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

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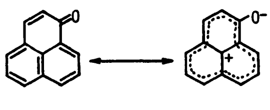
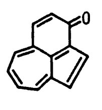
3-Phenyl-4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**5**) was prepared by saponification accompanied by the decarboxylation of the corresponding 1,2-bis(methoxycarbonyl) derivative, which was obtained by the DDQ oxidation of 5,6-dihydro one. Investigations concerning its spectral data and MO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



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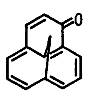

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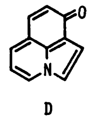
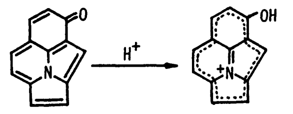


D



E F

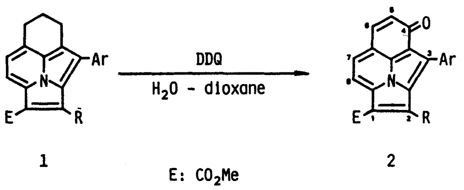
A more recent report[5)] on the synthesis and properties of 9*H*-pyrrolo[3,2,1-*ij*]quinolin-9-one (**D**) stimulated us to investigate 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-one (**E**), which involves a peripheral 10 π-electronic [3.2.2]cyclazine system instead of the indolizine nuclei of **D**. 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=C_6H_5, R=H; b: Ar=C_6H_5, R=E; b-d_5: Ar=C_6D_5, R=E; c: Ar=C_6H_4-OMe(*p*), R=E; d: Ar=C_6H_4-Br(*p*), R=E; e: Ar=4-Biphenyl, R=E; f: 2-Naphthyl, R=E.

Scheme 1.

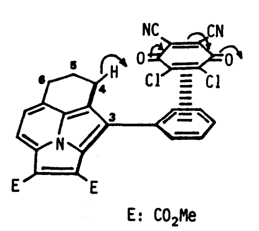


Fig. 1. CT complex formation between the phenyl group of **1a** and DDQ.

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.

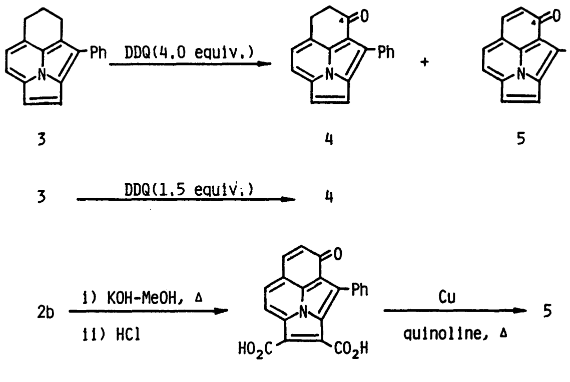
The saponification of **2b** with methanolic potassium hydroxide followed by acidification gave the corresponding dicarboxylic acid, which was decarboxylated in refluxing quinoline in the presence of copper dust to afford **5**. Similarly, the 3-pentadeuteriophenyl derivative **5**-d_5 was obtained from **2b**-d_5 (Scheme 2).

MO Calculations. In an attempt to obtain a better understanding of the properties of **5**, MO calculations using the MNDOA method[10] 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 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).

^{13}C NMR Spectra. A full assignment of the ^{13}C NMR spectrum for **5** was accomplished by a comparison with the spectra for **2a**, **2b**, **2c**, and **5**-d_5 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*-



Scheme 2.

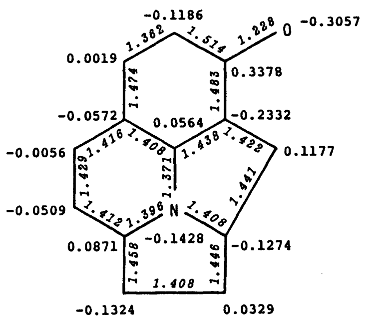
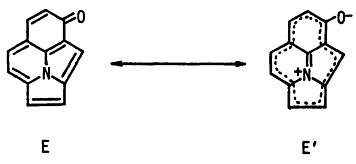


Fig. 2. Net atomic charge and atomic distance (Å) of E by MNDOA.



Scheme 3.

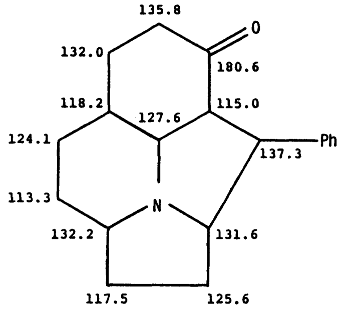


Fig. 3. Assignment of ^{13}C NMR spectrum of **5** in $CDCl_3$.

