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The Synthesis and Property of Dihydropyrene Derivatives Containing a Nitrogen Atom

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*Dihydropyrene (DHP) is 14π aromatic compound and applied as an aromatic probe by chemical shift of internal methyl groups in ^{1}H-NMR spectra. DHP containing a nitrogen atom **1a** and **2a** were designed as photochromic compounds which were restrained thermal-isomerization.*

***1a** and **2a** were confirmed as DHP types by ^{1}H-NMR spectra. Chemical shifts of internal methyl groups of **1a** and **2a** were observed at the lower magnetic field than that of DHP **3a**. According to optimized structures of **1a** and **3a**, it was expected that the internal methyl group located of the out at center of 14π annulene ring.*

*Isomerization to [2.2]metacyclophanediene **1b** from DHP **1a** by photo-irradiation of visible light was not observed.*

Keywords: aromaticity; dihydropyrene; [2.2]metacyclophanediene; photochromism; photo switching device

INTRODUCTION

Dihydropyrene (DHP) derivatives are 14π aromatic compounds and photo-, thermochromic compounds to [2.2]metacyclophanediene (MCPD)

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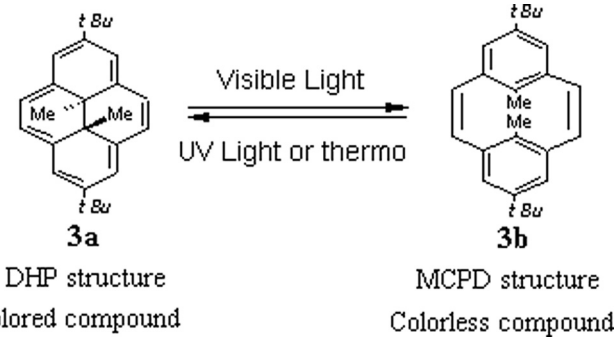


FIGURE 1 Isomerization of DHP and MCPD structures.

structure from DHP structure (Fig. 1)[1]. Therefore, *trans*-10b,10c-dimethyl-dihydropyrene derivatives are researched as a probe of aromaticity [2,3] and are expected to be photo switching devices [4–7].

On the other hand, the research that the atoms at internal position of DHP structure change to heteroatoms (nitrogen, oxygen etc.) from carbon have been limited [8]. Boekelheide tried synthesis of DHP derivative **4a**, that was replaced with two nitrogen atoms at 10b,10c-positions, but only MCPD structure **4b** was observed. The isomerization to DHP structure **4a** from MCPD structure **4b** was not occurred by heating or photo-irradiation (Fig. 2) [9].

We are interesting in that behavior for photo- and thermochromism and aromaticity of DHP derivatives containing heteroatoms at the internal position. Then, we synthesize DHP derivative **1a** (Scheme 1), and study about photo- and thermochromism of **1a**.

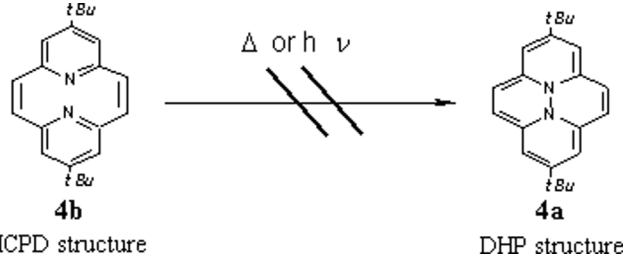
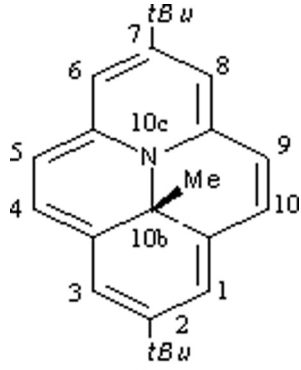


FIGURE 2 Isomerization of **4a** and **4b**.



1a

SCHEME 1 Target compound.

EXPERIMENTAL

Synthesis [10]

*Synthesis of 2,6-Bis(Bromomethyl)-4-*tert*-Butyl Toluene (6)*

To a suspension of zinc powder (2.0 g, 30 mmol) in dry tetrahydrofuran (100 ml), a solution of 1,2-dibromoethane (6.0 g, 32 mmol) in dry tetrahydrofuran (10 ml) was added dropwise. After the mixture was refluxed 6 h under nitrogen, a solvent was evaporated *in vacuo* to afford zinc dibromide.

