-methyl-1*H*-1,2,3-triazole and 1-phenyl-5-methyl-1*H*-1,2,3-triazole.[5)] The main product was **1e**, and the most sterically hindered isomer, **1f**, formed very little (**1e**:**1f**:**1g**=26:1:12). The 1:1 addition products of the above reaction, **3a** and **3b**, were employed to synthesize the unsymmetrical triazoles, **1h** and **1i**.

In order to prepare the parent compound, **1k**, following reactions were attempted. Hydrolysis of **1e** in alkaline solution led to carboxylic acid, **1j**. Heating crystals of **1j** up to 180 °C under a nitrogen atmosphere afforded **1k** almost quantitatively. In the similar manner, 1-naphthyltriazoles, **2a—h**, were synthesized from 1-azidonaphthalene.

Spectral properties of **1a—k** and **2a—h** are listed in Tables 1 and 2, respectively. In the ^{1}H NMR spectra of **1k**, the H-4 and H-5 protons appeared at higher field



3a: X=CO_2Et, Y=H
3b: X=H, Y=CO_2Et

Table 1. Spectroscopic Data of 1,1′-(1,8-Naphthylene)di-1*H*-1,2,3-triazoles

Product	^{1}H NMR ($CDCl_3$)[a]	IR(KBr)	UV(CH_3OH)	MS
	δ/ppm	ν/cm^{-1}	λ/nm (log ε)	m/z (rel intensity, %)
1a	3.81 (s, 6H, 5-CH_3), 4.01 (s, 6H, 4-CH_3), 7.49 (d, J=7.4Hz, 2H, H-2′), 7.72 (dd, J=8.4, 7.4Hz, 2H, H-3′), 8.27 (d, J=8.4Hz, 2H, H-4′)	1740, 1290, 1245, 1050, 830, 760	288(4.02), 220(4.89)	494(M^+, 67), 379(74), 351(52), 166(52), 152(90), 15(100)
1b	1.09 (t, J=7.2Hz, 6H, 5-CH_3), 1.45 (t, J=7.2Hz, 6H, 4-CH_3), 4.19 (q, J=7.2Hz, 4H, 5-CH_2), 4.45 (q, J=7.2Hz, 4H, 4-CH_2), 7.45 (d, J=7.3Hz, 2H, H-2′), 7.71 (dd, J=8.2, 7.3Hz, 2H, H-3′) 8.25 (d, J=8.2Hz, 2H, H-4′)	1735, 1730, 1285, 1205, 1055, 830	289(4.05), 221(4.94)	550(M^+, 25), 421(10) 274(16), 166(40) 152(48), 29(100)
1c	0.94 (d, J=6.3Hz, 3H, 5-CH_3), 1.01 (d, J=6.3Hz, 3H, 5-CH_3), 1.43 (d, J=6.3Hz, 3H, 4-CH_3), 1.44 (d, J=6.3Hz, 3H, 4-CH_3), 4.96 (m, 2H, 5-CH), 5.30 (m, 2H, 4-CH), 7.43 (d, J=7.3Hz, 2H, H-2′), 7.70 (dd, J=8.4, 7.3Hz, 2H, H-3′), 8.25 (d, J=8.4Hz, 2H, H-4′)	1750, 1735, 1725, 1715, 1290, 1200, 1050, 835	289(3.99), 221(4.87)	606(M^+, 7), 303(12), 276(14), 232(10), 152(15), 43(100)
1d	1.12 (s, 18H, 5-CH_3), 1.63 (s, 18H, 4-CH_3), 7.40 (d, J=7.3Hz, 2H, H-2′), 7.69 (dd, J=8.5, 7.3Hz, 2H, H-3′), 8.23 (d, J=8.5Hz, 2H, H-4′)	1730, 1300, 1245, 1160, 1060, 835	288(3.99), 222(4.88)	662(M^+, 5), 421(18), 366(23), 205(16), 56(48), 41(100)
