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Syntheses and Structures of Indolo[6,7-g]indoles, a New Heteroaromatic System[1)]

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Photolysis of 1,1′-(1,8-naphthylene)-bis(1*H*-1,2,3-triazole)s (**1**) in methanol has given new heteroaromatic system compounds, indolo[6,7-g]indoles (**2**). The spectral properties of these compounds were studied in comparison with those of the corresponding benz[g]indoles (**4**) obtained from the similar photolysis of 1-(1-naphthyl)-1*H*-1,2,3-triazoles (**3**). The ^{1}H NMR and IR spectra of **2** and **4** suggest the existence of a strong intramolecular hydrogen bonding in **2**. The X-ray crystallographic analysis of tetraethyl 1*H*, 10*H*-indolo[6,7-g]-indole-2,3,8,9-tetracarboxylate, **2a**, indicates that the molecule has almost twofold rotational symmetry, and the framework is distorted due to the steric overcrowding.

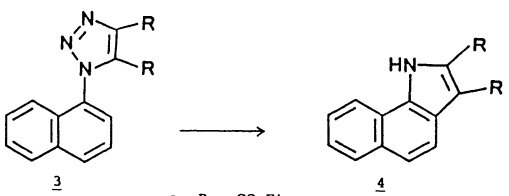
In order to know the properties of peri-substituted naphthalenes with heteroaromatic rings, we have synthesized novel 1,1′-(1,8-naphthylene)-bis(1*H*-1,2,3-triazole)s, which have triazole rings at 1 and 8 positions in the naphthalene ring, and investigated their structure by several spectroscopic analyses.[2)] According to the X-ray diffraction studies of these compounds, the naphthalene ring is considerably distorted owing to the steric repulsion between the two triazole rings.[3)] In addition to these studies, we have investigated photochemical reactions of these compounds. Products based on the interaction between the two triazole rings were expected, but they were not recognized in this reaction. Instead, new heteroaromatic system compounds, indolo[6,7-g]indoles, were produced by the denitrogenation from the triazole rings followed by the cyclization with the naphthalene ring.

In this paper, we describe the formation of these compounds by the photolysis of 1,1′-(1,8-naphthylene)-bis(1*H*-1,2,3-triazole)s (**1**) and their structural studies by spectroscopic analyses including X-ray crystallography.

Results and Discussion

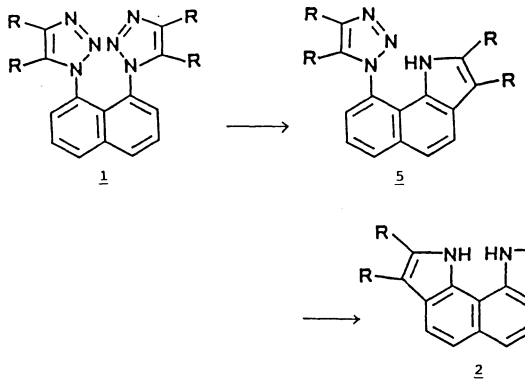
Photolysis of Naphthyltriazoles. Irradiation of **1a** in methanol for 15 min afforded tetraethyl 1*H*,10*H*-indolo[6,7-g]indole-2,3,8,9-tetracarboxylate (**2a**), which was produced by the elimination of nitrogen molecules from two triazole rings and cyclization toward the naphthalene ring. There are several kinds of indoloindole structures possible depending on the mode of condensation of the two indole rings. Although indolo[3,2-*b*]indole[4)] and indolo[7,6-g]-indole[5)] are known, the indolo[6,7-g]indole skeleton has not yet been synthesized to our knowledge. A similar reaction was observed on photolysis of the corresponding monotriazoles (**3**). Irradiation of **3a** in methanol for 15 min gave diethyl 1*H*-benz[g]indole-2,3-dicarboxylate (**4a**) almost quantitatively. Only a few studies have been investigated about the photochemical reaction of triazoles.[6)] Burgess et al. reported the formation of ketenimine derivatives by the photolysis of 1,4,5-triphenyl-1*H*-1,2,3-triazole.[7)] On the other hand, 1*H*-azirine derivatives were detected by the pyrolysis of triazole rings.[8)] We presumed the formation of similar compounds to the present reaction, but could not detect them to any extent under the experimental conditions. The isopropoxycarbonyl derivatives **2b** and **4b** were also produced by similar photolyses from **1b** and **3b** in excellent yield.