Secondly, to suspension of 4-*tert*-butyl toluene **5** (22 g, 150 mmol) and zinc dibromide and trioxane (11.3 g, 120 mol) in 30 wt% hydrobromic acid in acetic acid (100 ml) was stirred at 85°C for 4 d under nitrogen and then poured onto ice (100 ml). The mixture was carried out decantation with heat hexane (50 ml × 4) and the supernatent liquid was evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel (Waco-gel C-200E, 75 ~ 150 μm, eluent; hexane) and recrystalization with hexane, to afford **6** (33 g, 66%) as colorless needle: mp 120 ~ 121°C (lit. [11] 120 ~ 121°C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.48 (s, 3H), 4.50 (d, 4H), 7.26 (s, 2H).

*Synthesis of 2,6-Bis(Mercaptomethyl)-4-*tert*-Butyl Toluene (7)*

A suspension of **6** (0.73 g, 2.2 mmol) and thoiurea (0.50 g, 6.6 mmol) in ethanol (50 ml) was refluxed for 5 h under nitrogen. After the mixture was cooled, an aqueous 10% potassium hydroxide solution

(10 ml) was added and refluxed for 3 h under nitrogen. Diluted hydrochloric acid was added slowly until the reaction solution become slightly acidic and the mixture was extracted with chloroform. The extract was dried over $MgSO_4$ and evaporated *in vacuo* and recrystalized with hexane, to afford **4** (0.26 g, 50%) as white powder: mp 96 ~ 97°C (lit. [2] 90 ~ 91°C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 1.68 (t, J = 6.84 Hz, 2H), 2.48 (s, 3H), 4.50 (d, 4H), 7.26 (s, 2H).

Synthesis of Pyridine-2,6-Diethylester (9)

To ethanol (50 ml), thionyl chloride (1.7 ml. 22 mmol) was dropped slowly with ice cooling under nitrogen. To it, a pyridine-2,6-dicarboxylic acid **8** (1.7 g, 10 mmol) was added and the mixture was refluxed for 5 h under nitrogen. After the solvent was evaporated *in vacuo*. A toluene (50 ml × 3) was added to the residue and evaporated *in vacuo* 3 times. The residue was extracted with diethyl ether (30 ml × 3). The extract was washed with water, dried over $MgSO_4$ and evaporated *in vacuo*, to afford **9** (2.0 g, 90%) as colorless needle: mp 45 ~ 46°C (lit. [2] 41 ~ 42°C); IR (KBr) 1710 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.46 (t, J = 7.32 Hz, 3H), 4.50 (q, J = 7.32 Hz, 4H), 8.00 (t, J = 7.81 Hz, 1H), 8.29 (d, J = 7.81 Hz, 2H).

Synthesis of Pyridine-2,6-Dimethylalcohol (10)

To the suspension of **9** (1.8 g, 8.0 mmol) in ethanol (20 ml), the suspension of sodium borohydride (1.3 g, 35 mmol) in ethanol (20 ml) was dropwise during a period of 1 h with ice cooling under mechanical stirring. After the mixture was stirred at rt for 3 hour and was refluxed for 5 h under nitrogen, solvent was evaporated *in vacuo*, and the saturated aqueous solution of potassium carbonate was added to the residue. After the mixture was stirred at 60°C for 2 h, the mixture was extracted with chloroform (100 ml × 10). The extract was dried over $MgSO_4$ and evaporated *in vacuo*. to afford **10** (0.92 g, 83%). **10**: white powder: mp 113 ~ 115°C (lit. [2] 114 ~ 118°C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 2H), 4.60 (s, 4H), 7.20 (d, J = 7.81 Hz, 2H), 7.72 (t, J = 7.82 Hz, 1H).

Synthesis of 2,6-Bis(Bromomethyl)Pyridine (11)

A solution of **10** (0.75 g, 5.4 mmol) in 30 wt% hydrobromic acid in acetic acid (11 ml) was stirred at 100°C for 1.5 h and then poured onto ice (20 ml) and neutralized with aqueous 1 M NaOH. The resulting precipitate was collected and recrystallized with the mixture of hexane and ethyl acetate, to afford **11** (1.0 g, 70%) as colorless needle: mp 85 ~ 87°C (lit. [3] 84 ~ 89°C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 4H), 7.38 (d, J = 7.81 Hz, 2H), 7.71 (t, J = 7.82 Hz, 1H).

