Studies on Photochemical Reactivities of 2-(Alkylcarbamoyl)quinolines

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The photochemistry of three types of 2-(alklylcarbamoyl)quinolines was studied. The illumination of 2-(diethylcarbamoyl)quinolines (**1a**, **1b**, and **1c**) afforded 2-(2-ethylaminopropionyl)quinolines (**3a**, **3b**, and **3c**) with a small amount of five-membered cyclic products, 1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-ones (**4a**, **4b**, and **4c**), both of which were formed via Type-II hydrogen-atom abstraction from the T_1 state. 2-(Ethylcarbamoyl)quinoline (**1d**) did not undertake any photochemical change. The photochemical inactivity of **1d** could be attributed to the unfavorable orientation of its carbamoyl substituent for intramolecular hydrogen-atom abstraction by a ring nitrogen. The illumination of 2-(alkylcarbamoyl)-3-methyl quinolines (**2a** and **2b**) afforded 2-(*N*-acetyl-*N*-alkylcarbamoyl)-3-methyl quinolines (**5a** and **5b**), which were suggested to be formed by the atmospheric oxidation of an unstable photoproduct formed via the S_1 state.

The photochemistry of *N*-heterocyclic aromatics consisting of a simple six-membered skeleton, such as a pyridine or quinoline nucleus, is still an attractive subject.[1] Especially, the photochemical behavior of the pyridine derivatives bearing an electron–withdrawing substituent has been extensively studied by many investigators.[2] We have reported on the photochemical reactions of a series of similar quinoline derivatives.[3] Most of the photochemical reactions of those quinolines are initiated by intermolecular hydrogen-atom abstraction from solvents by a ring nitrogen at the S_1 state. However, 2-(dimethylcarbamoyl)quinoline was found to bring about Type-II hydrogen-atom abstraction by the ring nitrogen from the methyl group via the $T_1(\pi\ \pi^*)$state, followed by alkyl-insertion to the C(O)–N bond or five-membered cyclization (Scheme 1). 2-(Methylcarbamoyl)quinoline was, however, photochemically inactive.[3b] Its photochemical stability may be attributed to the trans-conformation of the substituent with respect to the quinoline nucleus, as reported by Gdaniec et al.[4] In recent years the photochemical behavior of some amide derivatives has received considerable attention, and a novel type of photochemical reaction has also been reported.[5,6] Such current research has urged us to extend our previous studies to several (alkylcarbamoyl)-quinolines (**1** and **2**) and to confirm a factor in determing the difference in the photochemical reactivities between dialkyl- and monoalkyl-carbamoylquinolines by means of an X-ray single crystal analysis method (Chart 1).

Results and Discussion

Photochemical Reaction of 1. The illumination of acetonitrile solutions of 2-(diethylcarbamoyl)quinolines (**1a**, **1b**, and **1c**) for 10 h in a nitrogen atmosphere gave 2-(2-ethylaminopropionyl)quinolines (**3a**, **3b**, and **3c**) and 2-ethyl-1-

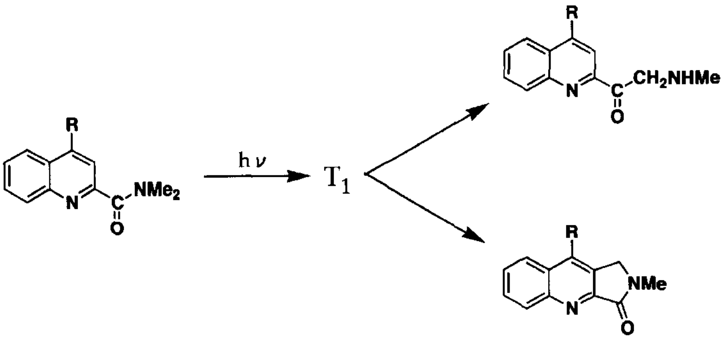
1

2

1a : R = H, $R_1 = R_2 = Et$
1b : R = Me, $R_1 = R_2 = Et$
1c : R = Cl, $R_1 = R_2 = Et$
1d : R = Me, $R_1 = Et$, $R_2 = H$

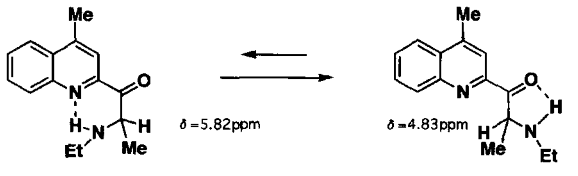
2a : $R_1 = R_2 = Et$
2b : $R_1 = Et$, $R_2 = Me$
2c : $R_1 = Et$, $R_2 = H$
2d : $R_1 = R_2 = Me$

Chart 1.



Scheme 1.

methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-ones (**4a**, **4b**, and **4c**) as minor products (Scheme 2). The NMR data showed that **3** has two different molecular conformations, as shown in the case of **3b** (Chart 2). One is that the hydrogen atom on the amino nitrogen forms hydrogen-bonding with the ring nitrogen; the other is that it forms hydrogen-bonding with the carbonyl oxygen. The ratio of the former type to the latter one at 20 °C was calculated to be 1 : 1.5 by integrating the peaks due to the methine protons at $\delta = 4.83$ and 5.82 ppm, respectively. The integration ratio of the methine proton peaks measured at 50 °C changed to 1 : 1.1. The equilibrium of two conformations shifted to an increase of the former type at higher temperature. The illumination of **1d** for 15 h did not undergo any photochemical change (Table 1). Photosensitization by xanthone ($E_T = 309\ \mathrm{kJ\,mol^{-1}}$[7]) of **1b** ($E_T = 250\ \mathrm{kJ\,mol^{-1}}$[3b]) afforded **3b** and **4b** in 68 and 5% yields. The photochemical reactions of **1** could be explained by the mechanism shown in Scheme 3 from an analogy with the photochemical reaction of 2-(dimethylcarbamoyl)quinoline.[3b] The initial step may be intramolecular hydrogen-atom abstraction by the ring nitrogen in the $T_1(\pi\,\pi^*)$ state; the resulting diradical leads to **3** and **4**.