Photolyses of **1** and **3** were followed by HPLC using an ODS column and methanol-water (90:10) as an eluent. The starting material (**3a**) disappeared completely after 2 min irradiation, while **1a** required 10 min for the complete decomposition. A similar difference was observed between **1b** and **3b**, indicating that triazolylnaphthalenes (**3**) decompose much faster than disubstituted ones (**1**). The decomposition of the triazole ring in **1** may be restricted by the adjacent triazole ring. As described above, 15 min irradiation of **1a** afforded indolo[6,7-g]indole derivatives, **2a**, while irradiation of **1a** for 2 min led to the intermediate diethyl 9-(4,5-diethoxycarbonyl-1*H*-1,2,3-triazol-



3 → 4

a; R = CO_2Et
b; R = CO_2Pr^i



1 → 5 → 2

a; R = CO_2Et
b; R = CO_2Pr^i

1-yl)-1*H*-benz[g]indole-2,3-dicarboxylate (**5a**), which was isolated from the solution. The amount of **5a** became maximum at 2 min irradiation and thereafter gradually decreased. Finally, **5a** could not detected after 15 min under the reaction condition.

Spectral Properties of Indoles. Spectral properties of **2a—b**, **4a—b**, and **5a—b** are listed in Table 1. In the ^{1}H NMR spectrum, the NH signal of **2a** is ca. δ 0.9 downfield from that of **4a**. This large low field shift is due to the intramolecular hydrogen bonding as well as the anisotropic effect between the two condensed indole rings. The N-H signal of **5a** is observed at ca. δ 2.3 upfield from that of **4a** in the ^{1}H NMR. The reason of this extremely upfield shift is due to the anisotropic effects of the triazole ring. Probably, the triazole ring is perpendicular to the benz[g]indole ring because of steric repulsion between the triazole ring and the pyrrole moiety. Then, the triazole ring faces toward the NH proton in short distance, and it makes such a large up-field shift.

In the IR spectrum, the N-H stretching frequency of **2a** is about 100 cm^{-1} lower than that of **4a**, which also suggests the existence of a strong intramolecular hydrogen bonding in **2a**. Since the IR spectra were measured in the very dilute concentration as low as 2 mM (1M=1 mol dm^{-3}), the effect of the intermolecular hydrogen bonding is ruled out for the low frequency shift. Owing to the enlargement of the condensed ring, the longest maximum wavelength band of **2a** shows about 30 nm red shift compared with that of **4a** in the UV spectrum. The spectral relationships observed for **2a**, **4a**, and **5a** as described above are also found in those between **2b**, **4b**, and **5b**. This means the substituted ester groups scarcely affect these spectroscopic properties.

Molecular and Crystal Structure of 2a. The molecular structure of **2a** with the atom numbering is presented by the ORTEP[9] drawing in Fig. 1. The selected bond distances and angles for **2a** are given in

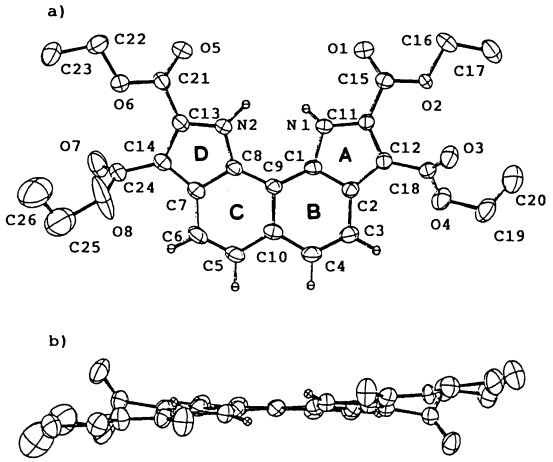


Fig. 1. Molecular structures of **2a**.
Non-hydrogen atoms are expressed as thermal ellipsoids with 40% probability level. Hydrogen atoms in ester groups are omitted for clarity.
(a) Side view. (b) Top view.

