

Synthesis and Properties of 4*H*-Benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-ones¹⁾

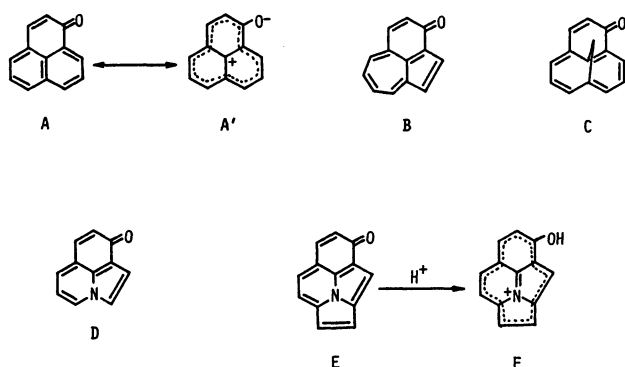
Michihiko NOGUCHI,* Takashi YAMAMOTO, Shoji KAJIGAESHI, Keiji SAITO,[†] and Tsuyoshi ARAI[†]
 Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

[†]UBE Scientific Analysis Laboratory, Kogushi, Ube 755

(Received May 14, 1987)

3-Phenyl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**5**) was prepared by saponification accompanied by the decarboxylation of the corresponding 1,2-bis(methoxycarbonyl) derivative, which was obtained by the DDQ oxidation of 5,6-dihydro one. Investigations concerning its spectral data and MO calculations revealed interesting electronic features for **5**, e.g., i) a highly polarized structure in the ground state, ii) the existence of a peripheral [12]annulene system in acidic media, and iii) a significant stabilization of the excited state by protonation.

Much attention has been paid to the chemistry of 1*H*-phenalen-1-one (**A**) owing to its unusual properties, e.g., high basicity, high dipole moment, low-frequency shift of carbonyl absorption, and so on. These properties have been ascribed to an important contribution of an ionic structure (**A'**) to the resonance hybrid.²⁾ From synthetic and physicochemical viewpoints, much effort has been made to prepare the iso π -electronic analogs of **A**, e.g., 3*H*-benz[*cd*]azulen-3-one (**B**)³⁾ and 2,14-dihydrotricyclo[7,3,2,0^{5,13}]tetradeca-1,3,5,7,9,11-hexaen-2-one (**C**).⁴⁾ Their interesting properties have been elucidated during the last two decades.



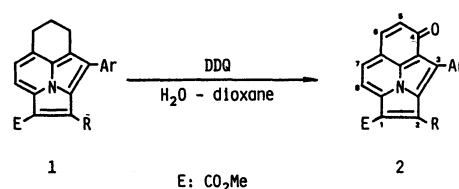
A more recent report⁵⁾ on the synthesis and properties of 9*H*-pyrrolo[3,2,1-*ij*]quinolin-9-one (**D**) stimulated us to investigate 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**E**), which involves a peripheral 10 π -electronic [3.2.2]cyclazine system instead of the indolizine nuclei of **D**. Therein, the [12]annulene system **F**, perturbed by an internal azomethinium ion, would be provided by the protonation of **E**.

In a preliminary paper,⁶⁾ we communicated a facile preparation of the derivatives of **E** and a few of their interesting electronic features. In the present paper, details concerning the syntheses of 3-aryl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-ones are described; also, their properties are discussed on the basis of spectral evidence and molecular orbital (MO) calculations.

Results and Discussion

Synthesis. According to the reported method for the introduction of a carbonyl function into the α -methylene moiety in azulene,⁷⁾ 5,6-dihydro-1-methoxycarbonyl- and 5,6-dihydro-1,2-bis(methoxycarbonyl)-3-aryl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizinenes (**1**) were oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (4 mol equiv.) in 10% aqueous dioxane to give selectively 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one derivatives (**2**) (Scheme 1). The structures of **2** were confirmed on the basis of analytical data and spectral evidence. These results and spectral data for **2** are summarized in Tables 3 and 4, respectively.