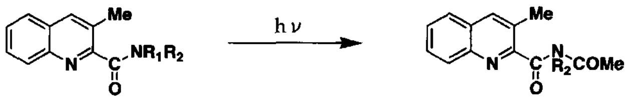
3b

Chart 2.

Table 1. Yields of the Photoproducts of 2-(Diethylcarbamoyl)quinolines

Compound	Conversion/%	Yield/%	
1a	68	**3a** (40),	**4a** (1)
1b	62	**3b** (57),	**4b** (3)
1c	63	**3c** (5),	**4c** (12)
1d	No reaction		

Photochemical Reaction of 2. The illumination of acetonitrile solutions of **2a** and **2b** induced the addition of oxygen to the methylene group of the carbamoyl group to afford 2-(*N*-acetyl-*N*-alkylcarbamoyl)-3-methylquinolines **5a** and **5b** (Scheme 4, Table 2). Photoproducts of **2c** and **2d** were unstable, the identifications of which were unsuccessful. Triplet quenching by 1,3-cyclohexadiene was ineffective on the quantum yield for the formation of **5a** in a nitrogen atmosphere (Fig. 1), indicating that the primary step of this photochemical reaction occurred through the S_1 state. In an oxygen atmosphere the quantum yield was 0.0045, the value of which was almost identical with that in a nitrogen atmosphere. This fact suggests that oxidation occurred when some unstable product, formed photochemically, was exposed to air through evaporation of the solution after illumination or isolation of the products. As shown in Table 3, the oxygen atmosphere extremely decreased the yield of **5a**. It shows that **5a** easily decomposed on light absorption in the presence of oxygen. Although we could not identify the unstable product and the mechanism of photochemical process to **5**, it is quite



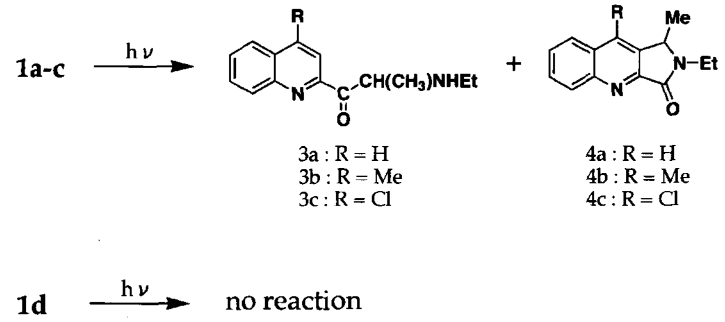
2a : $R_1 = R_2 = Et$
2b : $R_1 = Et,\ R_2 = Me$

5a : $R_2 = Et$
5b : $R_2 = Me$

Scheme 4.

Table 2. Yields of the Photoproducts of **2**

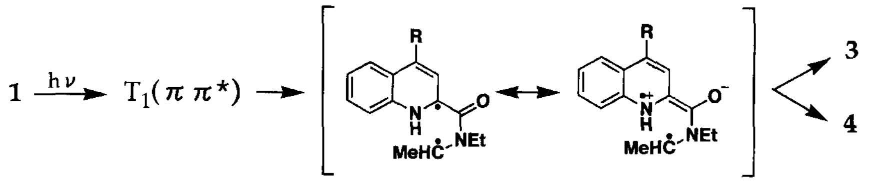
Compound	Conversion/%	Yield/%
2a	73	**5a** (45)
2b	65	**5b** (30)



3a : R = H
3b : R = Me
3c : R = Cl

4a : R = H
4b : R = Me
4c : R = Cl

Scheme 2.



Scheme 3.

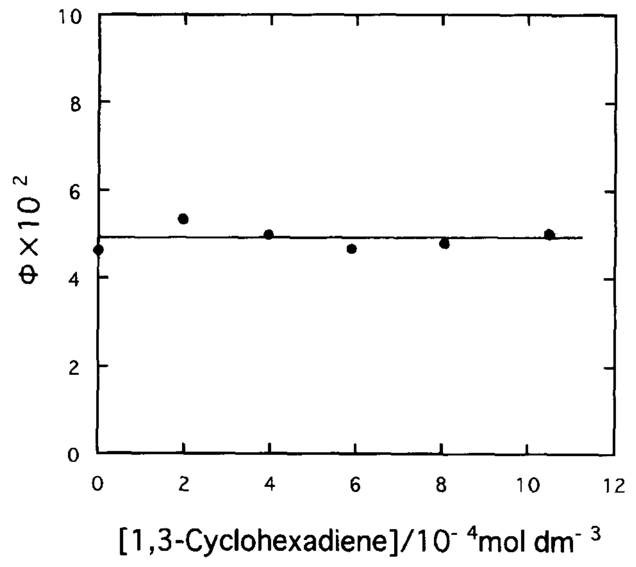


Fig. 1. Effect of triplet quencher on the quantum yield for the formation of **5a**.