Table 1. ^{1}H NMR Spectral Data for **3**-d_5 and **5**-d_5 in $CDCl_3$

Compd	δ/ppm				J/Hz	
	1-H	2-H	7-H	8-H	$J_{1\text{-}2}$	$J_{7\text{-}8}$
3-d_5	7.18	7.65	7.35	7.82	3.9	7.8
5-d_5	7.02	7.57	7.51	7.67	4.6	7.8
Δδ[a]	0.16	0.08	−0.16	0.15		

a) $\Delta\delta=\delta(\mathbf{3}\text{-}d_5)-\delta(\mathbf{5}\text{-}d_5)$.

Table 2. ^{1}H 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	$J_{1\text{-}2}$	$J_{5\text{-}6}$	$J_{7\text{-}8}$
$CDCl_3$	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) $\Delta\delta=\delta(CDCl_3)-\delta(CF_3COOD)$.

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**.

^{1}H NMR Spectra. The assignment and discussion concerning the cyclazine ring protons of **5** were achieved by an analysis of the spectrum of the pentadeuteriophenyl derivative **5**-d_5. The chemical shifts[12] 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 upperfield 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 (CF_3CO_2D) are summarized in Table 2. The positive charge resulting from the protonation caused relatively small downfield shifts for the protons (Δδ: within −0.6); interestingly, a small upfield shift was observed for 2-H in CF_3CO_2D in comparison with that in $CDCl_3$. The differences among the coupling constants became smaller in CF_3CO_2D, 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., Δδ=−0.7—−1.8 for 1*H*-phenalen-1-one,[13] Δδ=0.0—−1.3 for 7,9-dimethyl-3*H*-benz[*cd*]azulen-3-one,[3b] and Δδ=−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 (Δδ=−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]

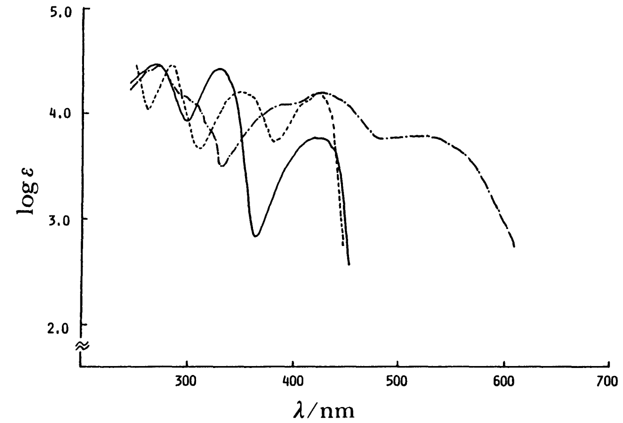


Fig. 4. Electronic spectra of **3** (——), **4** (----), and **5** (-·-·-) in $CHCl_3$.

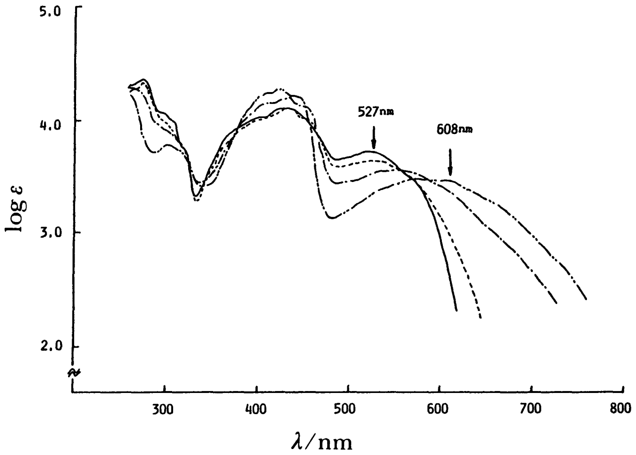


Fig. 5. Change of the electronic spectra of **5** with acid concentrations: (——) in $CHCl_3$; (----) in $CHCl_3$-CF_3COOH=100/1; (-·-·-) in 50/1; (-··-··-) in 3/2.