For this regioselective oxidation leading to **2**, we proposed a reaction pathway which initiates a CT complex formation between DDQ and aryl groups at the 3-position of **1** (Fig. 1). This was supported by the following results; at an earlier stage of the reaction, a dark-green solution was observed, which was in accordance with CT complex formation.⁸⁾ The progress of



a: Ar=C₆H₅, R=H; b: Ar=C₆H₅, R=E; b-*d*₅: Ar=C₆D₅, R=E; c: Ar=C₆H₄-OMe(*p*), R=E; d: Ar=C₆H₄-Br(*p*), R=E; e: Ar=4-Biphenyl, R=E; f: 2-Naphthyl, R=E.

Scheme 1.

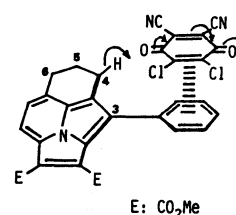


Fig. 1. CT complex formation between the phenyl group of **1a** and DDQ.

the oxidation was dependent upon the facility of the CT complex formation, which was also ascribed to the electron density of the aromatic ring at the 3-position.⁹⁾

In order to prepare the 3-phenyl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**5**), the corresponding 5,6-dihydro derivative **3** was treated with 1.5 mol equiv. of DDQ to give 5,6-dihydro-3-phenyl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**4**) in 42% yield. A similar treatment with 4.0 mol equiv. of DDQ gave the desired **5** and **4** in 33 and 16% yields, respectively. However, a successive oxidation of **4** to **5** was considerably sensitive to the reaction conditions employed; therefore, another synthetic approach to **5** was surveyed.

The saponification of **2b** with methanolic potassium hydroxide followed by acidification gave the corresponding dicarboxylic acid, which was decarboxylated in refluxing quinoline in the presence of copper dust to afford **5**. Similarly, the 3-pentadeuteriophenyl derivative **5-d₅** was obtained from **2b-d₅** (Scheme 2).

MO Calculations. In an attempt to obtain a better understanding of the properties of **5**, MO calculations using the MNDOA method¹⁰⁾ for the parent compound **E** were performed. All of its bond lengths and valence angles were reinvestigated using the structure optimization program therein (see Experimental section).

The results of these calculations indicate that there

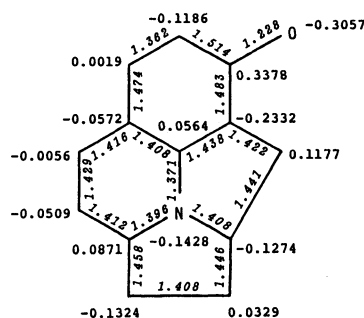
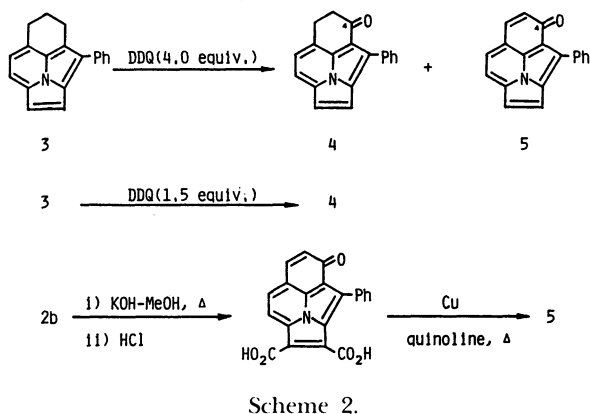


Fig. 2. Net atomic charge and atomic distance (Å) of **E** by MNDOA.

is no significant departure from planarity of molecule **E**. Among these results, the bond lengths and atomic charges for **E** are presented in Fig. 2. These suggest that the enone moiety attached to the peri position of [3.2.2]cyclazine nuclei is electron-withdrawing and that a considerable negative charge is located at the carbonyl oxygen atom. Consequently, the carbonyl group is highly polarized and the dipole moment was calculated to be 4.26 D, which is comparable to that of tropone.¹¹⁾