Table 3. Influence of Atmosphere on the Yield of **5a**

Atmosphere	Irradiation Time	Conversion	Yield
	min	%	%
N_2	90	73	45
O_2	60	100	12

interesting that the introduction of a methyl group at the 3-position of the quinoline ring brought about a novel type of photochemical reaction of the (carbamoyl)quinolines. The physicochemical studies of the photochemical reaction of **2** are presently in progress.

X-Ray Single Crystal Analysis. Taking into account the studies of Gdaniec et al. for 2-(methylcarbamoyl)quinoline by means of X-ray single crystal analysis, (monoalkylcarbamoyl)quinoline seems to have a molecular conformation that is unfavorable for intramolecular hydrogen-atom abstraction by the ring nitrogen, because the methylene group is situated at the opposite side of the ring nitrogen.[4] We performed X-ray single crystal analysis in order to obtain information about the orientation of the ethylcarbamoyl substituents of 2-(diethylcarbamoyl)-4-methylquinoline(**1b**) and 2-(ethylcarbamoyl)-4-methylquinoline (**1d**), which could be more readily prepared as a single crystal from recrystallization. Crystallographic data, data collection, and reduction parameters are summarized in Table 4. The positional and U_{iso} parameters are listed in Table 5 for **1b** and Table 7 for **1d** and intramolecular torsion angles in Table 6 for **1b** and Table 8 for **1d**, respectively.

An ORTEP drawing of **1b** is shown in Fig. 2. The plane of (C(14)–N(2)–C(11)–O(1)) in the carbamoyl group twists against the quinoline plane at 46.3°. The carbon atoms C(13) and C(15) do not lie in the former plane, the torsion angle of (C(11)–N(2)–C(14)–C(15)) being 82.8° and that of (C(11)–N(2)–C(12)–C(13)) being 109.0°. The distance between the methylene hydrogen, H(12B), of one ethyl group and the ring nitrogen (N(1)) is 2.527 Å, being shorter than the van der Waals (vdW) sum (2.75 Å [8]), where the formation of a six-membered-hydrogen bridge was ascertained. The hydrogen atom (H(14B)) of an alternative ethyl group has shorter contact with the carbonyl oxygen (O1), its distance of 2.431 Å being considerably less than the vdW sum (2.72 Å). This short intramolecular contact forms a cyclic

Table 4. Crystal Data, Data Collection, and Reduction Parameters for **1b** and **1d**

	1b	**1d**
Chemical formula	$C_{15}H_{18}N_2O$	$C_{13}H_{14}N_2O$
Formula weight	242.30	214.30
Crystal size	0.25×0.22×0.35 mm^3	0.35×0.25×0.20 mm^3
a/Å	8.564(3)	9.092(3)
b/Å	20.721(8)	15.463(7)
c/Å	7.677(2)	8.172(3)
β/deg	102.39(2)	95.45(3)
Volume of unit cell	1330.6(8) Å^3	1143.7(7) Å^3
Space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Z Value	4	4
D_{calc} / g cm^{-3}	1.21	1.24
D_{obs} / g cm^{-3}	1.17	1.26
Total reflection measured	3442	3011
Unique reflections	3044	2635
Least squares refinement method	Full matrix	Full matrix
Weight method	Unit weight	Unit weight
Reflections used in L.S.	1776	1817
Data reduction cut-off	3.00	3.00
L. S. parameters	163	146
Residuals, R	0.0614	0.0589
Residuals, R_w	0.0575	0.0566
Max shift/e.s.d	0.3305	0.2258
Goodness of fit	0.66061	0.54406

Table 5. Positional Parameters and Equivalent Isotropic Thermal Parameters for **1b**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso} [a)]
N(1)	1.0520(3)	0.3598(1)	0.0947(4)	0.048
O(1)	1.4123(3)	0.3410(1)	−0.0142(4)	0.075
N(2)	1.2851(3)	0.2550(1)	0.0712(3)	0.049
C(8)	0.9619(4)	0.4096(2)	0.1380(4)	0.049
C(9)	1.0315(4)	0.4671(2)	0.2235(4)	0.050
C(2)	1.2866(4)	0.4207(2)	0.2258(5)	0.052
C(7)	0.7942(4)	0.4039(2)	0.0915(5)	0.057
C(1)	1.2082(4)	0.3666(2)	0.1350(4)	0.049
C(3)	1.2010(4)	0.4713(2)	0.2702(4)	0.052
C(4)	0.9266(5)	0.5172(2)	0.2510(5)	0.064
C(12)	1.1829(4)	0.2251(2)	0.1771(5)	0.056
C(11)	1.3106(4)	0.3188(2)	0.0595(5)	0.051
C(6)	0.6985(5)	0.4538(2)	0.1190(5)	0.069
C(14)	1.3823(5)	0.2114(2)	−0.0137(5)	0.059
C(5)	0.7663(6)	0.5110(2)	0.1970(6)	0.075
C(10)	1.2838(5)	0.5308(2)	0.3581(5)	0.070
C(13)	1.0312(5)	0.1968(2)	0.0680(6)	0.074
C(15)	1.5446(5)	0.1982(2)	0.1017(6)	0.075
H(2)	1.40125	0.42185	0.25716	0.050
H(7)	0.74764	0.36427	0.03992	0.050
H(4)	0.97131	0.55590	0.30987	0.050
H(12A)	1.24004	0.19048	0.24605	0.050
H(12B)	1.15414	0.25678	0.25595	0.050
H(6)	0.58432	0.44997	0.08454	0.050
H(14A)	1.32774	0.17093	−0.03874	0.050
H(14B)	1.39644	0.23053	−0.12324	0.050
H(5)	0.69966	0.54675	0.21354	0.050
H(10A)	1.20594	0.56144	0.37929	0.050
H(10B)	1.34624	0.54974	0.28129	0.050
H(10C)	1.35274	0.51914	0.46939	0.050
H(13A)	0.96822	0.17776	0.14397	0.050
H(13B)	1.05732	0.16446	−0.01083	0.050
H(13C)	0.97142	0.23076	−0.00093	0.050
H(15A)	1.60474	0.16981	0.04216	0.050
H(15B)	1.53194	0.17881	0.21126	0.050
H(15C)	1.60054	0.23841	0.12676	0.050

