July, 1994] © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 1931—1935(1994)

Synthesis, Properties, and Crystal Structure of a 1,1′-Bis(ethoxycarbonyl)trichotomine Derivative

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(Received February 17, 1994)

On an oxidative dimerization in dichloromethane containing diisopropylamine, methyl 1-ethoxycarbonyl-2,5,6,11-tetrahydro-3-oxo-3*H*-indolizino[8,7-*b*]indole-5-carboxylate gave a trichotomine derivative bearing ethoxycarbonyl groups on C_1 and $C_1{}'$. In the presence of triethylamine, the initially formed trichotomine derivative changed to a blue compound, which had the skeleton of the trichotomine derivative and a =CH–CH= group. The X-ray crystallographic analysis of the trichotomine derivative showed the torsion around the central C–C double bond, and the dihedral angle of the adjacent two five-membered rings was 30.0°. This torsion is due to the steric interactions between the ethoxycarbonyl groups and the amido carbonyl groups, and might explain the difference of the $\lambda_{\max}$ between the trichotomine derivative (690 nm) and the blue compound (633 nm).

A blue pigment, trichotomine (**1**), was isolated from *Clerodendron trichotomum* Thunb, and its dimethyl ester **2** was synthesized by an oxidative dimerization of **3**.[1,2] The X-ray crystallographic analysis of a *p*-bromobenzoyl derivative **4** revealed that the two indole moities were not on a plane and the dihedral angle was 38.6 degree.[3] It was also documented that *N*,*N*′-diacylindigos (**5a**) were twisted around the central C_2–$C_2{}'$ double bond due to the steric interactions between the acyl groups and the amido carbonyl groups.[4] In a previous paper, we reported the similarity of **1** to indigo (**5b**).[5] Introduction of substituents on C_1 and $C_1{}'$ of **2** seemed to cause twisting of the central C_2–$C_2{}'$ double bond similar to that described in **5a**. This paper deals with the synthesis, properties, and crystal structure of a trichotomine derivative **6** bearing ethoxycarbonyl groups on C_1 and $C_1{}'$.

Results and Discussion

Synthesis and Properties of a Trichotomine Derivative 6. L-Tryptophan methyl ester was condensed with diethyl formylsuccinate to give four isomers **7a**—**7d**. The configurations of the C_1- and C_{11b}-protons in **7a**—**7d** were assigned as follows. The low-field C_5-proton signals of **7a** (δ=5.37) and **7d** (δ=5.39) indicated the β-orientations of the C_{11b}-proton in **7a** and **7d**, while the high-field C_5-proton signals of **7b** (δ=4.14) and **7c** (δ=4.00) suggested the α-orientations of the C_{11b}-proton in **7b** and **7c**.[5] In the NOESY spectra of **7b** and **7c**, the NOEs between the C_5- and C_{11b}-protons were observed, respectively, supporting the assignments mentioned above. The cis relationships of C_1- and C_{11b}-protons in **7c** and **7d** were determined by the NOEs in the NOESY spectra of **7c** and **7d**.

The isomer **7d** was dehydrogenated with *N*-bromosuccinimide (NBS) to give **8**. On autoxidation in dichloromethane containing diisopropylamine, **8** yielded a greenish blue pigment **6** and a trace of **9**. The structure of **6** was in line with its spectral data (^{1}H and ^{13}C NMR, and MS). Oxidation of **8** with pyridinium dichromate afforded **9**, which was identical with that obtained above. Conveniently, **6** was prepared from **7d** in a one-pot reaction. On stirring with NBS in dichloromethane at 20 °C for 20 min, and then with diisopropylamine at room temperature for 33 h, **7d** yielded **6** in 37% yield (Chart 1).