IR Spectra. The lower-frequency shift of 44 cm⁻¹ for the carbonyl absorption was caused by a conversion of the 5,6-dihydro derivative **4** (1650 cm⁻¹) into fully conjugated **5** (1606 cm⁻¹). The carbonyl absorptions at the 4-position for **2** were also observed at 1624–1592 cm⁻¹, which were somewhat lower than those of the other systems: **A**, **B**, and **D**.^{2,3,5)} These results indicate that the carbonyl groups of **2** and **5** are highly polarized and that the ionic structure **E'** is important to the resonance hybrid in the ground state of **E** (Scheme 3).

¹³C NMR Spectra. A full assignment of the ¹³C NMR spectrum for **5** was accomplished by a comparison with the spectra for **2a**, **2b**, **2c**, and **5-d₅** using several decoupling techniques (see Experimental section). The chemical shifts are presented in Fig. 3; these values for the benzopyrroloindolizinone moiety of **5** corresponded to the atomic charges of the 4*H*-

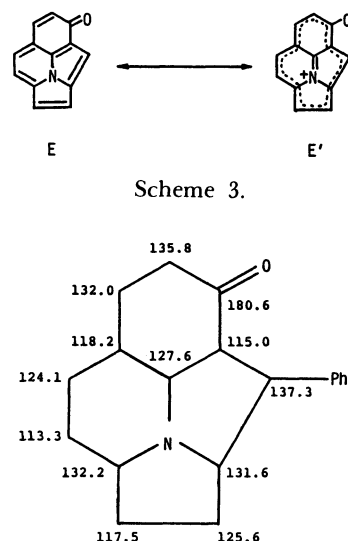


Fig. 3. Assignment of ¹³C NMR spectrum of **5** in CDCl₃.

Table 1. ¹H NMR Spectral Data for **3-d₅** and **5-d₅** in CDCl₃

Compd	δ/ppm				J/Hz	
	1-H	2-H	7-H	8-H	J ₁₋₂	J ₇₋₈
3-d₅	7.18	7.65	7.35	7.82	3.9	7.8
5-d₅	7.02	7.57	7.51	7.67	4.6	7.8
Δδ ^{a)}	0.16	0.08	-0.16	0.15		

a) Δδ=δ(**3-d₅**)-δ(**5-d₅**).

Table 2. ^1H NMR Spectral Data of 5- d_5 in CDCl_3 and CF_3COOD

Solvent	δ/ppm						J/Hz		
	1-H	2-H	5-H	6-H	7-H	8-H	J_{1-2}	J_{5-6}	J_{7-8}
CDCl_3	7.02	7.57	6.44	7.29	7.51	7.67	4.6	9.6	7.8
CF_3COOD	7.06	7.48	7.06	7.82	7.69	8.29	5.2	9.1	8.4
$\Delta\delta^{(a)}$	-0.04	0.09	-0.62	-0.53	-0.18	-0.62			

a) $\Delta\delta = \delta(\text{CDCl}_3) - \delta(\text{CF}_3\text{COOD})$.