1e	1.40 (t, J=7.2Hz, 6H, 4-CH_3), 4.38 (q, J=7.2Hz, 4H, 4-CH_2), 7.60 (d, J=7.3Hz, 2H, H-2′), 7.76 (dd, J=8.5, 7.3Hz, 2H, H-3′), 8.07 (s, 2H, H-5), 8.28 (d, J=8.5Hz, 2H, H-4′)	1715, 1270, 1220, 1040, 830	289(4.07) 223(4.91)	406(M^+, 38), 304(59) 277(32), 249(77), 205(100), 29(87)
1f	1.07 (t, J=7.2Hz, 6H, 5-CH_3), 4.15 (q, J=7.2Hz, 4H, 5-CH_2), 7.41 (d, J=7.3Hz, 2H, H-2′), 7.70 (dd, J=8.3, 7.3Hz, H-3′), 7.90 (s, 2H, H-4), 8.24 (d, J=8.3Hz, 2H, H-4′)	1735, 1310, 1285, 1200, 1075, 830	288(3.98), 222(4.91)	406(M^+, 100), 277(20), 249(60), 205(57), 152(32), 29(60)
1g	1.14 (t, J=7.2Hz, 3H, 5″-CH_3), 1.42 (t, J=7.2Hz, 3H, 4-CH_3), 4.17 (q, J=7.2Hz, 2H, 5″-CH_2), 4.42 (q, J=7.2Hz, 2H, 4-CH_2), 7.47—7.50 (m, 2H, H-2′,7″), 7.70—7.73 (m, 2H, H-3′,6′), 7.86 (s, 1H, H-5), 7.88 (s, 1H, H-4″), 8.25 (d, J=8.3Hz, 2H, H-4′,5′)	1740, 1730, 1720, 1250, 1205, 1080, 1030, 830	288(4.02), 223(4.90)	406(M^+, 78), 277(44), 249(100), 205(94) 152(47), 29(92)
1h	1.14 (t, J=7.2Hz, 3H, 5-CH_3), 1.42 (t, J=7.2Hz, 3H, 4″-CH_3), 1.44 (t, J=7.2Hz, 3H, 4-CH_3), 4.22 (q, J=7.2Hz, 2H, 5-CH_2), 4.39—4.46 (m, 4H, 4,4″-CH_2), 7.50—7.54 (m, 2H, H-2′,7′), 7.70—7.75 (m, 2H, H-3′,6′), 8.01 (s, 1H, H-5″), 8.24—8.28 (m, 2H, H-4′,5′)	1740, 1730, 1260, 1205, 1035, 835	288(4.02), 221(4.85)	478(M^+, 63), 349(20), 249(43), 205(38), 152(49), 29(100)
1i	1.02 (t, J=7.2Hz, 3H, 5″-CH_3), 1.12 (t, J=7.2Hz, 3H, 5-CH_3), 1.45 (t, J=7.2Hz, 3H, 4-CH_3), 4.13—4.20 (m, 4H, 5,5″-CH_2), 4.44—4.51 (m, 2H, 4-CH_2), 7.41—7.43 (m, 2H, H-2′,7″), 7.68—7.73 (m, 2H, H-3′,6′), 7.95 (s, 1H, H-4″), 8.23—8.27 (m, 2H, H-4′,5′)	1735, 1290, 1210, 1065, 835	288(3.95), 222(4.86)	478(M^+, 88), 349(27), 249(43), 205(38), 152(58), 29(100)
1j	7.77 (d, J=7.3Hz, 2H, H-2′), 7.87 (dd, J=8.3, 7.3Hz, 2H, H-3′), 8.48 (d J=8.3Hz, 2H, H-4′), 8.68 (s, 2H, H-5), 13.03 (s, 2H, COOH)	2985, 1745, 1730, 1185, 1060, 835	290(3.93), 225(4.75)	262(34), 206(85), 205(100), 166(18), 139(19),44(880)
1k	7.41 (d, J=1.0Hz, 2H, H-5), 7.47 (d, J=1.0Hz, 2H,H-4), 7.55 (d,J=7.3Hz, 2H, H-2′), 7.72 (dd, J=8.4, 7.3Hz, 2H, H-3′), 8.22 (d, J=8.4Hz, 2H, H-4′)	3140, 3120, 1460, 1215, 1025, 830	288(4.01), 224(4.91)	262(M^+, 68), 206(37) 205(100), 166(18), 140(19), 139(20)

a) Since **1j** was insoluble in $CDCl_3$, the ^{1}H NMR spectrum of **1j** was measured in DMSO-d_6.