a) $U_{\mathrm{iso}} = 1/3(\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j)/\text{Å}^2$.

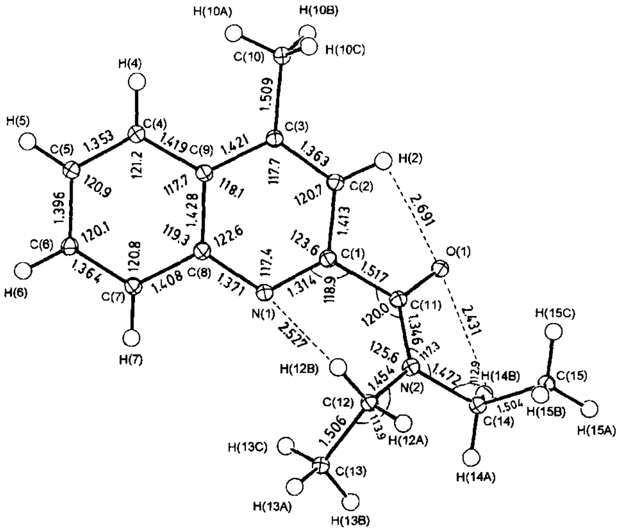


Fig. 2. An ORTEP drawing for **1b**. Numerical values along bond-axes rerpresent their bond lengths(Å), and another ones indicate bond angles (°). Short contacts are indicated with broken lines.

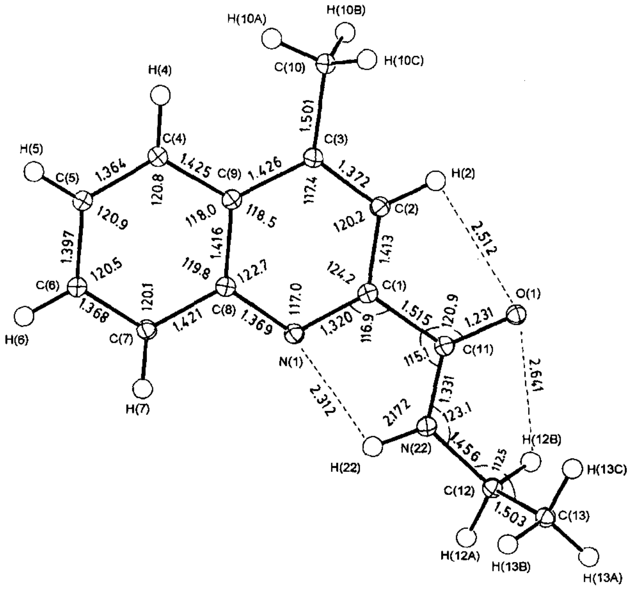


Fig. 3. An ORTEP drawing for **1d**. Numerical values along bond-axes rerpresent their bond lengths(Å), and another ones indicate bond angles (°). Short contacts are indicated with broken lines.

five-membered configuration. That is, the ring nitrogen and the carbonyl oxygen have short contacts with the hydrogen atoms (H(12B) and H(14B)) of each ethyl group of the carbamoyl substituent, respectively. The bond angles of ∠N(1)–H(12B)–C(12) and ∠H(12B)–N(1)–C(12) were estimated to be 112° and 17.1°, respectively. The hydrogen atom H(12B) is considered to be situated in a position favorable for undergoing intramolecular hyrogen-atom abstraction by the $2P_z$ orbital of the ring nitrogen in the $T_1(\pi\ \pi^*)$ state. Another shorter contact than the vdW sum was observed between N(1) and N(22) (N(1)- - -N(22) = 2.981 Å, vdW sum = 3.10 Å). There was no intermolecular short contact in the crystal structure.

An ORTEP drawing of **1d** is shown in Fig. 3. Its fundamental molecular conformation is approximately identical with that of 2-(methylcarbamoyl)quinoline, except for a conformational difference between the ethyl group and the methyl group. The molecule **1d** is also almost planar, the angle between the carbamoyl skeleton (C(12)–N(22)–C(11)–O(1)) and the quinoline ring being about 6.0°. The torsion angle of (C(11)–N(22)–C(12)–C(13)) is 74.6°. This shows that the methyl carbon C(13) deviates from the molecular plane because of sp^3 hybridization of C(12). Gdaniec et al. refered to the existence of short contacts between N(1) and H(22), and N(1) and N(22) of 2-(methylcarbamoyl)quinoline, the distances of which were 2.40 and 2.66 Å, respectively, but did not mention another intramolecular short contact.[4] In the case of **1d** the corresponding distances, N(1)- - -H(22) and N(1)- - -N(22), are 2.312 and 2.680 Å, respectively. It can be seen that the amide hydrogen of **1d** forms stronger hyrogen