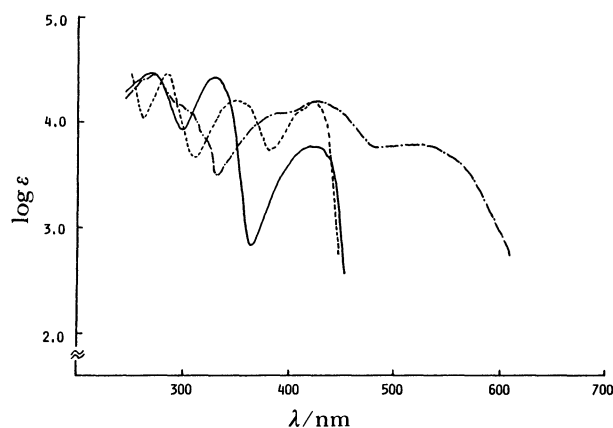
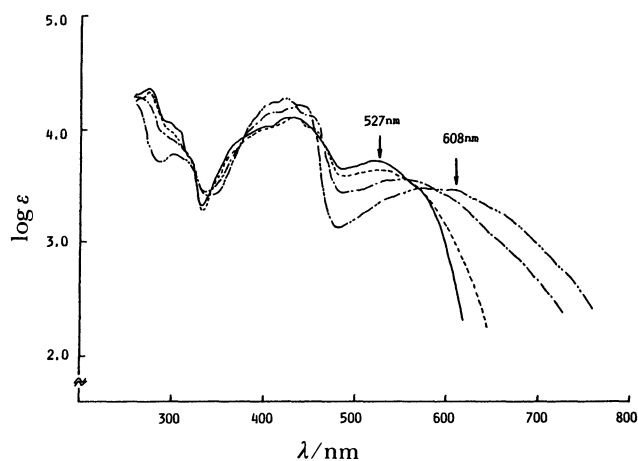
benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one system (**E**) calculated by MNDOA (Fig. 2). This implies that the results from the MNDOA calculations for **E** are useful for a qualitative discussion of the electronic features for **2** and **5**.

^1H NMR Spectra. The assignment and discussion concerning the cyclazine ring protons of **5** were achieved by an analysis of the spectrum of the penta-deuteriophenyl derivative 5- d_5 . The chemical shifts¹²⁾ and coupling constants of 3- d_5 and 5- d_5 are tabulated in Table 1. Therein, the introduction of the enone moiety into [3.2.2]cyclazine caused a small upfield shift for all protons other than 7-H. The spectral data for 5- d_5 in deuteriochloroform (CDCl_3) and in trifluoroacetic acid- d_1 ($\text{CF}_3\text{CO}_2\text{D}$) are summarized in Table 2. The positive charge resulting from the protonation caused relatively small downfield shifts for the protons ($\Delta\delta$: within -0.6); interestingly, a small upfield shift was observed for 2-H in $\text{CF}_3\text{CO}_2\text{D}$ in comparison with that in CDCl_3 . The differences among the coupling constants became smaller in $\text{CF}_3\text{CO}_2\text{D}$, which implied that the bond-alternation of the peripheral π -system was weakened by the protonation.

As is well-known, the protonation of other iso π -electronic systems caused considerable downfield shifts of all the ring protons, i.e., $\Delta\delta = -0.7$ — -1.8 for 1*H*-phenalen-1-one,¹³⁾ $\Delta\delta = 0.0$ — -1.3 for 7,9-dimethyl-3*H*-benz[*cd*]azulen-3-one,^{3b)} and $\Delta\delta = -0.4$ — -0.9 ¹⁴⁾ for 2-ethoxycarbonyl-7-phenyl-9*H*-pyrrolo[3,2,1-*ij*]quinolin-9-one. On the other hand, 5*H*-cyclopenta[*cd*]phenalen-5-one, a [13]annulenone perturbed by an internal vinyl π -system, exhibited both small up and downfield shifts for the ring protons on protonation ($\Delta\delta = -0.3$ — 0.3), for which the existence of the paramagnetic ring current arising from the peripheral 12 π -electronic system has been proposed.¹⁵⁾

The results in the present work are probably attributable to the ring current due to the peripheral [12]-annulene system, which is cross-linked by an azomethinium ion.

Electronic Spectra. The electronic spectra of **3**, **4**, and **5** are shown in Fig. 4. These reveal that the introduction of an enone moiety into the [3.2.2]cyclazine system causes a significant change in π -electronic features of the parent system. The solvent dependency of the spectra of **5** was also investigated. The spectra in chloroform, methanol, and methanol-sulfuric acid (100/1) do not show any solvent effect.¹⁶⁾

Fig. 4. Electronic spectra of **3** (—), **4** (---), and **5** (-·-) in CHCl_3 .Fig. 5. Change of the electronic spectra of **5** with acid concentrations: (—) in CHCl_3 ; (---) in CHCl_3 - CF_3COOH =100/1; (-·-) in 50/1; (-·-·-) in 3/2.