Synthesis of Dithiametacyclophane (12)

To a solution of potassium hydroxide (0.34 g, 6.1 mmol) and sodium borohydride (0.10 g, 2.6 mmol) in ethanol (1500 ml), a solution of **7** (0.45 g, 1.9 mmol) and **11** (0.50 g, 1.9 mmol) in ethanol (500 ml) was added dropwise over 24 h. After the solvent was evaporated *in vacuo*, the residue was extracted with chloroform (30 ml × 3). The extract was dried over $MgSO_4$ and evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel (Waco-gel C-200E, 75 ∼ 150 μm, eluent; hexane/ethyl acetate, 5/1), to afford **12** (0.32 g, 50%) as white powder: mp 133 ∼ 135°C; FT-IR 3021, 2954, 1591, 1571, 1480, 1451, 1360, 1214, 1082 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.56 (s, 3H), 3.61 (d, J = 14.16 Hz, 2H), 3.76 (d, J = 15.63 Hz, 2H), 3.89 (d, J = 15.13 Hz, 2H), 4.29 (d, J = 15.13 Hz, Hz, 2H), 6.86 (d, J = 7.81 Hz, 2H), 6.90 (d, 2H), 7.23 (t, J = 7.82 Hz, 1H), MS (TOF) m/z 347 ($M^+ + 4H$); MS (FAB+) m/z 344 ($M^+ - 1H$). Anal. Calcd for $C_{20}H_{25}S_2N$: C, 69.92; H, 7.33; N, 4.08. Found: C, 69.47; H, 7.40; N, 3.94.

Synthesis of [2.2]Metacyclophane SMe Derivative (13)

To stirred solution of **12** (1.0 g, 2.9 mmol) in dry tetrahydrofuran (20 ml), 6.0 ml of a hexane solution (1.58 mol/l) of *n*-butyllithium (15 mmol) was added with ice cooling under nitrogen. After the mixture was stirred for 3 h at rt, methyl iodide (1.0 ml, 15 mmol) was added to the reaction mixture. After the mixture was stirred for 30 min, it was worked up by addition of H_2O and dichloromethane. The extract was dried over $MgSO_4$ and evaporated *in vacuo*. The residue recrystallized with hexane, to afford **13** (0.82 g, 76%) as brown powder; mp 116 ∼ 118°C; FT-IR 2956, 2928, 2866, 1698, 1580, 1480, 1441, 1361, 1230, 1202, 1039 $cm^{-1;}$ ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.57 (s, 3H), 1.37 (s, 9H), 2.11 (s, 6H), 2.77 (t, J = 12.60 Hz, 2H), 3.20 (dd, J = 4.00 Hz, J = 11.72 Hz, 2H), 3.38 (dd, J = 4.00 Hz, J = 12.60 Hz, 2H), 7.15 (s, 2H), 7.64 (t, J = 7.82 Hz, 1H), 7.81 (d, J = 7.81 Hz, 2H); MS (FAB) m/z 375 ($M^+ + 1H$).

Preparation of Bis(Sulfonium) Salt (15)

To a solution of Trimethyl orthoformate (1.4 ml, 12 mmol) in dry dichloromethane (5 ml), Boron trifluoride diethylether complex (2.1 ml, 16 mmol) was added at −30°C under nitrogen. After the mixture was stirred at 0°C for 15 min, the solvent was decanted at −30°C. The dry dichloromethane (5 ml) was added to the reaction mixture and stirred at 0°C. Similarly, the decantation was performed 3 times, to afford dimethoxycarbonium tetrafluoroborate **14** as white liquid in the reactor.

Secondly, To dimethoxycarbonium tetrafluoroborate **14** in dichloromethane, a solution of **13** (0.92 g, 2.5 mmol) in dry dichloromethane (10 ml) was added at −30°C under nitrogen. The mixture was allowed to warm to rt and was stirred for 4 h. Then ethyl acetate (50 ml) was added, the mixture was stirred for 1 h, and the solvent was decanted. Fresh ethyl acetate (50 ml) was added to the only residue and the solution was stirred for 3 h more. After the solvent was decanted more, the resulting sticky residue was collected and dried in vacuo, to afford **15** (1.3 g, 90%) as brown powder: 139 ∼ 141°C; FT-IR 3031, 2957, 1724, 1602, 1431, 1363, 1286, 1031 cm^{-1}.