In the presence of triethylamine, **8** also underwent an oxidative dimerization to give **6**, identical to that obtained above by TLC and ^{1}H NMR comparisons. But, the initially formed **6** dissappeared gradually and a blue compound **10** was obtained in 10% yield. The ^{1}H and ^{13}C NMR spectra of 10 showed a good correspondence to those of **6**, respectively, except for a singlet proton signal at δ=9.30 (C_{12}–H) and a carbon signal at δ=133.6 (C-12). The COLOC NMR spectrum of **10** showed cross-peaks between the proton signal at δ=9.30 and the carbon signals at δ=102.3 (C-1) and 130.5 (C-2). The FABMS spectrum of **10** showed a molecular ion peak at m/z 730, which was larger than that of **6** by 26 mass unit. These spectral data suggested the presence of a =CH–CH= group, and were in line with the described structure of **10**. The geometry of the C_2–C_{12} double bond in **10** is undetermined. The absorption spectrum of **10** showed the $\lambda_{\max}$ at 633 nm, which was shorter than that of **6** ($\lambda_{\max}$=690 nm). Similar trend was reported between indigo (**5b**) and 2,2′-ethanediylidenebis[3-indolinone].[6] On autoxidation in the presence of triethylamine, **3** yielded **2** and **11**, and no such compound as **10** was obtained. Accordingly, **6** seemed to be more reactive than **2** because of the stereoelectronic effect of the C_1- and $C_1{}'$- ethoxycarbonyl groups, and the torsion around the central C_2–$C_2{}'$ double bond. The blue compound **10** might be formed via the cycloaddition reaction of the C_2–$C_2{}'$ double bond of the initially formed **6** with *N*,*N*-diethylethenamine generated in situ from triethylamine.[7,8]

Reaction of **6** with another nucleophile was examined. On treatment with crotonaldehyde and diisopropylamine, **6** afforded a red compound **12** ($\lambda_{\max}$=511 nm). The ^{1}H NMR spectrum of **12** showed signals of four

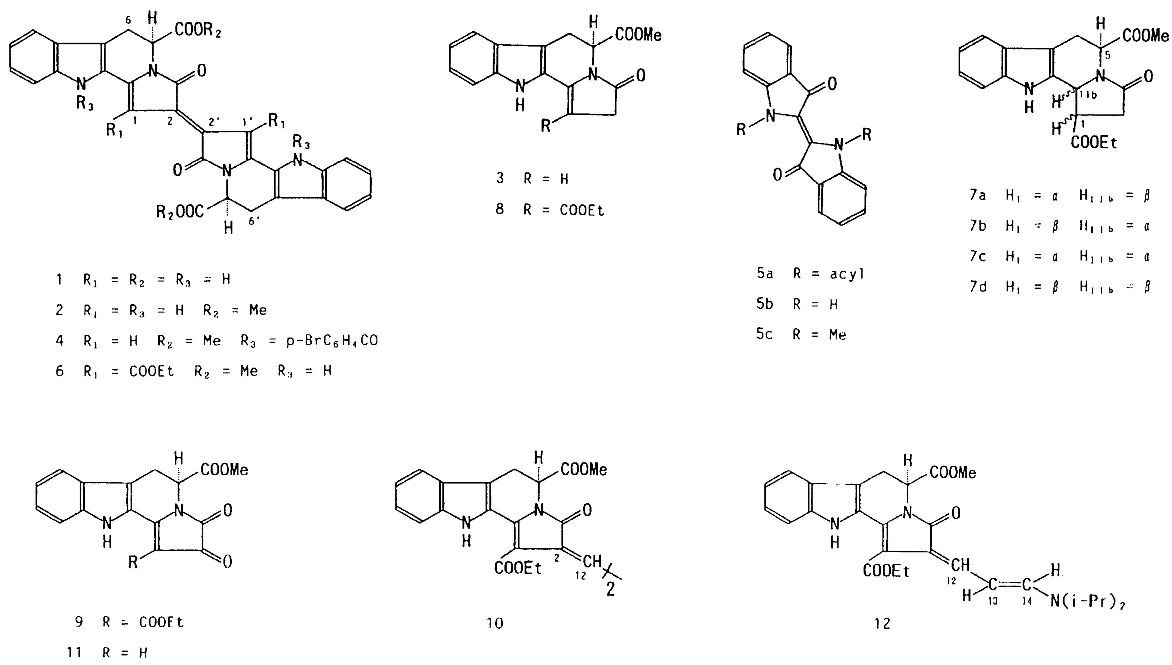

Chart 1.

secondary methyl groups (δ=1.29, d, 12H), and three olefinic proton signals at δ=7.01 (1H, d, J=12.5 Hz, C_{14}–H), 7.45 (1H, t, J=12.5 Hz, C_{13}–H), and 7.82 (1H, d, J=12.5 Hz, C_{12}–H). The ^{13}C NMR spectrum of **12** indicated olefinic carbon signals at δ=100.6 (C-13), 146.4 (C-12), and 150.6 (C-14) in addition to the corresponding carbon signals of **6**. The COLOC NMR spectrum of **12** showed cross peaks between the proton signal at δ=7.82 and the carbon signals at δ=102.0 (C-1), 150.6, and 166.5 (C-3), and between the proton signal at δ=7.45 and the carbon signal at δ=111.2 (C-2). The FABMS of **12** showed a molecular ion peak at m/z 491. These spectral data were in agreement with the described structure of **12**. The geometry of the C_{13}–C_{14} double bond of **12** was assigned to be E from the coupling constant, but that of the C_2–C_{12} double bond was undetermined. Under similar conditions used above, **2** was stable and did not give such a compound as **12**. Formation of **12** also seemed to proceed via the cycloaddition reaction of the reactive C_2–$C_2{}'$ double bond of **6** with *N*,*N*-diisopropyl-1,3-butadien-1-amine generated in situ from crotonaldehyde and diisopropylamine.[9]