Table 6. Intramolecular Torsion Angles for **1b**

Atoms	Angle (°)	Atoms	Angle (°)
C(1)–N(1)–C(8)–C(9)	0.0(4)	C(8)–N(1)–C(1)–C(2)	2.6(4)
C(1)–N(1)–C(8)–C(7)	178.3(5)	C(8)–N(1)–C(1)–C(11)	−168.8(5)
C(12)–N(2)–C(11)–O(1)	171.0(6)	C(12)–N(2)–C(11)–C(1)	−10.8(3)
C(11)–N(2)–C(12)–C(13)	109.0(5)	C(14)–N(2)–C(12)–C(13)	−78.2(4)
C(12)–N(2)–C(14)–C(15)	−90.6(4)	C(14)–N(2)–C(11)–O(1)	−1.7(4)
C(14)–N(2)–C(11)–C(1)	176.6(5)	C(11)–N(2)–C(14)–C(15)	82.8(4)
N(1)–C(8)–C(9)–C(3)	−2.2(4)	N(1)–C(8)–C(9)–C(4)	175.8(5)
N(1)–C(8)–C(7)–C(6)	−175.0(6)	C(7)–C(8)–C(9)–C(3)	179.5(5)
C(7)–C(8)–C(9)–C(4)	−2.5(4)	C(9)–C(8)–C(7)–C(6)	3.3(4)
C(8)–C(9)–C(3)–C(2)	1.8(4)	C(8)–C(9)–C(3)–C(10)	179.0(5)
C(8)–C(9)–C(4)–C(5)	−0.5(4)	C(4)–C(9)–C(3)–C(2)	−176.1(6)
C(3)–C(9)–C(4)–C(5)	177.4(6)	C(4)–C(9)–C(3)–C(10)	1.1(4)
C(3)–C(2)–C(1)–N(1)	−3.0(4)	C(1)–C(2)–C(3)–C(9)	0.6(4)
C(3)–C(2)–C(1)–C(11)	168.5(5)	C(1)–C(2)–C(3)–C(10)	−176.6(6)
C(8)–C(7)–C(6)–C(5)	−1.1(4)	N(1)–C(1)–C(11)–O(1)	129.9(5)
N(1)–C(1)–C(11)–N(2)	−48.5(4)	C(2)–C(1)–C(11)–O(1)	−42.1(4)
C(2)–C(1)–C(11)–N(2)	139.5(5)	C(9)–C(4)–C(5)–C(6)	2.7(4)
C(7)–C(6)–C(5)–C(4)	−1.9(4)		

Table 7. Positional Parameters and Equivalent Isotropic Thermal Parameters for **1d**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso} [a)]
O(1)	0.2633(3)	0.1500(1)	0.0847(2)	0.052
N(22)	0.2181(3)	0.2280(2)	0.3088(3)	0.044
N(1)	0.4554(3)	0.1597(2)	0.4816(3)	0.040
C(11)	0.2969(3)	0.1726(2)	0.2278(3)	0.040
C(9)	0.6745(3)	0.0673(2)	0.5036(3)	0.041
C(2)	0.5256(3)	0.0805(2)	0.2475(3)	0.044
C(1)	0.4333(3)	0.1369(2)	0.3256(3)	0.039
C(8)	0.5759(3)	0.1251(2)	0.5715(3)	0.040
C(7)	0.5982(3)	0.1473(2)	0.7408(4)	0.049
C(3)	0.6471(3)	0.0445(2)	0.3343(4)	0.044
C(12)	0.0793(3)	0.2653(2)	0.2386(4)	0.051
C(5)	0.8116(3)	0.0553(2)	0.7720(4)	0.055
C(10)	0.7440(4)	−0.0187(2)	0.2555(4)	0.061
C(6)	0.7140(4)	0.1124(2)	0.8381(4)	0.056
C(4)	0.7937(3)	0.0331(2)	0.6098(4)	0.053
C(13)	−0.0463(4)	0.2017(3)	0.2314(5)	0.075
H(2)	0.50421	0.06670	0.13287	0.050
H(7)	0.53113	0.18652	0.78647	0.050
H(12A)	0.05376	0.31403	0.30312	0.050
H(12B)	0.09096	0.28393	0.12852	0.050
H(5)	0.89190	0.03156	0.84279	0.050
H(10A)	0.82285	−0.03686	0.33425	0.050
H(10B)	0.78435	0.00864	0.16425	0.050
H(10C)	0.68655	−0.06806	0.21715	0.050
H(6)	0.72838	0.12741	0.95246	0.050
H(4)	0.86197	−0.00615	0.56633	0.050
H(13A)	−0.13558	0.22815	0.18312	0.050
H(13B)	−0.05988	0.18295	0.34092	0.050
H(13C)	−0.02258	0.15295	0.16632	0.050
H(22)	0.24638	0.24215	0.41354	0.06(1)

a) $U_{\mathrm{iso}} = 1/3(\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j)/\text{Å}^2$.

bonding with the ring nitrogen than that of **1b**. Consequently, the amino nitrogen of **1d** would be attracted more strongly to the ring nitrogen, so that the distance between both nitrogen atoms becomes short by 0.301 Å compared with that of **1b**. Two additional short contacts were also found in **1d** (H(12B)- - -O(1) = 2.641 Å, H(2)- - -O(1) = 2.540 Å, vdW sum = 2.72 Å). Those two short contacts and one hydrogen-bonding would act to make the conformation of **1d** planar and to hold the ethylene group at the opposite side of the ring nitrogen. It is evident that such a conformation is responsible for the photochemical inactivity of **1d**. In the crystal of **1d** there were short intermolecular contacts less than the vdW sum, which were observed between O(1) and H(22), and between O(1) and N(22) (O(1)- - -H(22) = 2.17 Å, O(1)- - -N(22) = 2.94 Å (vdW sum = 3.07 Å)).