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 (1M=1 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 phenalenones[2] 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 ^{1}H NMR spectra were obtained on JEOL FX-200 and/or JMN-MH-100 spectrometers and ^{13}C 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 $C_{21}H_{17}NO_2$: 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 $C_{24}H_{21}NO_5$: 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 $C_{23}H_{18}BrNO_4$: 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 $C_{29}H_{23}NO_4$: 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 $C_{27}H_{21}NO_4$: 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 $C_{21}H_{13}NO_3$: 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 $C_{23}H_{15}NO_5$: 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 $C_{24}H_{17}NO_6$: 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 $C_{23}H_{14}BrNO_5$: 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 $C_{29}H_{19}NO_5$: 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 $C_{27}H_{17}NO_5$: 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 h	**2** Yield/%
a	4	6	69
b	4	6	68
b-d_5	4	6	72
c	4	6	96
d	4	45	Trace
	6	54	34
e	4	24	47
f	6	42	55

Table 4. Spectral Data for 4*H*-Benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-ones **2**

Compd	IR ν(CO)	^{1}H NMR(CDCl$_3$) δ	M$^+$ *m/z*
2a	1692 1600	4.02 (3H, s, -OCH$_3$), 6.52 (1H, d, J=8 Hz, 5-H), 7.42 (1H, d, J=8 Hz, 6-H), 7.5—7.6 (3H, m, phenyl), 7.84 (1H, d, J=10 Hz, 7-H), 8.06 (1H, d, J=10 Hz, 8-H), 8.25 (1H, s, 2-H), 8.69 (1H, d, J=8 Hz, phenyl)	327
2b	1740 1716 1618	3.98, 4.02 (3H each, 2s, -OCH$_3$), 6.48 (1H, d, J=9.8 Hz, 5-H), 7.42 (1H, d, J=9.8 Hz, 6-H), 7.5—7.6 (3H, m, phenyl), 7.87 (1H, d, J=8.3 Hz, 7-H), 8.09 (1H, d, J=8.3 Hz, 8-H), 8.2—8.8 (2H, m, phenyl)	385
2c	1742 1711 1600	3.93 (3H, s, -OCH$_3$), 4.01 (6H, s, -OCH$_3$), 6.50 (1H, d, J=10 Hz, 5-H), 7.1 (2H, m, phenyl), 7.42 (1H, d, J=10 Hz, 6-H), 7.85 (1H, d, J=8 Hz, 8-H), 8.05 (1H, d, J=8 Hz, 8-H), 8.3 (2H, m, phenyl)	415
2d	1739 1721 1624	3.99, 4.01 (3H each, 2s, -OCH$_3$), 6.50 (1H, d, J=10 Hz, 5-H), 7.44 (1H, d, J=10 Hz, 6-H), 7.7 (2H, m, phenyl), 7.92 (1H, d, J= 8 Hz, 7-H), 8.14 (1H, d, J=8 Hz, 8-H), 8.2 (2H, m, phenyl)	465 463
2e	1728 1706 1603	4.02, 4.03 (3H each, 2s, -OCH$_3$), 6.51 (1H, d, J=10 Hz, 5-H), 7.42 (1H, d, J=10 Hz, 6-H), 7.3—7.8 (7H, m, aromatic), 7.89 (1H, d, J=8 Hz, 7-H), 8.10 (1H, d, J=8 Hz, 8-H), 8.4 (2H, m, phenyl)	461
2f	1718 1707 1592	3.59, 4.03 (3H each, 2s, -OCH$_3$), 6.53 (1H, d, J=10 Hz, 5-H), 7.46 (1H, d, J=10 Hz, 6-H), 7.6 (2H, m, naphthyl), 7.91 (1H, d, J=8 Hz, 7-H), 7.8—8.1 (3H, m, naphthyl), 8.12 (1H, d, J=8 Hz, 8-H), 8.3 (1H, dd, J=8, 2 Hz, naphthyl), 8.91(1H, br s, naphthyl)	438

h gave a mixture of **4** (16%) and **5** (33%).

4: Yellow needles (hexane-benzene); mp 99—100 °C; IR (KBr) cm^{-1}: 1650 (CO) and 1625 (C=C); ^{1}H NMR (CDCl$_3$) δ=2.99 (2H, t, 6-H, J=6 Hz), 3.38 (2H, t, 5-H, J=6 Hz), 7.17 (1H, d, 1-H, J=4 Hz), 7.2—7.6 (6H, m, 2- and 7-H and phenyl), and 8.1—8.2 (2H, m, phenyl); MS *m/z* (rel intensity): 271 (M$^+$, base peak), 270 (M$^+$ −H, 46), and 241 (26). Found: C, 84.04; H, 4.88; N, 5.37%. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16%.