In order to confirm the torsion around the C_2–$C_2{}'$ double bond, a crystal of **6** was subjected to X-ray crystallographic analysis.

X-Ray Crystallographic Analysis of 6. ORTEP drawing of the half of **6** is shown in Fig. 1. The numberings in Fig. 1 are arbitary, and not consistent with those of the IUPAC nomencleature. Figure 2 shows the perspective view of the unit cell along the b axis. The molecule has C_2 symmetry, and the geometry of the central double bond is E.

Each five-membered ring neighboring to the central double bond is planar with the maximum deviation of 0.02 Å, and the dihedral angles between them is 30.0°. It is reported that the shape of *N*,*N*′-dimethylindigo (**5c**) is a bent propeller, and the two halves of **5c** are twisted by 26° and tilted in the same direction by 9.5° with respect to the central C–C bond.[10] The shape of **6** is similarly a bent propeller, and the corresponding twisting and tilting angles are 19° and 11°, respectively. The carbonyl oxygen O(1) and the carbon C(17) of the ethoxycarbonyl group are bent away from the plane of the five-membered ring; the bending angle of O(1) is 6.7°, and that of C(17) is 12.2° in an opposite direction to the bending of O(1). The torsion around the central C_2–$C_2{}'$ double bond of **6** is due to the interactions

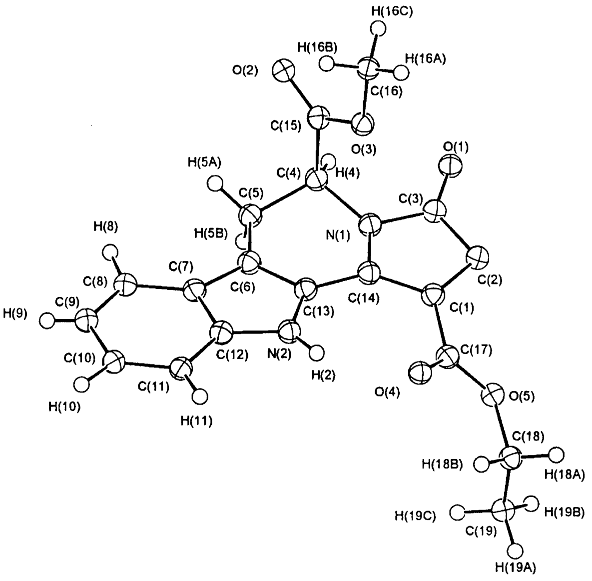

Fig. 1. ORTEP drawing of the half of **6**.

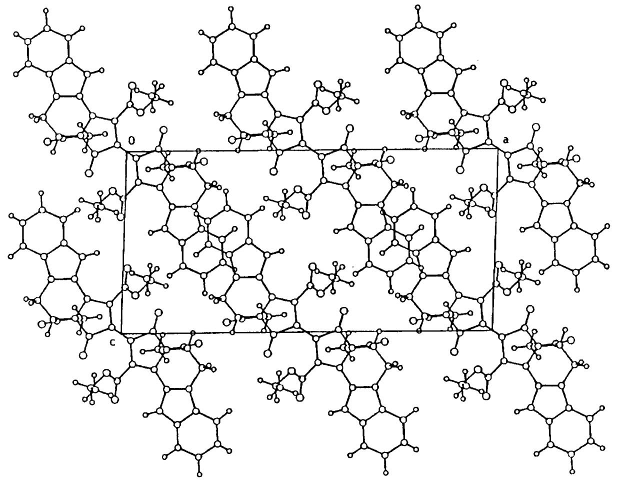

Fig. 2. Perspective view of the unit cell along the *b* axis.

between the ethoxycarbonyl groups and the amido carbonyl groups, and might explain the difference of the $\lambda_{\max}$ between **6** (690 nm) and **10** (633 nm).[11]

Each indole ring is also planar within the deviation of 0.02 Å. The dihedral angle between the indole ring and the five-membered ring in the half of **6** is 6.2°, and that between the two indole rings is 18.0°. As shown in Fig. 3, it is interesting that the ethoxycarbonyl and the methoxycarbonyl groups are located almost perpendicularly out of the molecular plane.