Experimental

The NMR spectra were measured in $CDCl_3$ on a JEOL GX-270 using TMS as an internal standard, and mass spectra were measured by a JEOL JMS-SX102. The phosphorescence spectra were recorded with a Shimadzu F-3010 attached to a phosphorescence accessory.

X-Ray Single Crystal Analysis. Suitable single crystals for an X-ray single crystal analysis were obtained by recrystallization from ethanol or its mixture with hexane. The diffraction data were measured using a Mac Science MXC18 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The data were collected with the 2θ–ω scan mode. The scan speed was 7.00 deg min^{-1}, where the maximum 2θ value was 55°. Crystan-GM was used as the computer program for the solution and refinement of the crystal structure. The structure was determined by a direct method using SIR 92, and was refined using a full–matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen-atoms. The positions of the hydrogen atoms were refined to have a fixed C–H bond length of 0.96 Å, the initial configuration being taken as sp^2 or sp^3.

Materials. All of the used solvents were of reagent grade from Wako Pure Chemical Industries. Acetonitrile was refluxed in the presence of phosphorus pentaoxide and distilled. Xanthone (Wako) was purified by sublimation after twice recrystallization from ethanol. 1,3-Cyclohexadiene (Tokyo Kasei Kogyo Co.) was used after

Table 8. Intramolecular Torsion Angles for **1d**

Atoms	Angle (°)	Atoms	Angle (°)
C(12)–N(22)–C(11)–O(1)	2.6(3)	C(12)–N(22)–C(11)–C(1)	−176.5(4)
C(11)–N(22)–C(12)–C(13)	74.6(4)	C(8)–N(1)–C(1)–C(11)	177.8(4)
C(1)–N(1)–C(8)–C(9)	0.1(3)	C(8)–N(1)–C(1)–C(2)	−0.5(3)
C(1)–N(1)–C(8)–C(7)	−178.2(4)	O(1)–C(11)–C(1)–N(1)	−175.3(4)
O(1)–C(11)–C(1)–C(2)	3.2(3)	N(22)–C(11)–C(1)–N(1)	3.8(3)
N(22)–C(11)–C(1)–C(2)	−177.7(4)	C(3)–C(9)–C(8)–N(1)	0.1(3)
C(8)–C(9)–C(3)–C(2)	0.1(3)	C(3)–C(9)–C(8)–C(7)	178.4(5)
C(8)–C(9)–C(3)–C(10)	−177.9(5)	C(4)–C(9)–C(8)–N(1)	−178.0(5)
C(4)–C(9)–C(8)–C(7)	0.3(3)	C(8)–C(9)–C(4)–C(5)	0.1(3)
C(4)–C(9)–C(3)–C(2)	178.1(5)	C(3)–C(9)–C(4)–C(5)	−177.9(5)
C(4)–C(9)–C(3)–C(10)	0.1(3)	C(3)–C(2)–C(1)–N(1)	0.7(3)
C(3)–C(2)–C(1)–C(11)	−177.6(5)	C(1)–C(2)–C(3)–C(9)	−0.4(3)
C(1)–C(2)–C(3)–C(10)	177.5(5)	N(1)–C(8)–C(7)–C(6)	177.8(5)
C(9)–C(8)–C(7)–C(6)	−0.6(3)	C(8)–C(7)–C(6)–C(5)	0.5(3)
C(6)–C(5)–C(4)–C(9)	−0.2(4)	C(4)–C(5)–C(6)–C(7)	−0.1(4)

distillation. The preparation of **1** and **2** was achieved according to the procedure described in an earlier paper.[3b]

2-(Diethylcarbamoyl)quinoline (1a): Colorless liquid; IR (neat) 3070, 2970, 1625 (CO) cm^{-1}; ^{1}H NMR δ = 1.21 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 1.30 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 3.41 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 3.58 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 7.30—8.30 (6H, m, ArH) ; MS m/z 228 (M$^+$).

2-(Diethylcarbamoyl)- 4-methylquinoline (1b): Mp 60—60.5 °C (from mixture of ethanol and hexane); IR (KBr) 3080, 2970, 1620 (CO) cm^{-1}; ^{1}H NMR δ = 1.20 (3H, t, J = 7.3 Hz, $CH_2C\underline{H}_3$), 1.30 (3H, t, J = 7.3 Hz, $CH_2C\underline{H}_3$), 2.70 (3H, s, CH_3 on ring), 3.43 (2H, q, J = 7.3 Hz, $C\underline{H}_2CH_3$), 3.60 (2H, q, J = 7.3 Hz, $C\underline{H}_2CH_3$), 7.33—8.23 (5H, m, ArH); MS m/z 242 (M$^+$).