by ca. 0.5 ppm than the corresponding protons in **2h**. Similar high field shifts of H-5 and H-4 were observed between **1e** and **2e** and between **1f** and **2f**, respectively. These high field shifts of each proton at the triazole ring can be explained by the considerable anisotropic effects of the other triazole ring. This suggests that the two triazole rings in **1** are facing to each other. On the other hand, according to the crystal structure of **1k**, which is determined by an X-ray diffraction study, the two triazole rings take a face-to-face arrangement and a trans conformation to each other.[6] Thus, the results obtained by NMR analyses about the conformation of these triazole rings are in well accordance with that by X-ray analyses. The extent of the high field shifts for these compounds are comparable to that for the facing benzene rings in 1,8-diphenylnaphthalene ($\Delta\delta$=0.53).[3]

Two kinds of ^{1}H NMR signal for methyl groups, which were assigned to 4- and 5- ester groups in the triazole ring, were observed in **1a**, **1b**, and **1d**. However, **1c** gave four kinds of methyl group resonance, each splitted by methine proton. This phenomenon shows that the two methyl moiety of the isopropyl group are not equivalent magnetically. Such nonequivalency is, as well as in the case of 1-phenyl-8-[3-(1-hydroxy-1-methylethyl)phenyl]naphthalene,[7] well explained by asymmetric environment of the molecule. Only two kinds of the methyl signals were observed in the isopropyl groups of **2c** at room temperature. These results indicate that the rotation around the pivot bond between triazole ring and naphthalene ring is restricted in **1c**. Probably, the two triazole rings hinder the rotation each other. On the

Table 2. Spectroscopic Data of 1-(1-Naphthylene)-1*H*-1,2,3-triazoles

Product	^{1}H NMR ($CDCl_3$)[a]	IR(KBr)	UV(CH_3OH)	MS
	δ/ppm	ν/cm^{-1}	λ/nm (log ε)	m/z (rel intensity, %)
2a	3.69 (s, 3H, 5-CH_3), 4.04 (s, 3H, 4-CH_3), 7.27 (d, J=8.4Hz, 1H, H-8′), 7.51—7.62 (m, 4H, arom.), 7.97 (d,J=8.2Hz, 1H, H-5′), 8.08 (d, J=8.2Hz, 1H, H-4′)	1735, 1300, 1215, 1075, 810	281(4.03), 220(4.86)	311(M^+, 58), 283(8), 251(37), 196(33), 193(58), 127(100)
2b	0.90 (t, J=7.2Hz, 3H, 5-CH_3), 1.46 (t, J=7.2Hz, 3H, 4-CH_3), 4.11 (q, J=7.2Hz, 2H, 5-CH_2), 4.52 (q, J=7.2Hz, 2H, 4-CH_2), 7.28 (d, J=8.4Hz, 1H, H-8′), 7.51—7.63 (m, 4H, arom.), 7.97 (d, J=8.2Hz, 1H, H-5′), 8.08 (d, J=8.1Hz, 1H, H-4′)	1740, 1730, 1200, 1070, 800, 770	282(3.96), 220(4.88)	339(M^+, 54), 265(45), 193(100), 169(61), 127(92), 29(85)
2c	0.85 (d, J=6.3Hz, 6H, 5-CH_3), 1.44 (d, J=6.3Hz, 6H, 4-CH_3), 4.91 (m, 1H, 5-CH), 5.39 (m, 1H, 4-CH), 7.29 (d, J=8.4Hz, 1H, H-8′), 7.50—7.60 (m, 4H, arom.), 7.95 (d J=8.2Hz, 1H, H-5′), 8.06 (d, J=8.1Hz, 1H, H-4′)	1740, 1715, 1260, 1235, 1100, 1065, 810	282(3.92), 220(4.91)	367(M^+, 39), 308(7), 211(37), 193(67), 127(42), 43(100)
2d	0.97 (s, 9H, 5-CH_3), 1.65 (s, 9H, 4-CH_3), 7.28 (d, J=8.4Hz, 1H, H-8′), 7.51—7.62 (m, 4H, arom.), 7.96 (d, J=8.2Hz, 1H, H-5′), 8.08 (d, J=8.1Hz, 1H, H-4′)	1745, 1715, 1260, 1120, 1070, 840	282(4.17), 220(5.10)	395(M^+, 12), 266(12), 211(60), 193(31), 127(20), 57(100)
2e	1.47 (t, J=7.2Hz, 3H, 4-CH_3), 4.51 (q, J=7.2Hz, 2H, 4-CH_2), 7.55—7.63 (m, 5H, arom.), 7.99 (d, J=8.2Hz, 1H, H-5′), 8.07 (m, 1H, H-4′), 8.47 (s, 1H, H-5)	1745, 1240, 1205, 1150, 1040, 810	282(3.98), 220(4.91)	267(M^+, 46), 194(42), 193(35), 167(97), 166(98), 127(100)
2f	0.99 (t, J=7.2Hz, 3H, 5-CH_3), 4.09 (q, J=7.2Hz, 2H, 5-CH_2), 7.11 (d, J=8.4Hz, 1H, H-8′), 7.45—7.61 (m, 4H, arom.), 7.95(d, J=8.1Hz, 1H, H-5′), 8.05 (d, J=8.2Hz, 1H, H-4′), 8.41 (s, 1H, H-4)	1730, 1200 1110, 810	281(4.00), 221(5.03)	267(M^+, 93), 194(42), 193(38), 167(87), 166(100), 127(76)
2g	7.46 (d, J=8.3Hz, 1H, H-8′), 7.63—7.82 (m, 4H, arom.), 8.15 (d, J=8.1Hz, 1H, H-5′), 8.24 (d, J=8.3Hz, 1H, H-4′), 9.25 (s, 1H, H-5), 13.24 (s, 1H, COOH)	2910, 1740, 1720, 1185, 1060, 805	282(3.90), 221(4.82)	239(M^+, 6), 195(13), 167(100), 166(42), 140(18), 127(58)
2h	7.92 (d, J=1.0Hz, 1H, H-5), 7.93 (d, J=1.0Hz, 1H, H-4), 7.47—7.57 (m, 5H, arom.), 7.86—7.95 (m, 2H, H-4′,5′),	3150, 1465, 1235, 1020, 800, 770	281(3.95), 221(4.92)	195(M^+, 55), 167(100), 166(58), 140(22), 139(18), 127(83)