A long conjugated system between the two indole rings in **6** is indicated by the bond lengths of C(13)–C(14), C(1)–C(14), C(1)–C(2), and C(2)–C(2), as shown in Table 1; the bond lengths of C(13)–C(14) and C(1)–C(2) are shorter than a normal single C–C bond length, and those of C(1)–C(14) and C(2)–C(2) are longer than that of ethene (1.337 Å).[12] The intermolecular distances are large (>3.0 Å), and the molecular interaction in a crystal would be a van der Waals force.

Experimental

All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC300 (300 MHz, 75 MHz) using $CDCl_3$ as a solvent. Absorption spectra were recorded on a Shimadzu-UV-3100. Mass spectra were obtained on a JEOL-DX303.

Preparation of 7a—7d. A mixture of L-tryptophan methyl ester (2.18 g, 10 mmol), diethyl formylsuccinate (2.22 g, 11 mmol), and molecular sieves 4A (8 g) in dry benzene (150 ml) was refluxed for 1 h. Molecular sieves were removed by filtration. To the filtrate was added 10-camphorsulfonic acid (0.3 g). The resulting mixture was refluxed for 40 h, washed with aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure to leave an oil, which showed the spots of **7a** (R_f 0.62), **7b** (R_f 0.55), **7c** (R_f 0.32), and **7d** (R_f 0.21) on TLC (SiO_2, MeOH : $CHCl_3$=1 : 20). Separation by column chromatography (SiO_2–$CHCl_3$) gave **7a** (0.98 g, 28%), **7b** (0.96 g, 27%), **7c** (23 mg, 0.6%), and **7d** (0.65 g, 18%).

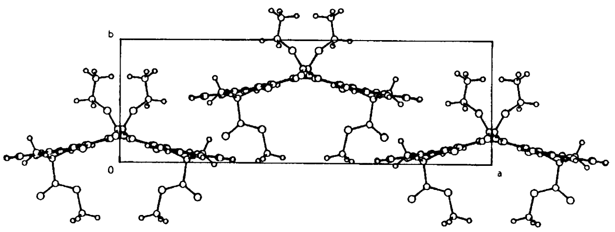

Fig. 3. Perspective view of the unit cell along the *c* axis.

Table 1. Bond Lengths (Å) of **6**

N(2)–C(13)	1.374(6)	N(2)–C(12)	1.378(6)
N(1)–C(14)	1.399(6)	N(1)–C(3)	1.380(6)
N(1)–C(4)	1.470(6)	C(13)–C(14)	1.414(6)
C(13)–C(6)	1.393(6)	O(1)–C(3)	1.201(6)
C(12)–C(11)	1.389(7)	C(12)–C(7)	1.411(7)
C(1)–C(14)	1.396(7)	C(1)–C(2)	1.440(6)
C(1)–C(17)	1.470(7)	C(3)–C(2)	1.503(6)
C(6)–C(7)	1.411(7)	C(6)–C(5)	1.493(7)
C(2)–C(2)	1.366(6)	C(4)–C(15)	1.528(8)
C(4)–C(5)	1.529(7)	C(11)–C(10)	1.378(8)
O(4)–C(17)	1.196(6)	C(7)–C(8)	1.415(7)
C(17)–O(5)	1.345(7)	O(5)–C(18)	1.467(9)
C(8)–C(9)	1.369(8)	O(2)–C(15)	1.192(8)
C(10)–C(9)	1.402(8)	O(3)–C(15)	1.323(7)
O(3)–C(16)	1.475(10)	C(18)–C(19)	1.310(18)

7a: Mp 190—191°C ($CHCl_3$–hexane); ^{1}H NMR δ=1.40 (3H, t, J=7.1 Hz), 2.79 (1H, dd, J=16.7 and 9.2 Hz), 2.98 (1H, dd, J=16.7 and 11.5 Hz), 3.07—3.23 (2H, m), 3.45 (1H, d, J=15.8 Hz), 3.65 (3H, s), 4.36 (2H, q, J=7.1 Hz), 5.29 (1H, d, J=9.2 Hz), 5.37 (1H, d, J=7.1 Hz), 7.08—7.52 (4H, m), and 8.96 (1H, br s). Anal. ($C_{19}H_{20}N_2O_5$) C,H,N.