4-Chloro-2-(diethylcarbamoyl)quinoline (1c): Mp 75.5—76 °C (from mixture of ethanol and hexane); IR (KBr) 3090, 2980, 1620 (CO) cm^{-1}; ^{1}H NMR δ = 1.28 (3H, t, J = 7.3 Hz, $CH_2C\underline{H}_3$), 1.32 (3H, t, J = 7.3 Hz, $CH_2C\underline{H}_3$), 3.56 (4H, quintet, J = 7.3 Hz, 2(CH_2)), 7.51—8.43 (5H, m, ArH) ; MS m/z 262/264 (M$^+$).

2-(Ethylcarbamoyl)-4-methylquinoline (1d): Mp 93.0 °C (from ethanol); IR (KBr) 3300 (NH), 3080, 2980, 1660 (CO) cm^{-1}; ^{1}H NMR δ = 1.32 (3H, t, J = 7.3 Hz, $CH_2C\underline{H}_3$), 2.76 (3H, s, CH_3 on ring), 3.52—3.62 (2H, m, $C\underline{H}_2CH_3$), 7.58—8.26 (6H, m, ArH and NH); MS m/z 214 (M$^+$).

2-(Diethylcarbamoyl)-3-methylquinoline (2a): Mp 73—74 °C (from diethyl ether–hexane); IR (KBr) 3060, 2980, 1635 (CO) cm^{-1}; ^{1}H NMR δ = 1.12 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 1.34 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.49 (3H, s, CH_3 on ring), 3.18 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 3.66 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 7.51—8.10 (5H, m, ArH); MS m/z 242 (M$^+$).

2-(*N*-Ethyl-*N*-methylcarbamoyl)-3-methylquinoline (2b): Colorless liquid; IR (neat) 3050, 2970, 1640 (CO) cm^{-1} ; ^{1}H NMR δ = 1.09 (1.6H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 1.26 (1.4H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.43 (1.4H, s, CH_3 on ring), 2.45 (1.6H, s, CH_3 on ring), 2.79 (1.4H, s, N–CH_3), 3.13 (1.6H, s, N–CH_3), 3.15 (1.07H, q, J = 7.2 Hz,$C\underline{H}_2CH_3$), 3.66 (0.93H, q, J = 7.2 Hz, -$C\underline{H}_2CH_3$), 7.45—8.03 (5H, m, ArH); MS m/z 228 (M$^+$).

2-(Ethylcarbamoyl)-3-methylquinoline (2c): Mp 114 °C (from cyclohexane); IR (KBr) 3280 (NH),3050, 2980, 1665 (CO) cm^{-1} ; ^{1}H NMR δ = 1.33 (3H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.88 (3H, s, CH_3 on ring), 3.55 (2H, m, $C\underline{H}_2CH_3$), 7.54—8.24 (6H, m, ArH and NH); MS m/z 214 (M$^+$).

2-(Dimethylcarbamoyl)-3-methylquinoline (2d): Mp 110 °C (from cyclohexane); IR (KBr) 3050, 2980, 1635 (CO) cm^{-1} ; ^{1}H NMR δ = 2.50 (3H, s, CH_3 on ring), 2.92 (3H, s, N–CH_3), 3.22 (3H, s, N–CH_3), 7.55—8.20 (5H, m, ArH); MS m/z 214 (M$^+$).

Direct Illumination of 1 and 2. **1** (50 mg) and **2** (100 mg) dissolved in 60 cm^3 of acetonitrile were illuminated in a Pyrex vessel with a 100-W high-pressure immersion mercury lamp (Riko Kagaku Sangyo Co.). After evaporation of the solvent, the residue was developed on thin-layer chromatography of Kieselgel (PF254, Merck) with a mixture of chloroform and diethyl ether.

Photosensitization of 1b by Xanthone. An acetonitrile solution of 35 cm^3 containing 27 mg of **1b** (3.0×10^{-3} mol dm^{-3}) and 27 mg of xanthone (4×10^{-3} mol dm^{-3}) was illuminated in a quartz cylindrical cell for 5 h under a nitrogen atmosphere with a 500-W high-pressure mercury lamp (USH-500D, Ushio Electric Inc). Exciting light shorter than 350 nm was removed by use of a UV-35 Toshiba cut-off filter. The amounts of **3b** and **4b** were spectrometrically determined after separation by the thin-layer chromatography of Kieselgel (PF254, Merck) with a mixture of chloroform and diethyl ether.

Triplet Quenching of 2a. The triplet excitation energy of **2a** was estimated to be 255 kJ mol^{-1} from the first maximum of its phosphorescence spectrum measured in ethanol at 77 K. 1,3-Cyclohexadiene was used as a triplet quencher (E_T = 219 kJ mol^{-1} [7]). The long phosphorescence lifetime of 1.5 s showed that the T_1 state of **2a** was of the $\pi\,\pi^*$ type. An acetonitrile solution (35 cm^3) containing 5×10^{-4} mol dm^{-3} of **2a** was illuminated in a cylindrical quartz cell by 313-nm light in a nitrogen atmosphere. Conversions of **2a** were in the range of 10—15%. The procedures of quantum yield measurements have been described elswhere.[3b] The amount of **5a** was spectrometrically determined after separation by thin-layer chromatography of Kieselgel (PF254, Merck) with a mixture of chloroform and diethyl ether.