Table 1. Spectroscopic Data of Indoles

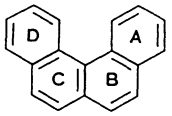
Product	^{1}H NMR ($CDCl_3$) δ/ppm	IR (CCl_4) ν/cm^{-1}	UV (CH_3OH) λ/nm	MS m/z (rel intensity, %)
2a	1.46 (t, J=7.1 Hz, 6H), 1.48 (t, J=7.1 Hz, 6H), 4.46—4.51 (m, 8H), 7.71 (d, J=8.8 Hz, 2H), 8.03 (d, J=8.8 Hz, 2H), 11.47 (s, 2H)	3351, 2984, 1730, 1698	376, 361, 278, 247, 208	494(M^+, 14) 448(100), 403(16), 376(14), 330(62), 259(16)
2b	1.45 (d, J=6.4 Hz, 12H), 1.49 (d, J=6.2 Hz, 12H), 5.31—5.42 (m, 4H), 7.74 (d, J=8.8 Hz, 2H), 7.99 (d, J=8.8 Hz), 11.50 (s, 2H)	3352, 2983, 1727, 1697	376, 315, 257, 216	550(M^+, 40), 490(100), 448(90), 405(60), 364(38), 302(42)
4a	1.43 (t, J=7.1 Hz, 3H), 1.47 (t, J=7.1 Hz, 3H), 4.44—4.52 (m, 4H), 7.50—7.61 (m, 3H), 7.91 (d, J=7.5 Hz, 1H), 7.99 (d, J=8.9 Hz, 1H), 8.23 (d, J=7.9 Hz, 1H), 10.52 (s, 1H),	3448, 2984, 1732, 1697	349, 335, 275, 249, 207	311(M^+, 76), 265(96), 193(100), 165(16), 164(14), 138(10)
4b	1.43 (d, J=6.2 Hz, 6H), 1.50 (d, J=6.2 Hz, 6H), 5.34—5.42 (m, 2H), 7.49—7.59 (m, 3H), 7.90 (d, J=7.5 Hz, 1H), 7.94 (d, J=9.0 Hz, 1H), 8.24 (d, J=7.7 Hz, 1H), 10.57 (s, 1H)	3449, 2980, 1734, 1700	349, 335, 274, 249, 207	339(M^+, 70), 297(12), 279(20), 237(100), 193(40), 164(12)
5a	0.83 (t, J=7.1 Hz, 3H), 1.40 (t, J=7.1 Hz, 3H), 1.43—1.49 (m, 6H), 4.07 (q, J=7.1 Hz, 2H), 4.36 (q, J=7.1 Hz, 2H), 4.45—4.56 (m, 4H) 7.54 (d, J=7.5 Hz, 1H), 7.64 (dd, J=8.1, 7.5 Hz, 1H), 7.76 (d, J=9.0 Hz, 1H), 8.19 (d, J=8.1 Hz, 1H), 8.21 (br, 1H), 8.24 (d, J=9.0 Hz, 1H)	3446, 2985, 1746, 1709	352, 335, 278, 253, 210	522(M^+, 22), 448(60), 421(28), 376(100), 258(50)
5b	0.78 (br, 6H), 1.37 (d, J=6.2 Hz, 6H), 1.45 (d, J=6.2 Hz, 12H), 4.88 (m, 1H), 5.22 (m, 1H), 5.34—5.42 (m, 2H), 7.52 (d, J=7.4 Hz, 1H), 7.63 (dd, J=8.3—7.4 Hz, 1H), 7.75 (d, J=9.1 Hz, 1H), 8.19 (d, J=8.3 Hz, 1H), 8.22 (br, 1H), 8.23 (d, J=9.1 Hz, 1H)	3448, 2983, 1744	351, 335, 278, 253, 209	578(M^+, 36), 404(30), 388(40), 362(100), 320(72), 276(54)