7b: Mp 89—94°C ($CHCl_3$–hexane); ^{1}H NMR δ=1.38 (3H, t, J=7.1 Hz), 2.67 (1H, dd, J=16.8 and 9.4 Hz), 2.93 (1H, dd, J=16.8 and 10.7 Hz), 3.00 (1H, dd, J=15.6 and 4.6 Hz), 3.21—3.33 (2H, m), 3.80 (3H, s), 4.14 (1H, dd, J=9.8 and 4.6 Hz), 4.33 (2H, q, J=7.1 Hz), 5.07 (1H, d, J=8.4 Hz), 7.08—7.50 (4H, m), and 8.88 (1H, br s). Found: m/z 356.1385. Calcd for $C_{19}H_{20}N_2O_5$: M, 356.1371.

7c: Mp 215—216°C ($CHCl_3$–hexane); ^{1}H NMR δ=1.23 (3H, t, J=7.1 Hz), 2.59 (1H, dd, J=17.4 and 10.5 Hz), 2.72 (1H, dd, J=17.4 and 9.0 Hz), 3.05 (1H, dd, J=15.8 and 4.5 Hz), 3.38 (1H, dd, J=15.8 and 11.5 Hz), 3.80 (1H, m), 3.87 (3H, s), 4.00 (1H, dd, J=11.5 and 4.5 Hz), 4.22 (2H, q, J=7.1 Hz), 5.40 (1H, br d, J=7.7 Hz), 7.09—7.54 (4H, m), and 8.65 (1H, br s). Found: m/z 356.1343. Calcd for $C_{19}H_{20}N_2O_5$: M, 356.1371.

7d: Mp 212—214°C ($CHCl_3$–hexane); ^{1}H NMR δ=0.74 (3H, t, J=7.1 Hz), 2.77 (1H, d, J=16.8 Hz), 2.89 (1H, dd, J=16.8 and 7.6 Hz), 3.08 (1H, dd, J=15.6 and 7.0 Hz), 3.42 (1H, d, J=15.6 Hz), 3.62 (3H, s), 3.65 (1H, m), 3.77 (2H, q, J=7.1 Hz), 5.39 (1H, d, J=7.0 Hz), 5.56 (1H, d, J=7.1 Hz), 7.07—7.51 (4H, m), and 8.52 (1H, br s). Anal. ($C_{19}H_{20}N_2O_5$) C,H,N.

Preparation of 8. To a solution of **7d** (107 mg, 0.30 mmol) in CH_2Cl_2 (20 ml) was added NBS (70 mg, 0.39 mmol). The solution was stirred at 20 °C for 20 min, and worked up in the usual way to give **8** (77 mg, 73%): Mp 176—179 °C ($CHCl_3$—hexane); UV (CH_3OH) 223 (ε 23200), 300 (9000), 354 (21700), and 372 nm (17600); ^{1}H NMR δ= 1.37 (3H, t, J=7.1 Hz), 3.35 (1H, dd, J=16.8 and 7.5 Hz), 3.51 (1H, d, J=24.3 Hz), 3.64 (1H, d, J=24.3 Hz), 3.64 (3H, s), 3.76 (1H, d, J=16.8 Hz), 4.31 (2H, m), 5.22 (1H, d, J=7.5 Hz), 7.12—7.63 (4H, m), and 11.42 (1H, br s). Found: m/z 354.1207. Calcd for $C_{19}H_{18}N_2O_5$: M, 354.1213.

Autoxidation of 8. A solution of **8** (30 mg) an i-Pr_2NH (0.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temperature for 48 h, and concentrated under reduced pressure. The residue was separated by column chromatography (SiO_2–$CHCl_3$) to give **6** (10 mg, 33%) and **9** (0.2 mg, 0.7%). **6**: Mp 271—272°C ($CHCl_3$–CH_3OH); UV ($CHCl_3$) 376 (ε 24400) and 690 nm (77900); ^{1}H NMR δ=1.30 (3H×2, t, J=7.1 Hz), 3.42 (1H×2, dd, J=16.9 and 7.5 Hz), 3.59 (3H×2, s), 3.86 (1H×2, d, J=16.9 Hz), 4.37 (2H×2, q, J=7.1 Hz), 5.28 (1H×2, d, J=7.5 Hz), 7.12—7.64 (4H×2, m), and 10.80 (1H×2, br s); ^{13}C NMR δ=14.3 ($OCH_2\underline{C}H_3$), 23.9 (C-6), 50.8 (C-5), 53.2 (OCH_3), 61.3 ($O\underline{C}H_2CH_3$), 105.4 (C-1), 112.7 (C-10), 117.3 (C-6a), 120.2 (C-7), 121.0 (C-8), 123.9 (C-11a), 125.7 (C-6b), 126.8 (C-9), 127.6 (C-2), 139.4 (C-10a), 140.7 (C-11b), 166.2 (C-3), 167.0 ($\underline{C}$OOEt), and 170.0 ($\underline{C}$OOMe); MS m/z 704 (M^+). Anal. ($C_{38}H_{32}N_4O_{10}$) C,H, N.

