

New Heterocyclic Compounds Derived from Diethyl 2,5-Dioxo-1,4-cyclohexanedicarboxylate and 2-Aminobenzophenone

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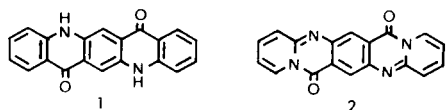
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The synthesis and properties of a new class of heterocyclic compounds **5-8** derived from 2-aminobenzophenone and diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate were investigated.

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As quinacridone (**1**) revealed excellent characteristics as an organic pigment, many derivatives of **1** have been synthesized [1]. Recently, a dimethyl derivative of **1** was utilized for the photoconductor in an organic solar cell [2]. Compound **1** was generally prepared from diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate (**3**) and aniline in several steps [1]. When 2-aminopyridine instead of aniline was employed, a new aza analogue of **1**, namely pyrido[2,1-*b*]pyrido[1',2':1,2]pyrimido[4,5-*g*]quinazoline-7,15-dione (**2**) was obtained [3]. We now report the synthesis



and properties of new heteropolycyclic compounds derived from **3** and 2-aminobenzophenone (**4**) which are important as the raw materials for the preparation of benzodiazepines [4]. Furthermore, the thermal and photochemical properties of the intermediates were studied.

It is known that the reaction of **3** with aniline afforded diethyl 2,5-dianilino-3,6-dihydroterephthalate in ethanol containing an acid catalyst under a nitrogen atmosphere. Using **4** as the aromatic amine under the same conditions, a Friedländer type condensation [5] proceeded to form diethyl 6,13-dihydro-7,14-diphenylbenzo[*b*]quinolino[2,3-*j*]quinoline-6,13-dicarboxylate (**5**). The ¹H and ¹³C-nmr

of **5** showed the methine proton at 5.35 ppm and its carbon at 54.14 ppm, respectively. In the uv spectra, there was the spectral pattern similar to quinoline (Figure 1).

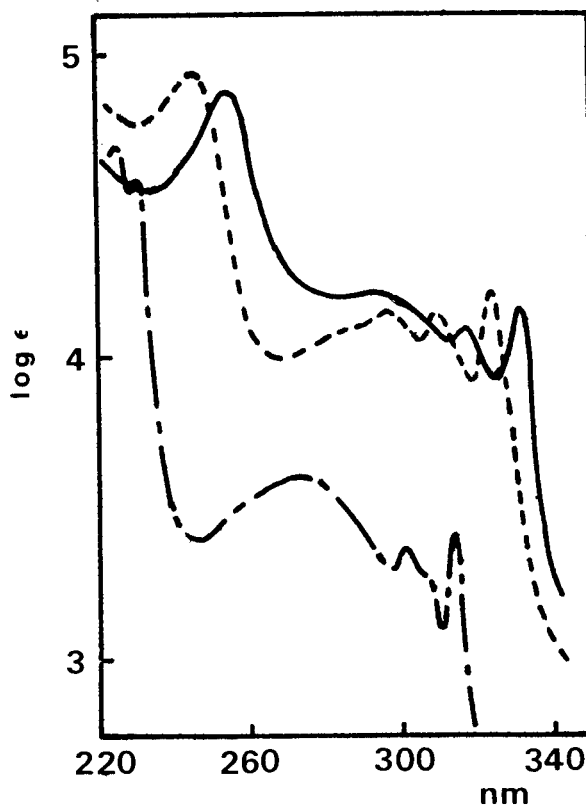
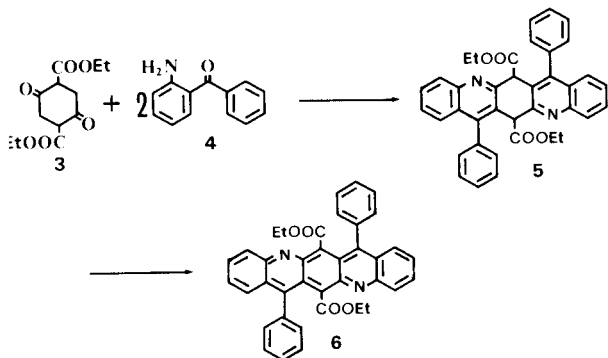


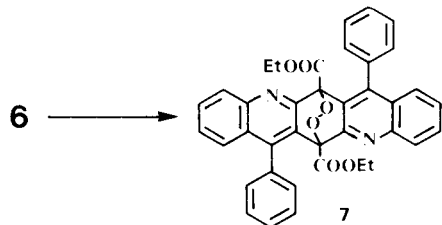
Figure 1. Uv spectra of the compounds **5**, **7** and quinoline in dioxane: **5**: (---); **7**: (—); quinoline: (-·-·).