Table 2. Selected Bond Lengths and Bond Angles in **2a** with Estimated Standard Deviations in Parentheses

Bond length *l*/Å				C(6)-C(5)-C(10)	122.8(4)	C(5)-C(6)-C(7)	119.2(5)
C(1)-C(2)	1.417(7)	C(1)-C(9)	1.413(6)	C(6)-C(7)-C(8)	119.4(5)	C(6)-C(7)-C(14)	133.3(4)
C(1)-N(1)	1.374(5)	C(2)-C(3)	1.427(6)	C(8)-C(7)-C(14)	107.4(4)	C(7)-C(8)-C(9)	122.5(4)
C(2)-C(12)	1.417(6)	C(3)-C(4)	1.346(7)	C(7)-C(8)-N(2)	107.2(4)	C(9)-C(8)-N(2)	130.4(4)
C(4)-C(10)	1.436(8)	C(5)-C(6)	1.341(8)	C(1)-C(9)-C(8)	128.3(4)	C(1)-C(9)-C(10)	116.1(4)
C(5)-C(10)	1.419(7)	C(6)-C(7)	1.419(7)	C(8)-C(9)-C(10)	115.6(4)	C(4)-C(10)-C(5)	120.3(4)
C(7)-C(8)	1.413(6)	C(7)-C(14)	1.427(7)	C(4)-C(10)-C(9)	119.5(4)	C(5)-C(10)-C(9)	120.3(4)
C(8)-C(9)	1.418(7)	C(8)-N(2)	1.380(6)	C(12)-C(11)-C(15)	132.2(4)	C(12)-C(11)-N(1)	109.4(4)
C(9)-C(10)	1.438(6)	C(11)-C(12)	1.374(6)	C(15)-C(11)-N(1)	118.2(4)	C(2)-C(12)-C(11)	106.7(4)
C(11)-C(15)	1.471(6)	C(11)-N(1)	1.361(6)	C(2)-C(12)-C(18)	125.6(4)	C(11)-C(12)-C(18)	127.4(4)
C(12)-C(18)	1.474(7)	C(13)-C(14)	1.377(6)	C(14)-C(13)-C(21)	131.4(4)	C(14)-C(13)-N(2)	109.7(4)
C(13)-C(21)	1.475(7)	C(13)-N(2)	1.371(6)	C(21)-C(13)-N(2)	118.7(4)	C(7)-C(14)-C(13)	106.6(4)
C(14)-C(24)	1.470(7)	C(15)-O(1)	1.205(7)	C(7)-C(14)-C(24)	124.6(4)	C(13)-C(14)-C(24)	128.4(4)
C(15)-O(2)	1.324(6)	C(18)-O(3)	1.195(5)	C(11)-C(15)-O(1)	123.1(5)	C(11)-C(15)-O(2)	112.4(4)
C(18)-O(4)	1.340(7)	C(21)-O(5)	1.197(6)	C(1)-C(15)-O(2)	124.4(4)	C(12)-C(18)-O(3)	126.6(5)
C(21)-O(6)	1.324(6)	C(24)-O(7)	1.168(6)	C(12)-C(18)-O(4)	111.4(4)	O(3)-C(18)-O(4)	121.9(5)
C(24)-O(8)	1.307(7)			C(13)-C(21)-O(5)	123.5(5)	C(13)-C(21)-O(6)	111.8(4)
				O(5)-C(21)-O(6)	124.7(5)	C(14)-C(24)-O(7)	126.4(4)
Bond angles ϕ/°				C(14)-C(24)-O(8)	111.9(4)	O(7)-C(24)-O(8)	121.3(5)
C(2)-C(1)-C(9)	122.8(4)	C(2)-C(1)-N(1)	106.3(4)	C(1)-N(1)-C(11)	110.0(4)	C(8)-N(2)-C(13)	109.2(4)
C(9)-C(1)-N(1)	130.9(4)	C(1)-C(2)-C(3)	119.6(4)	C(15)-O(2)-C(16)	116.9(4)	C(18)-O(4)-C(19)	115.8(4)
C(1)-C(2)-C(12)	107.6(4)	C(3)-C(2)-C(12)	132.9(5)	C(21)-O(6)-C(22)	116.9(4)	C(24)-O(8)-C(25)	118.8(5)
C(2)-C(3)-C(4)	118.5(5)	C(3)-C(4)-C(10)	123.4(4)				