However, when the protonation of carbonyl oxygen atom of **5** was complete,¹⁷⁾ the absorption maximum due to the first electronic transition was shifted to a longer wavelength, and the spectra were changed as the acid concentrations decreased (Fig. 5). The longer wavelength shift by the protonation of **5** did not depend on the concentrations of substrate **5** in the range 8.0×10^{-7} to 3.6×10^{-6} M ($1\text{M} = 1 \text{ mol dm}^{-3}$). The addition of *p*-dimethoxybenzene or 1,4-dimethoxynaphthalene caused no changes of the spectra in acidic media. Also, the 1,2-bis(methoxycarbonyl) derivative

2a showed the same behavior under acidic conditions as those of **5**.

From these results, we suggest that the shift was not due to an intermolecular interaction, e.g., a CT complex formation between **5** and its protonated species, but due to inherent changes in the electronic system of **5** by protonation.¹⁸⁾

On the other hand, the spectra of phenalenones²⁾ or 3*H*-benz[*cd*]azulen-3-one^{3b)} in acidic media exhibited considerable hypsochromic shifts, which were ascribed to a stabilization of their ground states. Accordingly, the present results indicate that protonation onto the carbonyl oxygen atom of **5** results in a more significant stabilization of its excited state, rather than of its ground state.

In order to confirm this point, MO calculations for **F**, the protonated species of **E**, were attempted. The HOMO and LUMO energy levels of **F** were calculated to be -8.52 and -3.98 eV, respectively. This means that a very small instabilization of the HOMO and a large stabilization of the LUMO are caused by the protonation, in comparison with those of **E** (HOMO: -8.62 eV; LUMO: -1.54 eV). Also, as shown in Fig. 6, the positive charge caused by the protonation was delocalized over the peripheral system of **F**, and the peripheral bond lengths were averaged, indicating the bond alternations of the π -system were less significant.

In conclusion, 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]-indolizin-4-one (**E**) has the following characteristic properties: i) a highly-polarized structure in the ground state and ii) a significant stabilization of the LUMO of **E** by protonation, which is considerably different from its π -electronic analogs, such as 1*H*-phenalen-1-one (**A**), 3*H*-benz[*cd*]azulen-3-one (**B**), and 9*H*-pyrrolo[3,2,1-*ij*]quinolin-9-one (**D**).

Experimental

General. All melting points are uncorrected. The IR spectra were measured on a JASCO IRA-1 spectrometer. The ¹H NMR spectra were obtained on JEOL FX-200 and/or JMN-MH-100 spectrometers and ¹³C NMR spectra were recorded on a JEOL FX-200 spectrometer at 50.1 MHz. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane. The mass spectra were determined with a JEOL JMS-D spectrometer at 75 eV using a direct inlet method. The electronic spectra were taken by a Hitachi 220 spectrophotometer. The elemental analyses were performed on a Hitachi 026 CHN analyzer. Most of the reactions were monitored by thin-layer chromatography (Silica gel 60F-254, Merck). The visualization was made with ultraviolet light (254 and 365 nm). Wakogel C-200 and C-300 (Wako Pure Chemical Industries LTD) and Aluminium Oxide 90 (Merck) were used for preparative column chromatography.

The unknown starting materials **1a**, **1c**, **1d**, **1e**, and **1f** were prepared from reactions of the corresponding benzo[*hi*]indolizines and acetylenes in a similar manner to the reported method.¹⁹⁾

1a: Mp 140–141 °C. Found: C, 80.11; H, 5.50; N, 4.18%.

Calcd for C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44%.

1c: Mp 153–154 °C. Found: C, 71.58; H, 5.32; N, 3.62%.

Calcd for C₂₄H₂₁NO₅: C, 71.45; H, 5.25; N, 3.47%.

1d: Mp 194–195 °C. Found: C, 61.09; H, 4.07; N, 3.29%.