Oxidation of **5** with chloranil in methylcellosolve afforded diethyl 7,14-diphenylbenzo[*b*]quinolino[2,3-*j*]quinoline-6,13-dicarboxylate (**6**) in excellent yield. In the ¹H-nmr of **6** the methylene protons of the ethyl group were observed to be the broad doublet at 3.85 ppm. It is considered to be due to the influence of the phenyl group at a *peri* position of the ethyl group. Compound **6** in organic solvents exhibited a red color and it was discolored by irradiation with light. Photooxidation of polyacenes afforded their endoperoxides [6]. The elemental analysis and spectral



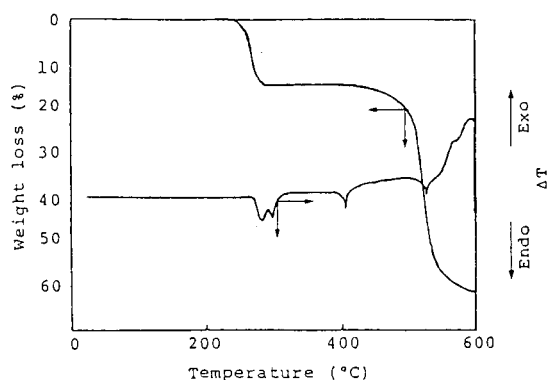
Scheme 1

data of the product agree with oxygen adduct of **6**. The uv spectra shown in Figure 1 indicated the presence of the quinoline skeleton. From the above evidences, it is proposed that the structure of the photochemical reaction product is diethyl 7,14-diphenyl-6,13-epidioxybenzo[*b*]quinolino[2,3-*j*]quinoline-6,13-dicarboxylate **7**.

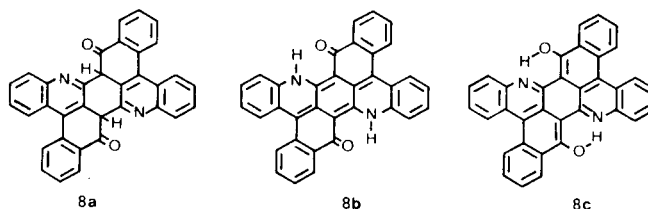


Scheme 2

On the other hand, since the color change was observed by heating **5** the thermal behavior was investigated in solid phase by TG-DTA under a nitrogen atmosphere at a heating rate of 10°/minute. The TG-DTA curves for **5** are shown in Figure 2. The first weight loss at 250-285°

Figure 2. TG-DTA curves for the compound **5**.

reaches 14.9% which agrees with the calculated value of 15.0% for the elimination of two moles of ethanol from **5**. Next, the endothermic curve corresponding to the melting point of the thermal treatment product appears at 400-410. Treatment of **5** in refluxing 1-chloronaphthalene gave metallic green needles of **8**. As **8** was insoluble in organic solvents at room temperature, the nmr could not be measured. The ms and elemental analysis consist of molecular formula $C_{34}H_{18}N_2O_2$. The structure of **8** is shown in Figure 3, three structures can be proposed. But the ir did not show ν NH and ν OH. Therefore, the structure of **8** is assigned as 5,15-diaza-5b,15b-dihydro-tetra-benzo[*a,g,j,p*]perylene-6,13-dione **8a**. Compound **8a** colors reddish purple in polyvinyl chloride and shows good characteristics for an organic pigment.

Figure 3. Structure of the thermal treatment product of **5**.