Table 2.[10]

The molecule has an approximate twofold rotational symmetry with respect to the C(9)-C(10) bond. The fused angle C(1)-C(9)-C(8), 128.3 (4)°, is fairly large compared with the corresponding angle in naphthalene itself, 121.5°.[11] In a four-ring helicene, benzo[*c*]phenanthrene (**6**), the angle is 124.6°, which is smaller than that in **2a**.[12] These results reflect the



(6)

remarkable steric overcrowding in **2a**.

The dihedral angles between the four rings of **2a** defined in Fig. 1 are listed in Table 3 together with the corresponding data in **6**. The twistings are observed at same intervals from the ring A to the ring D in **2a**. Thus, the dihedral angle of the two pyrrole rings A and D is 9.8 (2)°, while the angle of the corresponding two benzene rings in **6** is 26.5°.[12] These results indicate that the molecule **2a** relieves the steric hindrance by enlargement of the angle C(1)-C(9)-C(8) and by rather small twists in the fused four rings, while the molecule **6** twists largely in order to relieve the steric hindrance. Although the two N-H bonds twist away from each other, the distance between the N-H hydrogen atoms is nearly equal to the sum of the van der Waals radii. The carbonyl groups bonded at the C(11) and C(13) atoms are almost coplanar to the pyrrole rings A and D, respectively, but the carbonyl groups at the C(12) and C(14) twist from the pyrrole ring planes by 55—60°.

The packing modes of molecules in the crystal is shown in Fig. 2. The crystal packing mainly results from intermolecular hydrogen bonds; the shortest

Table 3. Dihedral Angles (°) between the Four Rings of **2a** and **6**[a]

	2a	**6**
Ring A-Ring B	3.6(2)	10.3(2)
Ring B-Ring C	3.3(2)	7.1(2)
Ring C-Ring D	3.2(2)	9.7(2)
Ring A-Ring D	9.8(2)	26.5(2)

a) Calculated with Ref. 12.

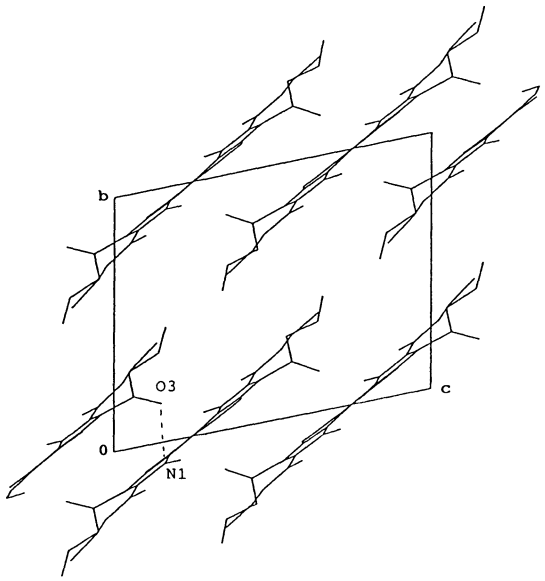


Fig. 2. Crystal structure of **2a**. Projected along the a axis.

intermolecular distance is 3.005(6) Å for N(1)-O(3^i) ($i=1-x,-y,1-z$).