Calcd for C₂₃H₁₈BrNO₄: C, 61.07; H, 4.01; N, 3.10%.

1e: Mp 224–225 °C. Found: C, 77.60; H, 5.20; N, 3.24%.

Calcd for C₂₉H₂₃NO₄: C, 77.48; H, 5.16; N, 3.12%.

1f: Mp 201–203 °C. Found: C, 76.38; H, 5.03; N, 3.37%.

Calcd for C₂₇H₂₁NO₄: C, 76.58; H, 5.00; N, 3.31%.

Oxidation of 1 with DDQ to 2. General Procedure: To a 10% aqueous dioxane solution (30 mL) of **1a** (500 mg, 1.59 mmol), DDQ (1.44 g, 6.36 mmol) was added portionwise at room temperature; the reaction mixture was heated under reflux for 6 h. The resultant hydroquinone was filtered off and the filtrate was evaporated to dryness. The residue was subjected to a short column chromatography (alumina-chloroform) in order to remove any unreacted DDQ. The chloroform elution was collected and concentrated to give a residue. The residue was chromatographed on silica gel to afford **2a** (359 mg, 69%) as a chloroform eluent.

2a: Red needles (ethanol); mp 274–275 °C. Found: C, 76.87; H, 4.15; N, 4.56%. Calcd for C₂₁H₁₃NO₃: C, 77.05; H, 4.00; N, 4.28%.

A similar oxidation of **1b–f** gave the corresponding 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one derivatives **2b–2f**.

2b: Red needles (ethanol); mp 189–190 °C. Found: C, 71.42; H, 4.09; N, 3.43%. Calcd for C₂₃H₁₅NO₅: C, 71.68; H, 3.92; N, 3.64%.

2c: Red needles (ethanol); mp 225–226 °C. Found: C, 69.16; H, 4.17; N, 3.35%. Calcd for C₂₄H₁₇NO₆: C, 69.39; H, 4.13; N, 3.37%.

2d: Deep red needles (ethanol); mp 227–229 °C. Found: C, 59.44; H, 3.18; N, 3.24%. Calcd for C₂₃H₁₄BrNO₅: C, 59.44; H, 3.18; N, 3.24%.

2e: Red needles (ethanol); mp 256–258 °C. Found: C, 75.56; H, 4.21; N, 3.28%. Calcd for C₂₉H₁₉NO₅: C, 75.48; H, 4.15; N, 3.04%.

2f: Deep red needles (ethanol); mp 219–220 °C. Found: C, 74.64; H, 4.11; N, 3.44%. Calcd for C₂₇H₁₇NO₅: C, 74.47; H, 3.93; N, 3.22%.

These results and the spectral data for **2** are presented in Tables 3 and 4, respectively.

Oxidation of 3 with DDQ to 4 and 5. A mixture of **3** (265 mg, 1.03 mmol) and DDQ (350 mg, 1.54 mmol) in 10% aqueous dioxane (10 mL) was stirred at room temperature for 18 h. After similar procedures as mentioned above, **4** was obtained in 42% yield. Also, the oxidation of **3** with DDQ (4.0 mol equiv.) in 10% aqueous dioxane under reflux for 12

Table 3. Oxidation of **1** with DDQ in Refluxing Dioxane Leading to **2**

Run	Molar ratio DDQ/1	Time	2 Yield/%
		h	
a	4	6	69
b	4	6	68
b-d₅	4	6	72
c	4	6	96
d	4	45	Trace
	6	54	34
e	4	24	47
f	6	42	55

The structural optimization for **F**, the protonated species of **E**, was performed using the attained geometries for **E** as an