5: Red needles (hexane-benzene); mp 121—122 °C; IR (KBr) cm^{-1}: 1606 (CO) and 1593 (C=C); ^{1}H NMR (CDCl$_3$) δ=6.23 (1H, d, 5-H, J=10 Hz), 6.79 (1H, d, 1-H, J=4 Hz), 7.06 (1H, d, 6-H, J=10 Hz), 7.2—7.8 (6H, m, 2-, 7-, and 8-H and phenyl), and 8.3—8.5 (2H, m, phenyl); MS *m/z* (rel intensity): 269 (M$^+$, 96), 268 (M$^+$ −H, base peak), and 239 (46). Found: C, 84.47; H, 4.40; N, 5.12%. Calcd for $C_{19}H_{10}NO$: C, 84.74; H, 4.12; N, 5.20%.

Preparation of 5 from 2b. Compound **2b** (570 mg, 1.48 mmol) was heated under reflux in 5% methanolic potassium hydroxide (30 mL) for 12 h and the methanol was removed to give a residue. The residue was made acidic with concd hydrochloric acid. The resultant diacid was filtered, dried, and subjected to the next decarboxylation without further purification. A solution of the diacid in quinoline (30 mL) was refluxed for 0.5 h in the presence of copper dust (100 mg). The copper dust was filtered off and the filtrate was evaporated to give a residue. The residue was dissolved in benzene (50 mL) and washed with 0.5 M hydrochloric acid (50 mL×3) in order to completely remove the quinoline. The organic layer was collected, dried and evaporated to dryness. The residue was subjected to a chromatography on alumina to afford **5** (74% from **2b**) as a chloroform eluent.

Similarly, the pentadeuteriophenyl derivative **5**-d_5 was obtained from **2b**-d_5 in 80% yield.

MO Calculations. The calculations were carried out by using the ACOS system 1000 computer in the Computation Center of Osaka University. For an optimization of the structure, the initial structure was taken as follows: for the geometries of the cyclazine moiety of **E**, the X-ray analytical data for 1,4-dibromopyrrolo[2,1,5-*cd*]indolizine[20] were used. Those of the enone part were estimated by using the molecular models fused by the above cyclazine system. The distance of the C=O bond was taken from that of acrylaldehyde (1.23 Å). A structure optimization was performed for the bond length and valence and dihedral angles of all the atoms of **E**, except for the hydrogen atoms. Among the results, the net atomic charge and bond length for **E** are demonstrated in Fig. 2. A structure optimization for the 3-phenyl derivative **5** was also performed. For the geometries of the benzopyrroloindolizinone moiety and of the phenyl one of **5**, the data for **E** obtained above and for biphenyl were taken, respectively. An optimization was performed for the C-C bond length and the dihedral angle between the mother nuclei and the phenyl one. The results showed that the dihedral angle was calculated to be 76.7°. This showed that the π-electronic system of the phenyl ring had little effect on the mother nuclei.

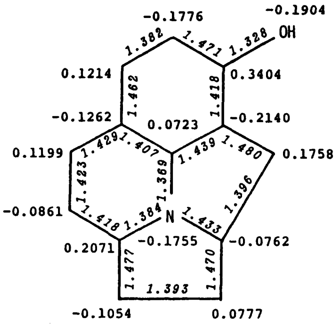


Fig. 6. Net atomic charge and atomic distance (Å) of **F** by MNDOA.

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		^{1}H	**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 ^{1}H 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 ^{1}H signals were superimposed on each other; therefore, the relationships between the ^{1}H 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 quartery 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 δ=131.6, 132.2, and 133.2 due to C-2a, -8a, and -1′. The replacement of the phenyl group of **5** by pentadeuteriophenyl one, **5**-d_5, resulted in changes of the coupling patterns of the signal due to C-1′: the carbon signal at δ=133.2 (NON: t) for **5** was changed to a singlet (δ=132.9) for **5**-d_5, and, therefore, assigned to be C-1′. The LPSEL technique irradiating the 7-H (δ=7.57) of **5**-d_5 caused a simplification of the signal patterns at δ=132.3, and the signal at δ=132.2 of **5** was assignable to be C-8a. Consequently, the signal at δ=131.8 of **5** was deduced to be C-2a.

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

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17) No significant changes of its electronic spectra were observed at higher acid concentrations than $CHCl_3$-CF_3CO_2H (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 $CDCl_3$-CF_3CO_2D (2/3).

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