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 JASCO 5MP 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 analyzer.

Materials. Compounds **1** and **3** were prepared from 1,8-diazidonaphthalene and 1-azidonaphthalene, respectively, by 1,3-dipolar cycloaddition with acetylene dicarboxylate as previously reported.[2]

Photolyses of 1 and 3. A solution of **1a** (120 mg, 0.22 mmol) in 400 ml of methanol under nitrogen atmosphere was irradiated with a Ushio 450 W high-pressure mercury lamp through a quartz well at 30—35 °C for 15 minutes. Then, the solvent was evaporated, and the residue was chromatographed over silica gel (diethyl ether-hexane as eluent) to give pure **2a**.

2a: pale yellow needles, mp 209—210 °C, 76 mg (70%). Found: C, 63.08; H, 5.39; N, 5.62%. Calcd for $C_{26}H_{26}N_2O_8$: C, 63.15; H, 5.30; N, 5.66%.

Similarly, the photoreactions of **1b**, **3a**, and **3b** (0.22 mmol) in methanol gave **2b**, **4a**, and **4b**, respectively.

2b: pale yellow needles, mp 168—169°C, 72%. Found: C, 65.47; H, 6.16; N, 5.04%. Calcd for $C_{30}H_{34}N_2O_8$: C, 65.44; H, 6.22; N, 5.09%.

4a: colorless needles, mp 133—134 °C, 95%. Found: C, 69.52; H, 5.58; N, 4.53%. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50%.

4b: colorless needles, mp 116—117 °C, 94%. Found: C, 70.63; H, 6.31; N, 4.19%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

Irradiation of **1** for 2 min gave **5** together with the starting material (**1**) and indoloindole, and they were separated with silica-gel chromatography as in case of **2**.

5a: colorless needles, mp 93—94°C, 25%. Found: C, 59.65; H, 4.97; N, 10.65%. Calcd for $C_{26}H_{26}N_4O_8$: C, 59.77; H, 5.02; N, 10.72%.

5b: colorless needles, mp 67—68 °C, 30%. Found: C, 62.33; H, 5.95; N, 9.59%. Calcd for $C_{30}H_{34}N_4O_8$: C, 62.27; H, 5.92; N, 9.68%.

X-Ray Analysis of Compound 2a. Pale yellow needle-like crystals of **2a** were obtained by a slow evaporation of hexane-diethyl ether solution at room temperature. The crystal, approximate dimension of 0.75×0.25×0.10 mm, was used for intensity data measurements.

Crystal data of **2a**; $C_{26}H_{26}N_2O_8$, M=494.5, triclinic, space group $P\bar{1}$, a=9.366(1), b=10.330(1), c=13.052(2) Å, α=101.85(2), β=90.76(2), γ=104.35(4)°, V=1194.6(1) Å^3, D_m=1.39 Mg m^{-3} (by floatation in carbon tetrachloride and hexane), D_c=1.38 Mg m^{-3} for Z=2, μ(Mo$K\alpha$)=0.111 mm^{-1}. The cell dimension and diffraction intensity were measured on a Rigaku AFC-4 four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ=0.71069 Å) at room temperature. Unit cell dimensions were determined by least-squares fits using 25 reflections in the range $20°<2\theta<30°$. Intensity data were collected by the ω-2θ scan mode at a rate of 2° (2θ)min^{-1}. The scan range was from 2° to 55°. Three standard reflections (202, 022, and 2—20) were measured after every 50 reflections, showing no significant intensity decay throughout the data collection. Totals of 5532 reflections were measured, of which 3111 with $|F_o|>3\sigma|F_o|$ were used. The usual Lorentz and polarization corrections were applied, but no absorption corrections were made. The structure was solved by the direct method using MULTAN78.[13] An E-map using 244 ($|E|>1.2$) revealed all non-hydrogen atoms. Hydrogen atoms in the rings were found from a difference electron density map and those in the ester groups were placed at the calculated positions. The structure was refined by a full-matrix least-squares method, using the UNICS III system.[14] Anisotropic thermal parameters were assumed for the non-hydrogen atoms, and isotropic parameters, for the hydrogen atoms. The final refinement, employing a weighting scheme of $w=(0.011\,|F_o|^2-0.161|F_o|+1.245)^{-1}$, led to R and R_w values of 0.085 and 0.090, respectively. The final atomic parameters are listed in Table 4. Atomic scattering factors were taken from International Tables for X-Ray Crystallog-