EXPERIMENTAL

The melting points and the thermal properties of the colored compounds were measured by Rigaku TG-DTA. The melting points of the other compounds were not corrected. The ^1H - and ^{13}C -nmr, ir, ms and electronic absorption spectra were recorded by means of a JEOL PMX-60SI, a JEOL FX90Q, a JASCO IRA-2, a JEOL JMS-01SG-2, and a Hitachi ESP-3T spectrometers, respectively.

Reaction of **3** with **4**.

A mixture of **3** (1.32 g, 5.2 mmoles) and **4** (2.56 g, 13 mmoles) in ethanol (40 ml) and 6*N* hydrochloric acid (0.4 ml) was refluxed under a nitrogen atmosphere for 4 hours. After cooling, the precipitate was filtered off, washed with ethanol, dried and recrystallized from methylcellosolve to give 1.19 g (72 %) of pale orange plates **5**; ^1H -nmr (deuteriochloroform): 1.12 (t, 6H), 4.04 (q, 4H), 5.35 (s, 2H), 7.31-8.17 (m, 18H); ^{13}C -nmr (deuteriochloroform): 14.00 (CH_3), 54.14 (CH), 61.89 (CH_2), 205.56 (COO); ms: *m/e* 578 (M^+); uv (dioxane): λ max 246 (log ϵ 4.94), 297 (4.12), 310 (4.14), 324 (4.22).

Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_4$: C, 78.86; H, 5.24; N, 4.84. Found: C, 78.85; H, 5.24; N, 4.73.

Oxidation of **5**.

A mixture of **5** (3.00 g, 5.1 mmoles) and chloranil (1.25 g, 5.1 mmoles) in methylcellosolve (20 ml) was refluxed for 5 hours. The mixture was filtered off while still hot, washed with ethanol and recrystallized from *o*-dichlorobenzene to give **6** as a purple powder (2.70 g, 92%), mp 363°; ^1H -nmr (deuteriochloroform): 1.37 (t, 6H), 3.85 (d of br, 4H), 7.19-8.05 (m, 18H); ^{13}C -nmr (deuteriochloroform): 13.89 (CH_3), 61.24 (CH_2), 201.56 (COO); ms: *m/e* 576 (M^+); uv-vis (dioxane): λ max 255 (log ϵ 4.55), 302 (5.13), 331 (4.02), 347 (3.76), 409 (3.71), 431 (4.05), 478 (3.13), 510 (3.58), 547 (3.88), 591 (3.94).

Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{O}_4$: C, 79.14; H, 4.90; N, 4.86. Found: C, 79.26; H, 4.88; N, 4.84.

Thermal Treatment of **5**.

A solution of **5** (0.20 g, 0.3 mmole) in 1-chloronaphthalene (10 ml) was refluxed for 5 minutes. The solids separated, and they were collected on a filter, washed with hot methanol and water, dried and recrystallized from nitrobenzene to give **8** as metallic green needles (0.12 g, 83%), mp 405°; ms: *m/e* 486 (M^+); vis (*N*-methyl-2-pyrrolidone): λ max 535 (log ϵ 4.36), 580 (4.26), 636 (4.59).

Anal. Calcd. for $\text{C}_{34}\text{H}_{18}\text{N}_2\text{O}_2$: C, 83.93; H, 3.74; N, 5.76. Found: C, 83.84; H, 3.83; N, 5.75.

Photolysis of **6**.

A solution of **6** (0.20 g, 0.3 mmole) in DMF (50 ml) was subjected to photolysis and then treated with a large volume of water. The resulting solid was filtered, washed with water, dried and recrystallized from benzene-ethanol (1:1) to give **7** as white crystals (0.11 g, 61%), mp 149-150°; ^1H -nmr (deuteriochloroform): 1.30 (t, 6H), 3.24-4.34 (m, 4H), 7.04-8.04 (m, 18H); ms: *m/e* 608 (M^+); uv (dioxane): λ max 255 (log ϵ 4.91), 292 (4.21), 317 (4.08), 332 (4.16).

Anal. Calcd. for $\text{C}_{38}\text{H}_{18}\text{N}_2\text{O}_6$: C, 74.99; H, 4.64; N, 4.60. Found: C, 74.85; H, 4.74; N, 4.56.

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