Table 5. The Full Assignments of ^{13}C NMR Spectra of **5** and **2b**

Assign	5 / ^{13}C		^1H	2b / ^{13}C		
	δ	NON; J/Hz		δ	NON; J/Hz	Method
1	117.5	dd(177, 4)	6.90	118.0	s	b)
2	125.6	dd(174, 4)	a)	123.7	s	b)
2a	131.6	s		133.6	s	LPSEL
3	137.3			141.6	t(5)	NOE, SEL
3a	115.0			117.1	d(5)	LPSEL
4	180.6	d(10)		180.7	d(10)	
5	135.8	d(164)	6.34	136.1	d(164)	NOE, LPSEL
6	132.0	dd(164, 3)	7.15	132.6	dd(164, 4)	NOE, SEL
6a	118.2	dd(12, 8)		119.4	dd(12, 8)	LPSEL
7	124.1	d(163)	a)	125.8	d(164)	NOE, SEL
8	113.3	d(167)	a)	116.5	d(174)	NOE, SEL
8a	132.2	m		131.5	t(7)	LPSEL
8c	127.6			129.1	dd(9, 3)	LPSEL
1'	133.2	t(7)		131.7	t(10)	LPSEL
2'	128.7	dd(165, 7)	8.55	130.3	d(160)	NOE, SEL
3'	129.5	dt(161, 6)	a)	128.6	d(164)	SEL
4'	130.0	dt(162, 7)	a)	131.1	dt(161, 8)	SEL

a) Overlapped with each other. b) Assigned by the comparison with **2a**.

initial structure. The net atomic charge and bond length for **F** are presented in Fig. 6.

^{13}C NMR Spectra. On the basis of the ^1H NMR spectral data, assignments for the ^{13}C signals were made by using the nuclear Overhauser effect (NOE) and complete decoupling (COM), non-decoupling (NON), proton selective decoupling (SEL), and/or low-power selective proton decoupling techniques (LPSEL).²¹⁾

It seemed to be difficult to directly assign the ^{13}C signals of **5**, since its ^1H signals were superimposed on each other; therefore, the relationships between the ^1H and ^{13}C signals were obscure. Thus, first the assignment for **2b** was attempted; the SEL technique for the ring protons accomplished the assignment for C-5, -6, -7, and -8, and the quaternary C-3a, -6a, and -6b were confirmed by using LPSEL measurements. The assignments for C-1 and -2 were accomplished through comparisons with those of the 1-methoxycarbonyl derivative **2a**; also, the phenyl carbons (C-2', -3', and -4') were assigned by the comparisons with those of the 3-(*p*-methoxyphenyl) derivative **2c**. On the basis of the above results for **2b**, the assignment for **5** was attained, except for the signals at $\delta=131.6$, 132.2, and 133.2 due to C-2a, -8a, and -1'. The replacement of the phenyl group of **5** by pentadeuterio-phenyl one, **5-*d*₅**, resulted in changes of the coupling patterns of the signal due to C-1': the carbon signal at $\delta=133.2$ (NON: t) for **5** was changed to a singlet ($\delta=132.9$) for **5-*d*₅**, and, therefore, assigned to be C-1'. The LPSEL technique irradiating the 7-H ($\delta=7.57$) of **5-*d*₅** caused a simplification of the signal patterns at $\delta=132.3$, and the signal at $\delta=132.2$ of **5** was assignable to be C-8a. Consequently, the signal at $\delta=131.8$ of **5** was deduced to be C-2a.

These assignments for **5** and **2b** are summarized in Table 5.

The authors wish to thank Professor Masashi Tashiro, Research Institute of Industrial Science, Kyushu University, for the elemental analyses. The author (M. N.) is grateful to the Ministry of Education, Science and Culture for financial support through a

Grand-in-Aid for Scientific Research (No 59750691).

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maxima were shifted wholly to shorter wavelength (ca. 10 nm), and fine structures were observed over the ranges of 480–570 nm.

17) No significant changes of its electronic spectra were observed at higher acid concentrations than CHCl₃-CF₃-CO₂H (8/1). On the contrary, the downfield shifts of the ring protons on the ¹H NMR spectra were observed up to the acid concentration of CDCl₃-CF₃CO₂D (2/3).

18) Similar behaviors on the electronic spectra were found in 6*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-6-one system, a regio-isomer of **E**. Those results would be published elsewhere.

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