a) Since **2g** was insoluble in $CDCl_3$, the ^{1}H NMR spectrum of **2g** was measured in DMSO-d_6.

other hand, the racemization may occur in **2c** because the rotation around the bond is so fast.

The ^{1}H NMR signals for the methyl moiety in the ester group of 5-position at the triazole ring are at higher field than those of 4-position in **1a—i**. As the similar relationships were observed in **2a—f**, it may be explained by the anisotropic effect of the naphthalene ring.

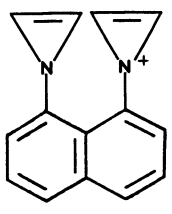
The UV spectra of **1** are almost identical with each other (ca. 221 and 288 nm) and independent of the substituents on the triazole ring, and show a red shift from those of **2**. The extent of the red shift is about 7 nm for the longest wavelength absorption band. Since the absorption band due to the triazole ring exists at ca. 210 nm,[8] the longest wavelength band is assigned to naphthalene ring. The same kind of red shift has been observed between the absorption of 1,8-diphenylnaphthalene and 1-phenylnaphthalene.[9]

In IR spectra, absorptions of C=O (ca. 1700—1750 cm^{-1}) and C-O-C (ca. 1200—1300 cm^{-1}) groups were observed in addition to those of the triazole (ca. 1000—1100 cm^{-1}) and naphthalene rings (ca. 750—850 cm^{-1}) in **1a—j** and **2a—g**. Both **1k** and **2h** show C-H stretching in triazole ring at ca. 3100—3150 cm^{-1}. No significant spectral differences between **1** and **2** were observed in the IR spectra.