Hofmann Elimination of 15 to Give (2a)

A suspension of **15** (100 mg, 0.17 mmol) and potassium *tert*-butoxide (100 mg, 0.9 mmol) in dry tetrahydrofuran (50 ml) was stirred at rt overnight under nitrogen. The mixture was washed with aqueous 10% potassium hydroxide solution (50 ml × 3), water phase was extracted with hexane (50 ml × 3). The extract was dried over $MgSO_4$ and evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel absorbed 3 wt% aqueous 25% NH_3 (Silica Gel 60, 70 ∼ 230 mesh, eluent; hexane/ethyl acetate, 20/1), to afford **2a** (1.5 mg, 3%) as dark purple powder: 83 ∼ 85°C; FT-IR 3037, 2962, 2913, 2868, 1577, 1535, 1437, 1389, 1260, 1091, 1020, 862, 798 $cm^{-1;}$ ^{1}H-NMR (400 MHz, C_6D_6); δ −2.55 (s, 3H), 1.57 (s, 9H), 2.34 (s, 3H), 7.47 (d, J = 7.82 Hz, 1H), 7.80 (t, J = 7.81 Hz, 1H), 7.93 (d, J = 1.21 Hz, J = 7.81 Hz, 1H), 8.22 (s, 1H), 8.28 (s, 1H), 8.43 (d, J = 7.82 Hz, 1H), 8.96 (s, 1H), 9.59 (dd, J = 1.22 Hz, J = 7.81 Hz, 1H); MS (TOF): *m/z* 322 ($M^+ + 1H$), 308 ($M^+ - 1CH_3 + 2H$), 293 ($M^+ - 2CH_3 + 1H$), 276 ($M^+ - 1SCH_3 + 1H$), 262 ($M^+ - 1SCH_3 - CH_3 + 1H$); MS (FAB): *m/z* 322 ($M^+ + 1H$). Anal. Calcd for $C_{21}H_{23}NS$: C, 78.46; H, 7.21; N, 4.36. Found: C, 78.01; H, 7.33; N, 4.30.

Hofmann Elimination of 15 to Give (1a)

A suspension of **15** (100 mg, 0.17 mmol) and sodium hydride (81 mg, 3.4 mmol) in dry tetrahydrofuran (50 ml) was refluxed 13 h under nitrogen. The mixture was washed with aqueous 10% potassium hydroxide solution (50 ml × 3), water phase was extracted with hexane (50 ml × 3), The extract was dried over $MgSO_4$ and evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel absorbed 3 wt% aqueous 25% NH_3 (Silica Gel 60, 70 ∼ 230 mesh, eluent; hexane/ethyl acetate, 20/1), to afford **1a** (3.9 mg, 8%) as dark purple powder: 113 ∼ 114°C; FT-IR 3037, 2958, 2909, 2864, 1527, 1391, 1229, 1141, 1070, 985, 797 $cm^{-1;}$ ^{1}H-NMR

(400 MHz, C_6D_6) δ −2.62 (s, 3H), 1.62 (s, 9H), 7.54 (d, J = 7.82 Hz, 2H), 7.70 (t, J = 7.81 Hz, 1H), 8.04 (d, J = 7.81 Hz, 2H), 8.34 (s, 2H), 8.56 (d, J = 8.30 Hz, 2H); MS (FAB): m/z 277 ($M^+ + 1H$). Anal. Calcd for ($C_{20}H_{21}N + 1/4H_2O$): C, 85.82; H, 7.74; N, 5.00. Found: C, 85.79; H, 7.84; N, 5.09. $\lambda_{cyclohexane}$; 355 nm (ε 25887 l mol^{-1} cm^{-1}), 530 nm (ε 4537 l mol^{-1} cm^{-1}), 718 nm (ε 2007 l mol^{-1} cm^{-1}).