Preparation of 9. To a solution of **8** (30 mg, 0.085 mmol) in dry CH_2Cl_2 (30 ml) was added pyridinium dichromate (160 mg, 0.43 mmol). The mixture was stirred at 20°C for 7 h, and worked up in the usual way. Purification by column chromatography (SiO_2–$CHCl_3$) gave **9** (5 mg, 16%), which was identical with that obtained above by TLC and ^{1}H NMR comparisons. **9**: Mp 181—184°C ($CHCl_3$–hexane); UV (CH_3OH) 206 (ε 22800), 367 (16700), and 443 nm (22500); ^{1}H NMR δ=1.45 (3H, t, J=7.1 Hz), 3.53 (1H, dd, J=17.6 and 7.5 Hz), 3.66 (3H, s), 3.95 (1H, d, J=17.6 Hz), 4.44 (2H, m), 5.33 (1H, d, J=7.5 Hz), 7.20—7.72 (4H, m), and 12.67 (1H, br s). Found: m/z 368.1027. Calcd for $C_{19}H_{16}N_2O_6$: M, 368.1007.

One-Pot Preparation of 6 from 7d. A mixture of **7d** (71 mg, 0.20 mmol) and NBS (47 mg, 0.26 mmol) in CH_2Cl_2 (15 ml) was stirred at 20°C for 20 min. To this solution was added i-Pr_2NH (0.5 ml). The resulting solution was stirred at room temperature for 33 h, washed successively with aqueous HCl, water, and brine, and then dried over Na_2SO_4. Evaporation of the solvent and separation by column chromatography (SiO_2–$CHCl_3$) gave **6** (26 mg, 37%) and **9** (0.6 mg, 1%).

Formation of 10. A solution of **8** (30 mg) and Et_3N (0.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temperature for 48 h, and concentrated under reduced pressure. The residue was separated by column chromatography (SiO_2–$CHCl_3$) to give **10** (3 mg, 10%): Mp >300°C ($CHCl_3$–CH_3OH); UV ($CHCl_3$) 366 (ε 21200), 585 (70300), and 633 nm (86700); ^{1}H NMR δ=1.62 (3H×2, t, J=7.1 Hz), 3.44 (1H×2, dd, J=16.6 and 7.2 Hz), 3.59 (3H×2, s), 3.78 (1H×2, d, J=16.6 Hz), 4.50 (2H×2, m), 5.32 (1H×2, d, J=7.2 Hz), 7.02—7.54 (4H×2, m), 9.30 (1H×2, s), and 11.51 (1H×2, br s); ^{13}C NMR δ=14.3 ($OCH_2\underline{C}H_3$), 23.4 (C-6), 50.2 (C-5), 53.1 (OCH_3), 61.5 ($O\underline{C}H_2CH_3$), 102.3 (C-1), 112.4 (C-10), 116.5 (C-6a), 119.9 (C-7), 120.6 (C-8), 123.8 (C-11a), 125.4 (C-6b), 126.3 (C-9), 130.5 (C-2), 133.6 (C-12), 138.4 (C-10a), 141.4 (C-11b), 165.9 (C-3), 166.5 ($\underline{C}$OOEt), and 170.4 ($\underline{C}$OOMe). Found: m/z 730.2247. Calcd for $C_{40}H_{34}N_4O_{10}$: M, 730.2246.

Autoxidation of 3. A solution of **3** (30 mg) and Et_3N (0.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temperature for 24 h, and concentrated under reduced pressure. The residue was separated by column chromatography (SiO_2–$CHCl_3$) to give **2** (8 mg, 27%) and **11** (0.2 mg, 0.6%), the latter of which was identical with that prepared according to G. Palmisano's procedure by TLC and ^{1}H NMR comparisons.$^{13)}$