Table 4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters with e.s.d.'s in Parentheses

$B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_ia_j$

Atom	x	y	z	B_{eq}/Å^2
O(1)	7689(4)	1740(4)	976(3)	5.1(1)
O(2)	6801(3)	2620(3)	−248(3)	2.8(1)
O(3)	3868(4)	1546(4)	−1478(3)	4.8(1)
O(4)	2864(4)	3035(4)	−466(3)	5.1(1)
O(5)	6802(4)	−1844(5)	4038(3)	5.6(1)
O(6)	5475(3)	−2676(4)	5277(3)	4.3(1)
O(7)	3055(5)	−1572(5)	6477(3)	6.3(1)
O(8)	1423(8)	−3194(6)	5463(4)	11.9(2)
N(1)	4850(4)	872(4)	1603(3)	3.0(1)
N(2)	4404(4)	−968(4)	3387(3)	3.2(1)
C(1)	3368(4)	599(4)	1765(3)	3.0(1)
C(2)	2704(4)	1106(4)	1003(3)	3.0(1)
C(3)	1167(5)	1048(5)	1013(4)	3.6(1)
C(4)	393(5)	522(5)	1759(4)	3.8(1)
C(5)	141(5)	−561(5)	3295(4)	3.7(1)
C(6)	670(5)	−1088(5)	4030(4)	4.0(1)
C(7)	2156(5)	−1183(4)	4018(3)	3.2(1)
C(8)	3059(4)	−684(4)	3252(3)	3.0(1)
C(9)	2555(4)	−40(4)	2510(3)	2.9(1)
C(10)	1023(4)	−31(5)	2526(3)	3.3(1)
C(11)	5122(5)	1472(4)	766(3)	3.0(1)
C(12)	3822(4)	1613(4)	360(3)	3.0(1)
C(13)	4388(4)	−1570(4)	4231(3)	3.2(1)
C(14)	3030(5)	−1710(4)	4651(3)	3.2(1)
C(15)	6666(5)	1929(5)	510(3)	3.5(1)
C(16)	8286(6)	3137(6)	−551(4)	4.4(2)
C(17)	8169(9)	3969(9)	−1340(6)	6.1(2)
C(18)	3578(5)	2045(4)	−623(3)	3.2(1)
C(19)	2582(8)	3554(8)	−1395(5)	5.9(2)
C(20)	3912(12)	4514(11)	−1616(9)	7.6(3)
C(21)	5691(5)	−2032(5)	4491(3)	3.5(1)
C(22)	6683(7)	−3171(7)	5607(5)	5.0(2)
C(23)	6169(9)	−3907(7)	6464(5)	5.7(2)
C(24)	2577(5)	−2143(5)	5628(4)	3.7(1)
C(25)	518(13)	−3548(14)	6427(9)	9.3(4)
C(26)	1273(20)	−4473(21)	6578(12)	12.0(6)

raphy.[15] All the calculations were carried out on a FACOM M-780 computer at Tsukuba Research Center.

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