Measurements

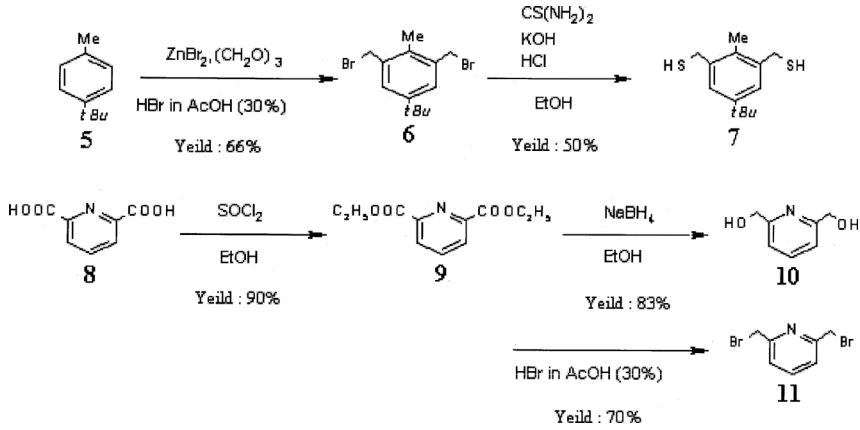
^{1}H-NMR spectra were recorded on a JOEL JNM-EX400 spectrometer at 25°C. IR spectra were recorded as a KBr disk on a Shimazu JR-408. FT-IR spectra were recorded on a Perkin-Elmer Instruments Spectrum One FT-IR Spectrometer. UV-Vis spectra were recorded on a HITACHI U-3210 spectrometer. TOF mass spectral analyses were performed on a PerSeptive Biosystems Voyager™ RP. FAB mass spectral analyses were performed on a JOEL JMS-DX303HF.

RESULTS AND DISCUSSION

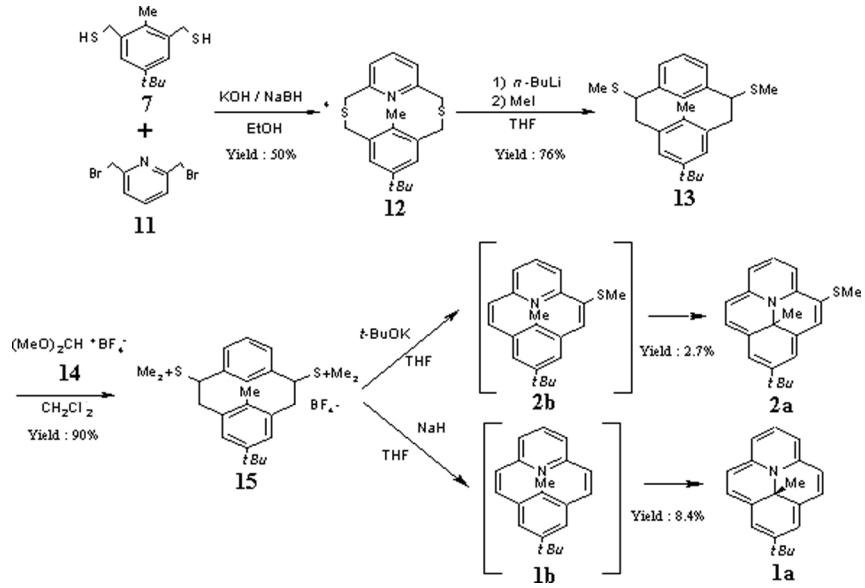
Syntheses of starting materials **7** and **11** are shown in Scheme 2. Compound **7** was yielded from **5** by two steps, and compound **11** was obtained from **8** by three steps.

Syntheses of **1a** and **2a** are shown in Scheme 3.

Dithia[3.3]metacyclophane **12** was synthesized with KOH under the high dilution condition from **7** and **11**. SMe derivative **13** was obtained by Witting rearrangement reaction and confirmed its



SCHEME 2 Synthesis of starting materials.



SCHEME 3 Synthesis of DHP derivatives **1a** and **2a**.

structure by ^{1}H-NMR and H-H COSY, H-H NOESY spectra. The structure of **13** is shown in Figure 3. Bis-sulfonium salt derivative **15** was continuously produced by treating with dimethoxycarbonium tetrafluoroborate **14**. Hofmann elimination reaction of **15** by using *t*-BuOK gave DHP derivative **2a** which have a -SMe group. In the case of using NaH, DHP derivative **1a** was yielded. It was expected that Hofmann elimination reaction of **15** produced MCPDs **1b** and **2b**, and following thermal isomerization of the MCPDs **1b** and **2b** gave DHPs **1a** and **2a**, respectively. Since both **1a** and **2a** were unstable

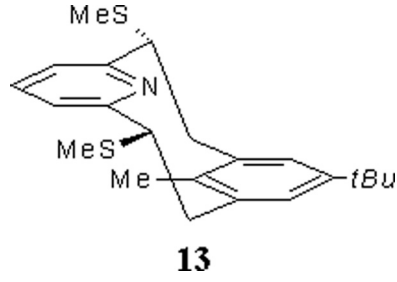


FIGURE 3 Structure of Sme derivative **13**.