Formation of 12. A mixture of **6** (30 mg, 0.043 mmol), crotonaldehyde (0.4 ml, 4.9 mmol), and i-Pr_2NH (0.3 ml, 2.1 mmol) in acetonitrile (20 ml) was stirred at room temperature for 2 d, and then concentrated under reduced pressure. The residue was separated by column chromatography (SiO_2–$CHCl_3$) to give **12** (9 mg, 43%) as an oil: UV (CH_3OH) 511 nm (ε 22400); ^{1}H NMR δ=1.29 (12H, d, J=6.6 Hz), 1.50 (3H, t, J=7.1 Hz), 3.34 (1H, dd, J=16.5 and 7.5 Hz), 3.59 (3H, s), 3.65 (1H, m), 3.75 (1H, d, J=16.5 Hz), 4.23 (1H, m), 4.46 (2H, m), 5.38 (1H, d, J=7.5 Hz), 7.01 (1H, d, J=12.5 Hz), 7.08—7.56 (4H, m), 7.45 (1H, t, J=12.5 Hz), 7.82 (1H, d, J=12.5 Hz), and 11.28 (1H, br s); ^{13}C NMR δ=14.6 ($OCH_2\underline{C}H_3$), 19.9 ($\underline{C}H_3$–CH–$\underline{C}H_3$), 23.4 (C-6), 47.7 (CH_3–$\underline{C}$H–CH_3), 50.1 (C-5), 52.8 (OCH_3), 60.4 ($O\underline{C}H_2CH_3$), 100.6 (C-13), 102.0 (C-1), 110.9 (C-6a), 111.2 (C-2), 111.9 (C-10), 119.0 (C-7), 119.9 (C-8), 123.9 (C-9), 125.5 (C-11a), 125.9 (C-6b), 132.5 (C-11b), 137.0 (C-10a), 146.4 (C-12), 150.6 (C-14), 166.5 (C-3), 166.6 ($\underline{C}$OOEt), and 171.2 ($\underline{C}$OOMe). Found: m/z 491.2444. Calcd for $C_{28}H_{33}N_3O_5$: M, 491.2421.

X-Ray Crystallographic Analysis of 6. Single crystals of **6** were grown from $CHCl_3$–CH_3OH solution by slow evaporation of the solvent. A crystal of dimension of

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2)

Atom	x/a	y/b	z/c	$U_{(\mathrm{iso})}$$^{a)}$
N(2)	0.10958(15)	0.11983(65)	0.42539(32)	0.043
N(1)	0.12388(14)	0.11967(56)	0.08970(29)	0.034
C(13)	0.12792(19)	0.11587(73)	0.30707(36)	0.037
O(1)	0.09986(13)	0.10999(58)	−0.11521(26)	0.048
C(12)	0.1596(2)	0.0907(8)	0.5021(4)	0.044
C(1)	0.03324(19)	0.19332(71)	0.16778(38)	0.036
C(14)	0.09289(19)	0.14159(67)	0.19776(37)	0.036
C(3)	0.08611(19)	0.14201(67)	−0.01247(37)	0.036
C(6)	0.19009(19)	0.08253(76)	0.30609(38)	0.040
C(2)	0.02573(19)	0.19324(67)	0.03675(39)	0.036
C(4)	0.18236(19)	0.02539(72)	0.08281(40)	0.040
C(11)	0.1637(2)	0.0842(9)	0.6288(4)	0.053
O(4)	−0.01140(15)	0.21527(67)	0.36110(30)	0.062
C(7)	0.2105(2)	0.0694(8)	0.4293(4)	0.043
C(17)	−0.00686(19)	0.26907(78)	0.25893(43)	0.044
O(5)	−0.03541(15)	0.41666(58)	0.21360(33)	0.056
C(8)	0.2682(2)	0.0423(8)	0.4876(5)	0.054
O(2)	0.2130(2)	−0.2813(7)	0.0566(5)	0.087
C(10)	0.2207(3)	0.0578(10)	0.6819(5)	0.063
O(3)	0.11534(18)	−0.22521(55)	0.08989(44)	0.071
C(15)	0.1726(2)	−0.1790(8)	0.0755(4)	0.050
C(5)	0.22454(19)	0.07548(87)	0.19153(42)	0.048
C(9)	0.2724(2)	0.0392(10)	0.6125(5)	0.060
C(18)	−0.0770(3)	0.5088(11)	0.2945(7)	0.093
C(16)	0.1011(4)	−0.4200(11)	0.0840(10)	0.130
C(19)	−0.0664(10)	0.6827(20)	0.3048(24)	0.447

a) $U_{(\mathrm{iso})}=(1/3)\sum_i\sum_j u_{ij}\, a_i^*\, a_j^*\, \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Bond Angles (°) of **6**