In the MS spectra of **1**, molecular ions were observed except for the carboxylic acid, **1j**. The MS spectrum data show that the molecular ion peaks become weaker with the size of the ester groups at the triazole ring become bulkier, as seen in usual carboxyric acid and esters. The fragment ion (m/z=167) of the azirine type, which was generated by the nitrogen elimination from molecular ion, was found in the parent molecules, **2h**. Such fragmentation was reported in the MS spectra of 1-phenyl-1*H*-1,2,3-triazoles.[10] Moreover, the fragment ion (m/z=206) with two azirine groups at peri-position in the naphthalene ring **4** was found in **1k**. The m/z 166 ion, which was produce by the further elimination of one azirine ring from **4**, was also observed in **1k**.

Experimental

Instruments. All melting points were determined on a Mettler FP61 instrument and were uncorrected. ^{1}H NMR spectra were obtained by a JEOL GX-400 spectrometer (399.65 MHz for ^{1}H nuclei) using TMS as an internal standard. IR and UV spectra were measured on a Nicolet 170SX



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and a Shimadzu MPS-2000 spectrometer, respectively. MS spectra were measured with a JEOL JMS-01SG-2 spectrometer at 75 eV of ionization energy. Elemental analyses were performed on a Yanaco MT-3 CHN micro analyzer.

Materials. 1,8-Diazidonaphthalene and 1-azidonaphthalene were prepared from 1,8-diaminonaphthalene and 1-aminonaphthalene as previously reported, respectively.[11,12] Diisopropyl acetylenedicarboxylate was prepared from acetylenedicarboxyric acid and isopropyl alcohol,[13] and di-*t*-butyl acetylenedicarboxylate was synthesized from acetylenedicarboxylic acid and 1-butene according to the synthetic method of di-*t*-butyl malate.[14] Dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, and ethyl propiolate were commercially available.

Reaction of 1,8-Diazidonaphthalene with Acetylene Carboxylates. To a solution of 1,8-diazidonaphthalene (1.0 g, 4.8 mmol) in diethyl ether (10 ml), a large excess of dimethyl acetylenedicarboxylate (5.0 g, 35.2 mmol) was added and the mixture was allowed to react at room temperature in the dark. It took 14 d until the products with two triazole rings were formed. After the completion of the reaction was checked by TLC (silica gel, diethyl ether), the mixture was purified by chromatographic separation on silica gel (Waco gel C-100) with a diethyl ether-dichloromethane mixture to give **1a**.

Tetramethyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-4,5-dicarboxylate(**1a**): Colorless prisms from methanol; mp 222—223 °C, 2.1 g (89%). Found: C, 53.72; H, 3.66; N, 16.86%. Calcd for $C_{22}H_{18}N_6O_8$: C, 53.44; H, 3.67; N, 17.00%.

Similarly, the reactions of 1,8-diazidonaphthalene (1.0 g, 4.8 mmol) with about 8 times as much excess of diethyl, diisopropyl, and di-*t*-butyl acetylenedicarboxylates gave **1b**, **1c**, and **1d**, respectively.

Tetraethyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-4,5-dicarboxylate (**1b**): Colorless prisms from methanol; mp 138—139 °C, 2.2 g (85%). Found: C, 56.81; H, 4.63; N, 15.14%. Calcd for $C_{26}H_{26}N_6O_8$: C, 56.72; H, 4.76; N, 15.27%.

Tetraisopropyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-4,5-dicarboxylate (**1c**): Colorless needles from methanol; mp 107—108 °C, 2.5 g (86%). Found: C, 59.30; H, 5.50; N, 13.71%. Calcd for $C_{30}H_{34}N_6O_8$: C, 59.40; H, 5.65; N, 13.85%.

Tetra-*t*-butyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-4,5-dicarboxylate(**1d**): Colorless needles from methanol; mp 160—161 °C, 2.5 g (80%). Found: C, 61.83; H, 6.62; N, 12.50%. Calcd for $C_{34}H_{42}N_6O_8$: C, 61.62; H, 6.39; N, 12.68%.

In the similar reaction of the 1,8-diazidonaphthalene (1.0 g, 4.8 mmol) with ethyl propiolate (3.5 g, 35.7 mmol) for 14 d, the following three possible products were all isolated by chromatography on silica gel with a diethyl ether-dichloromethane mixture.

Diethyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-4-carboxylate (**1e**): Colorless needles from methanol; mp 173—174 °C, 1.0 g (52%). Found: C, 58.88; H, 4.22; N, 20.59%. Calcd for $C_{20}H_{18}N_6O_4$: C, 59.11; H, 4.46; N, 20.68%.