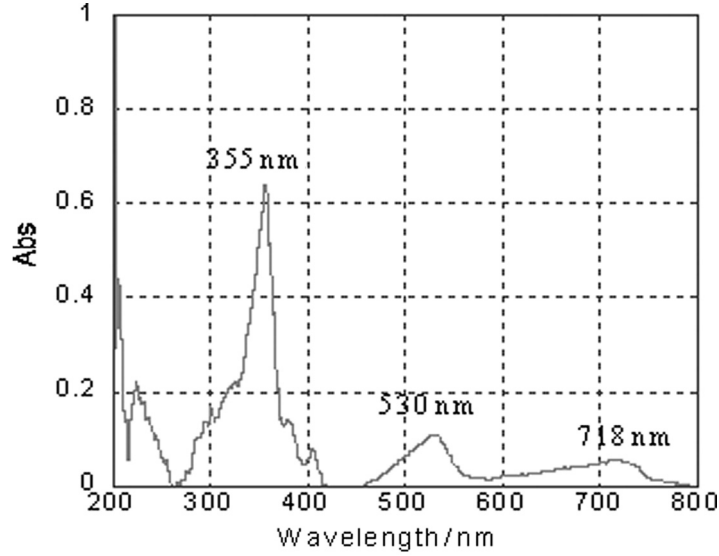


FIGURE 4 UV-Vis spectra of **1a** (cyclohexane, 2.12×10^{-5} mol/l).

on silica gel, alumina, under the acid condition, they were 8.4% and 2.7% yield, respectively. Structures of **1a** and **2a** were confirmed by ^{1}H-NMR and H-H COSY, H-H NOESY spectra.

UV-Vis spectra of **1a** and **3a** are shown in Figures 4 and 5. Absorption maximum of **1a** shifted to the longer wavelength than that of **3a**.

Energy gap between HOMO and LUMO of **1a** and **3a** calculated with AM1 (software; Hyperchem Ver 5.1 for windows) is shown in Figure 6.

As show in Figure 6, energy gap of **1a** was smaller than that of **3a** about 0.78 eV by AM1 calculation. This calculation was supported by UV-Vis spectra, in which absorption maximum of **1a** shift to the longer wavelength than that of **3a**.

The optimized structures of **1a** and **3a** with AM1 (software; Hyperchem Ver 5.1 for windows) are shown in Figures 7 and 8.

While the internal methyl groups of **3a** locate at the center of 14π annulene ring, **1a** is the bowl type structure and the internal methyl group of **1a** shifts from the center of the 14π annulene ring.

Chemical shifts of the internal methyl groups and aromatic protons of various DHP derivatives are shown in Table 1.

The peaks of internal methyl groups of **1a** and **2a** shifted the lower magnetic field than that of **3a**. The quantities of the chemical shifts were not so remarkable compared with **16a**. According to optimized

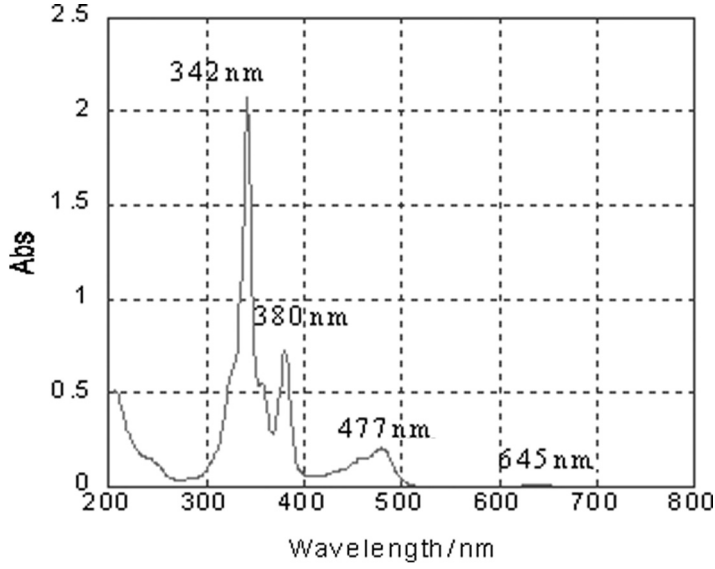


FIGURE 5 UV-Vis spectra of **3a** (cyclohexane, 1.80×10^{-5} mol/l).

structures of **1a** and **3a**, it is suggested that the low field shift was depend on the position of internal methyl groups which located at the out of center of 14π annulene ring for DHP derivatives [12,13].