C(13)–N(2)–C(12)	108.4(4)	C(14)–N(1)–C(3)	112.0(4)
C(14)–N(1)–C(4)	123.8(4)	C(3)–N(1)–C(4)	121.2(4)
N(2)–C(13)–C(14)	128.8(4)	N(2)–C(13)–C(6)	109.6(4)
C(14)–C(13)–C(6)	121.5(4)	N(2)–C(12)–C(11)	129.5(5)
N(2)–C(12)–C(7)	107.9(4)	C(11)–C(12)–C(7)	122.6(5)
C(14)–C(1)–C(2)	107.8(4)	C(14)–C(1)–C(17)	122.0(4)
C(2)–C(1)–C(17)	129.0(5)	N(1)–C(14)–C(13)	115.7(4)
N(1)–C(14)–C(1)	108.5(4)	C(13)–C(14)–C(1)	135.7(4)
N(1)–C(3)–O(1)	124.9(4)	N(1)–C(3)–C(2)	104.7(4)
O(1)–C(3)–C(2)	130.1(4)	C(13)–C(6)–C(7)	106.5(4)
C(13)–C(6)–C(5)	123.0(4)	C(7)–C(6)–C(5)	130.4(4)
C(1)–C(2)–C(3)	106.8(4)	C(1)–C(2)–C(2)	130.5(4)
C(3)–C(2)–C(2)	121.0(4)	N(1)–C(4)–C(15)	110.5(4)
N(1)–C(4)–C(5)	110.7(4)	C(15)–C(4)–C(5)	111.1(5)
C(12)–C(11)–C(10)	116.8(5)	C(12)–C(7)–C(6)	107.6(4)
C(12)–C(7)–C(8)	118.7(5)	C(6)–C(7)–C(8)	133.7(5)
C(1)–C(17)–O(4)	125.7(5)	C(1)–C(17)–O(5)	110.0(5)
O(4)–C(17)–O(5)	124.1(5)	C(17)–O(5)–C(18)	116.6(5)
C(7)–C(8)–C(9)	118.6(5)	C(11)–C(10)–C(9)	122.1(5)
C(15)–O(3)–C(16)	116.7(6)	C(4)–C(15)–O(2)	122.2(5)
C(4)–C(15)–O(3)	112.5(5)	O(2)–C(15)–O(3)	125.4(6)
C(6)–C(5)–C(4)	110.5(4)	C(8)–C(9)–C(10)	121.1(5)
O(5)–C(18)–C(19)	113.3(12)		

$0.35\times0.28\times0.21$ mm was chosen, and intensity data were collected by Mac-Science MXC3 diffractometer system. The used X-ray was graphite-monochromated Cu $K\alpha$.

A trichotomine derivative **6** is monoclinic and the space group is $C2$ with the lattice constants of $a=22.040(3)$, $b=7.391(1)$, $c=10.964(2)$ Å, and $\beta=92.18(1)^\circ$. The observed density of the crystal was 1.31 g cm^{-3} and the unit cell contains two molecules. The calculated density is 1.39 g cm^{-3}. Intensity measurement was carried out by $2\theta/\omega$ scan at 21°C, and the scan speed was 6° min^{-1} in ω. Standard reflections of −14 0 1, −4 −2 6, and −6 4 1 were observed every 100 measurements. Independent reflections of 1608 were observed, and 94% of them were larger than 5σ (I). Intensity data observed were corrected for Lorentz-polarization factors, but absorption correction was ignored.

The atomic parameters of the half molecule were determined. The atomic positions of atoms in the rings were solved by the direct method of Mithril 91 in Crystan-GM.[14)] The subsequent difference Fourier syntheses revealed the atomic positions in the methoxycarbonyl and the ethoxycarbonyl groups. Block diagonal least-squares refined the atomic positions and the anisotropic temperature factors to the R-factor of 0.080. Unit weights were adopted. The temperature factors of the terminal carbons of the methoxycarbonyl and the ethoxycarbonyl groups were abnormally large, indicating the disorder of the terminal atoms in the crystal. Further attempts to resolve these carbon atom positions were not carried out. Hydrogen atoms were placed at the ideal positions, with the bond length of 0.96 Å, but the isotropic temperature factors were refined. The final R-factor was 0.050, and the R_w was 0.053.

The atomic coordinates and their estimated standard deviations were listed in Table 2. The bond distances and the bond angles were listed in Tables 1 and 3, respectively. The atomic coordinates including hydrogen atoms, the anisotropic temperature factors, and the observed and calculated structure factors are deposited as Document No. 67042 at the office of the Editor of the Bull. Chem. Soc. Jpn.

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