Diethyl 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazole-5-carboxylate (**1f**): Colorless needles from methanol; mp 175—176 °C, 35 mg (2%). Found: C, 58.80; H, 4.46; N, 20.47%. Calcd for $C_{20}H_{18}N_6O_4$: C, 59.11; H, 4.46; N, 20.68%.

Ethyl 1-[8-(5-ethoxycarbonyl-1*H*-1,2,3-triazol-1-yl)-1-naphthyl]-1*H*-1,2,3-triazole-4-carboxylate (**1g**): Colorless needles from methanol; mp 128—129 °C, 460 mg (24%). Found: C, 59.36; H, 4.26; N, 20.57%. Calcd for $C_{20}H_{18}N_{60}O_4$: C, 59.11; H, 4.46; N, 20.47%.

Identical reaction for 24 h gave the intermediate 1 : 1 adducts, **3a** and **3b**, in the maximum yields, and they were isolated by chromatography on silica gel with a hexane-diethyl ether mixture.

Ethyl 1-(8-azido-1-naphthyl)-1*H*-1,2,3-triazole-4-carboxylate (**3a**): Pale yellow needles from methanol; mp 135—136 °C, 700 mg (48%). ^{1}H NMR ($CDCl_3$) δ=1.48 (t, J=7.2 Hz, 3H, CH_3), 4.51 (q, J=7.2 Hz, 2H, CH_2), 7.31 (d, J=7.5 Hz, 1H, H-7′), 7.47 (d, J=7.3 Hz, 1H, H-2′), 7.58 (dd, J=8.1, 7.5 Hz, 1H, H-6′), 7.60 (dd, J=8.3, 7.3 Hz, 1H, H-3′), 7.77 (d, J=8.1 Hz, 1H, H-5′), 8.06 (d,J=8.3 Hz, 1H, H-4′), 8.34 (s, 1H, H-5). IR (KBr) 2130 (N_3), 1730 (C=O) cm^{-1}. MS m/z (rel intensity, %) 308 (10), 280 (9), 208 (96), 180 (35), 126 (100). Found: C, 58.34; H, 3.88; N, 27.03%. Calcd for $C_{15}H_{12}N_6O_2$: C, 58.44; H, 3.92; N, 27.26%.

Ethyl 1-(8-azido-1-naphthyl)-1*H*-1,2,3-triazole-5-carboxylate (**3b**): Pale yellow needles from methanol; mp 109—110 °C, 250 mg (17%). ^{1}H NMR ($CDCl_3$) δ=1.07 (t, J=7.2 Hz, 3H, CH_3), 4.14 (m, 2H, CH_2), 7.27 (d, J=7.4 Hz, 1H, H-7′), 7.42 (d, J=7.3 Hz, 1H, H-2′), 7.55 (dd, J=8.2, 7.4 Hz, 1H, H-6′), 7.60 (dd, J=8.3, 7.3 Hz, 1H, H-3′), 7.77 (d, J=8.2 Hz, 1H, H-5′), 8.05 (d, J=8.3 Hz, 1H, H-4′), 8.34 (s, 1H, H-4). IR (KBr) 2125 (N_3), 1730 (C=O) cm^{-1}. MS m/z (rel intensity, %) 308 (28), 280 (37), 208 (10), 180 (100), 126 (96). Found: C, 58.27; H, 3.86; N, 27.15%. Calcd for $C_{15}H_{12}N_6O_2$: C, 58.44; H, 3.92; N, 27.26%.

The reaction of **3a** (200 mg, 0.65 mmol) and **3b** (200 mg, 0.65 mmol) with 5 times as much excess of diethyl acetylenedicarboxylate for 14 d at room temperature gave **1h** and **1i**, respectively.

Diethyl 1-[8-(4-ethoxycarbonyl-1*H*-1,2,3-triazol-1-yl)-1-naphthyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate(**1h**): Colorless needles from methanol; mp 130—131 °C, 210 mg (68%). Found: C, 57.74; H, 4.66; N, 17.49%. Calcd for $C_{23}H_{22}N_6O_6$: C, 57.74; H, 4.63; N, 17.56%.