Thermal isomerization from **1b** to **1a** was confirmed by the synthetic procedure of **1a** by Hofmann elimination of **15**.

When C_6D_6 solution of **1a** was irradiated by visible light from the halogen lamp (500 W), the C_6D_6 insoluble material was generated. When ^{1}H-NMR spectrum of C_6D_6 insoluble material was measured

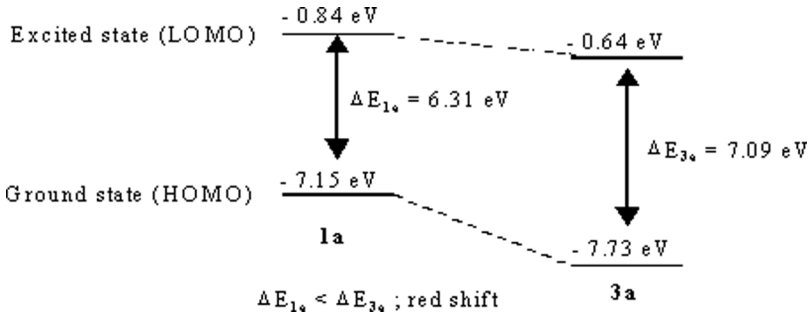


FIGURE 6 Energy gaps of DHP **1a** and **3a**.

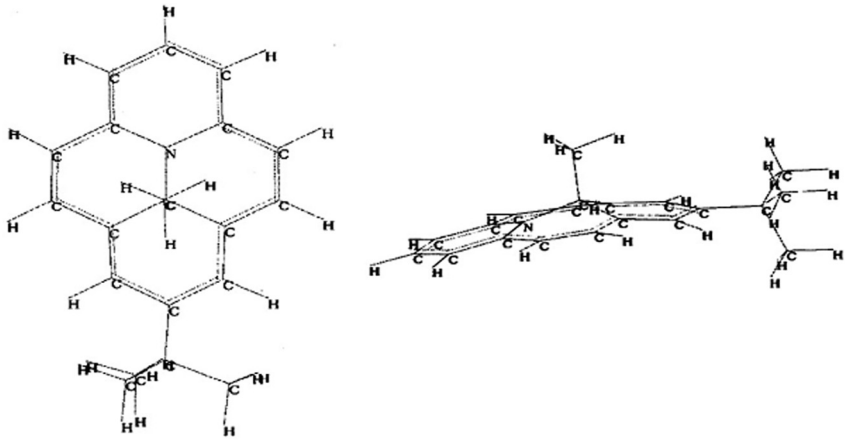


FIGURE 7 Optimized structure of **1a** (AM1, HyperChem Pro Ver 5.1 for Windows).

in $CDCl_3$, no peak of **1a** and **1b** was detected and broad peaks were observed.

CONCLUSIONS

DHP derivatives **1a** and **2a** replaced with a nitrogen atom at 10c-position was synthesized. Absorption maximum of **1a** shifted to the