2-(2-Ethylaminopropionyl)quinoline (3a): Colorless liquid, picrate 155.0—155.5 °C (from EtOH); IR (neat) 3300 (vw), 3050, 2950, 1655 (CO) cm^{-1}; ^{1}H NMR δ = 0.97 (3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.75 (1.4H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 1.84 (1.6H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 3.33 (2H, m, $C\underline{H}_2CH_3$), 5.06 (0.6H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 5.84 (0.4H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 7.24—8.34 (7H, m, ArH and NH); MS m/z 228 (M$^+$). Found (for picrate): C, 52.41; H, 4.22; N, 15.14%. Calcd for $C_{20}H_{19}N_5O_8$: C, 52.46; H, 4.18; N, 15.30%.

2-(2-Ethylaminopropionyl)-4-methylquinoline (3b): Mp 83.0—83.6 °C (from ethanol–hexane); IR (KBr) 3300 (NH), 3080, 2980, 2940, 1650 (CO), 1560, 1515, 1430 cm^{-1}; ^{1}H NMR δ = 1.01

(3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.74 (1.2H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 1.79 (1.8H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 2.66 (3H, s, CH_3 on ring), 3.29 (2H, q, J = 7.25 Hz, $C\underline{H}_2CH_3$), 4.83 (0.6H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 5.82 (0.4H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 7.12—8.42 (6H, m, ArH and NH); MS m/z 242 (M^+). Found: C, 74.33; H, 7.50; N; 11.56%. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56%.

4-Chloro-2-(2-ethylaminopropionyl)quinoline (3c). Mp 72—73 °C (from ethanol–hexane); IR (KBr) 3280 (NH), 3050, 2950, 1655 (CO) cm^{-1}; ^1H NMR δ = 1.05 (3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.70 (1.2H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 1.87 (1.8H, d, J = 7.25 Hz, $CHC\underline{H}_3$), 3.31 (2H, q, J = 7.25 Hz, $C\underline{H}_2CH_3$), 4.86 (0.6H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 5.76 (0.4H, q, J = 7.25 Hz, $C\underline{H}CH_3$), 7.40—8.40 (6H, m, ArH and NH). HRMS: Found: m/z 262.0862. Calcd for $C_{14}H_{15}ClN_2O$: M, 262.0873.

2-Ethyl-1-methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (4a). Mp 105—106 °C (from ethanol–hexane); IR (KBr) 3050, 2920, 1690 (CO) cm^{-1} ; ^1H NMR δ = 1.33 (3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.66 (3H, d, J = 6.85 Hz, $CHC\underline{H}_3$), 3.30—3.50 (2H, m, $C\underline{H}_2CH_3$), 4.71 (1H, q, J = 6.85 Hz, $C\underline{H}CH_3$), 7.58—8.63 (5H, m, ArH). HRMS: Found : m/z 226.1114. Calcd for $C_{14}H_{14}N_2O$: M, 226.1107.

2-Ethyl-1,9-dimethyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (4b). Mp 80—80.5 °C (from ethanol–hexane); IR (KBr) 3040, 2990, 1690 (CO) cm^{-1}; ^1H NMR δ = 1.30 (3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.62 (3H, d, J = 6.85 Hz, $CHC\underline{H}_3$), 3.37—3.42 (2H, m, $C\underline{H}_2CH_3$), 4.63 (1H, q, J = 6.85 Hz, $C\underline{H}CH_3$), 7.61—8.19 (4H, m, ArH). HRMS: Found : m/z 240.1231. Calcd for $C_{15}H_{16}N_2O$: M, 240.1263.

9-Chloro-2-ethyl-1-methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (4c). Mp 135—136 °C (from ethanol–hexane); IR (KBr) 3050, 2950, 1680 (CO) cm^{-1}; ^1H NMR δ = 1.30 (3H, t, J = 7.25 Hz, $CH_2C\underline{H}_3$), 1.63 (3H, d, J = 6.85 Hz, $CHC\underline{H}_3$), 3.33 (2H, m, $C\underline{H}_2CH_3$), 4.65 (1H, q, J = 6.85 Hz, $C\underline{H}CH_3$), 7.51—8.55 (4H, m, ArH); MS: m/z 260/262 (M^+). Found: C, 64.12; H, 4.99; N, 10.65%. Calcd for $C_{14}H_{15}ClN_2O$: C, 64.50; H, 5.03; N, 10.75%.

2-(*N*-Acetyl-*N*-ethylcarbamoyl)-3-methylquinoline (5a). Colorless liquid; IR (neat) 3010, 2980, 1710 (CO), 1690 (CO), 1490, 1460 cm^{-1}; ^1H NMR δ = 1.25 (3H, t, J = 6.92 Hz, $CH_2C\underline{H}_3$), 2.33 (3H, s, $COCH_3$), 2.52 (3H, s, CH_3 on ring), 3.82 (2H, q, J = 6.92 Hz, $C\underline{H}_2CH_3$), 7.52—8.05 (5H, m, ArH); MS m/z 256 (M^+). Found: C, 70.29; H, 6.22; N, 10.92%. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.28; H, 6.28; N, 10.84%.

2-(*N*-Acetyl-*N*-methylcarbamoyl)-3-methylquinoline (5b). Colorless liquid; IR (neat) 3050, 2900, 1710 (CO), 1690 (CO), 1490, 1460 cm^{-1}; ^1H NMR δ = 2.35 (3H, s, $COCH_3$), 2.47 (3H, s, CH_3 on ring), 3.23 (3H, s, $N–CH_3$), 7.49—8.01 (5H, m, ArH); MS m/z 242 (M^+). Found: C, 69.22; H, 5.85; N, 11.60%. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56%.

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