Diethyl 1-[8-(5-ethoxycarbonyl-1*H*-1,2,3-triazol-1-yl)-1-naphthyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate(**1i**): Colorless needles from methanol; mp 170—171 °C, 190 mg (61%). Found: C, 57.58; H, 4.45; N, 17.52%. Calcd for $C_{23}H_{22}N_6O_6$: C, 57.74; H, 4.63; N, 17.56%.

Hydrolysis of 1e. A suspension of **1e** (500 mg, 1.2 mmol) in aqueous NaOH (1.0 g, 25 mmol, 40 ml) was refluxed for 12 h. On adjusting the solution to pH 5 with aqueous HCl, a precipitate was formed immediately. The precipitate was collected by filtration and recrystallized from water to give **1j** as colorless needles.

1,1′-(1,8-Naphthylene)di-1*H*-1,2,3-triazole-4-carboxylic acid (**1j**): mp 253—254 °C, 350 mg (81%). Found: C, 54.99; H, 2.94; N, 24.02%. Calcd for $C_{16}H_{10}N_6O_4$: C, 54.86; H, 2.88; N, 23.99%.

Decarboxylation of 1j. The crystals of **1j** (320 mg, 0.91 mmol) were decarboxylated by heating at 180 °C for 3 h under a nitrogen atmosphere. Sublimation of the crude product gave pure **1k** as colorless needles.

1,1′-(1,8-Naphthylene)di-1*H*-1,2,3-triazole(**1k**): mp > 300 °C, 235 mg (92%). Found: C, 63.98; H, 3.78; N, 32.05%. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04%.

Preparation of 1-(1-Naphthyl)-1*H*-1,2,3-triazoles. By the reaction of 1-azidonaphthalene (1 g, 5.92 mmol) with 5 times as much excess of acetylenecarboxylates at room temperature for 72 h, **2a—f** were synthesized and purified by silica-gel chromatography with hexane-diethyl ether.

Dimethyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate

(**2a**): Colorless needles from hexane-diethyl ether, mp 122—123 °C, 1.5 g (81%). Found: C, 61.54; H, 4.21; N, 13.39%. Calcd for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50%.

Diethyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (**2b**): Oil, 1.5 g (75%). Found: C, 63.56; H, 5.16; N, 12.52%. Calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38%.

Diisopropyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (**2c**): Colorless prisms from hexane-diethyl ether, mp 105—106 °C, 1.9 g (87%). Found: C, 65.22; H, 5.73; N, 11.37%. Calcd for $C_{20}H_{21}N_3O_4$: C, 65.38; H, 5.76; N, 11.44%.

Di-*t*-butyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (**2d**): Colorless prisms from hexane-diethyl ether, mp 142—143 °C, 1.9 g (81%). Found: C, 66.75; H, 6.25; N, 10.48%. Calcd for $C_{22}H_{25}N_3O_4$: C, 66.82; H, 6.37; N, 10.63%.

Ethyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4-carboxylate (**2e**): Colorless needles from hexane-diethyl ether, mp 101—102 °C, 1.1 g (71%). Found: C, 67.31; H, 4.83; N, 15.64%. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.90; N, 15.72%.

Ethyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-5-carboxylate (**2f**): Colorless needles from hexane-diethyl ether, mp 102—103 °C, 280 mg (18%). Found: C, 67.50; H, 4.72; N, 15.77%. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.90; N, 15.72%.

Hydrolysis of **2e** (1 g, 3.7 mmol) as in the case of **1e** gave **2g**.

1-(1-Naphthyl)-1*H*-1,2,3-triazole-4-carboxylic acid (**2g**): Colorless needles from water, mp 147—148 °C, 0.8 g (89%). Found: C, 65.23; H, 3.76; N, 17.56%. Calcd for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56%.

Decarboxylation of **2g** (0.5 g, 2.1 mmol) was performed in a similar manner to that of **1j**, and pure **2h** was obtained by sublimation as colorless needles.

1-(1-Naphthyl)-1*H*-1,2,3-triazole (**2h**): mp 102—103 °C, 380 mg (93%). Found: C, 73.77; H, 4.51; N, 21.60%. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52%.

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