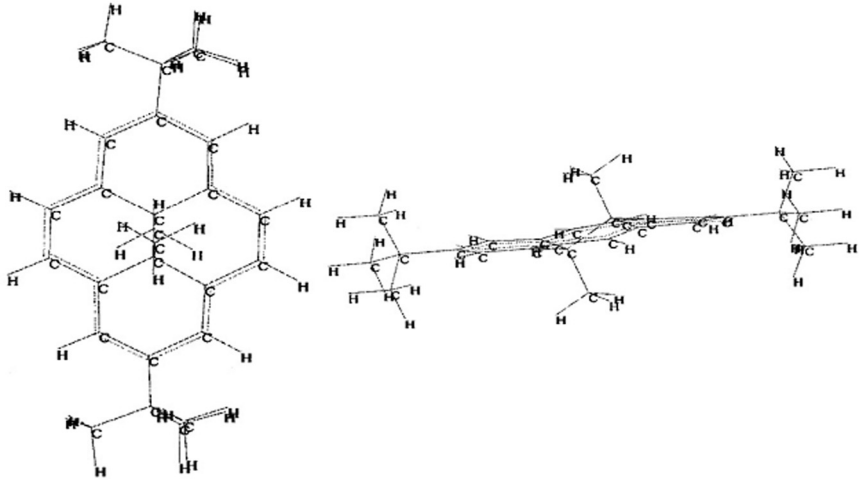
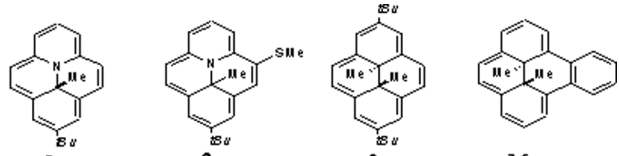


FIGURE 8 Optimized structure of **3a** (AM1, HyperChem Pro Ver 5.1 for Windows).

TABLE 1 Chemical Shifts of Internal Methyl Groups and Aromatic-Protons



	1a	2a	3a	16a
Average δMe (ppm)	-2.62	-2.55	-3.67	-1.85
Average δH_{ary} (ppm)	8.04	8.43	8.57	7.62

a) in C_6D_6 b) in $CDCl_3$

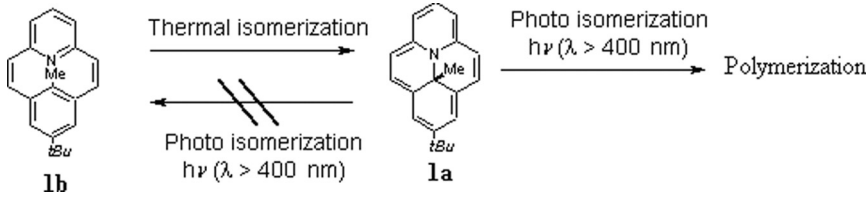


FIGURE 9 Photoisomerization of **1a**.

longer wavelength compared with them of **3a**. According to structural optimization by AM1, structure of DHP **1a** was not suggested the plane type structure but the bowl type structure. Photo isomerization to **1b** from **1a** was not observed. The irradiation of visible light seems to cause polymerization of **1a** (Fig. 9).

REFERENCES

[1] Boekelheide, V. & Phillips, J. B. (1967). *J. Am. Chem. Soc.*, *89*, 1695.
[2] Mitchell, R. H. & Ward, T. R. (2001). *Tetrahedron*, *57*, 3689.
[3] Mitchell, R. H., Iyer, V. S., Khalifa, H., Mahadevan, R., Venugopalan, S., & Weerawarna, S. A. (1995). *J. Am. Chem. Soc.*, *117*, 1514.
[4] Murphy, R. S., Chen, Y., Ward, T. R., Mitchell, R. H., & Bohne, C. (1999). *Chem. Comm.*, *20*, 2097.
[5] Sheepwash, M. A. L., Mitchell, R. H., & Cohne, C. (2002). *J. Am. Chem. Soc.*, *124*, 4693.
[6] Mitchell, R. H., Ward, T. R., & Wang, Y. (2001). *Heterocycles*, *54*, 249.
[7] Mitchell, R. H. & Eur. J. (1999). *Org. Chem.*, *64*, 2695.
[8] Boekelheide, V. & Pepperdine, W. (1970). *J. Am. Chem. Soc.*, *92*, 3684.
[9] Boekelheide, V. & Lawson, J. A. (1970). *J. Chem. Soc. Chem. Comm.*, *14*, 1558.
[10] Mitchell, R. H. & Boekelheide, V. (1974). *J. Am. Chem. Soc.*, *96*, 1547.

[11] Yamato, T., Tsuchihashi, K., Nakamura, N., Hirahara, M., & Tanaka, K. (2002). *Canadian Journal of Chemistry*, *80*, 510.
[12] Mao, Y. & Boekelheide, V. (1980). *J. Org. Chem.*, *45*, 2746.
[13] Bodwell, G. J., Bridson, J. N., Chen, S., & Poirier, R. A. (2001). *J. Am. Chem. Soc.*, *123*, 4704.