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Syntheses and Electronic Properties of 6-Methylene- and 6-Iminocyclohepta[*a*]phenalen-12(6*H*)-one Derivatives

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Synopsis. Some new polyfused nonbenzenoid quinone derivatives, 6-(disubstituted methylene)- and 6-iminocyclohepta[*a*]phenalen-12(6*H*)-ones, were synthesized. The effects of substituents on electronic states were studied.

The benzenoid quinonemethides have been known as biologically important compounds[1] and, like quinodimethanes, they have been extensively studied from the viewpoint of advanced materials.[2] The unique reactivity of quinonemethides arises from their electronic properties, such as a dipolar structure which depends on their substituent on the methylene moiety and the in-between conjugated systems, like compound **1** and its dipolar structure **1′** shown in Fig. 1.[3] However, few examples of fused nonbenzenoid compounds of this type have appeared.[4] It is of interest to know the electronic states of fused nonbenzenoid quinonemethide to explore the uses mentioned and to evaluate the possibility for use as a new probase.[5] We have reported the synthesis of cyclohepta[*a*]phenalenediones[6] which are composed of tropone and phenalenone moieties in neutral state, these quinones are considered to be potential precursors for such quinonemethides.[7] Here, we wish to report the regioselective syntheses and electronic properties of 6-(disubstituted methylene) cyclohepta[*a*]phenalen-12-(6*H*)-one derivatives as the first example of a polyfused nonbenzenoid quinonemethide.

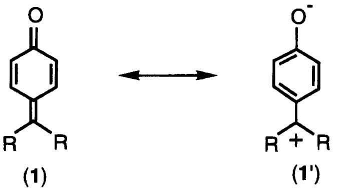
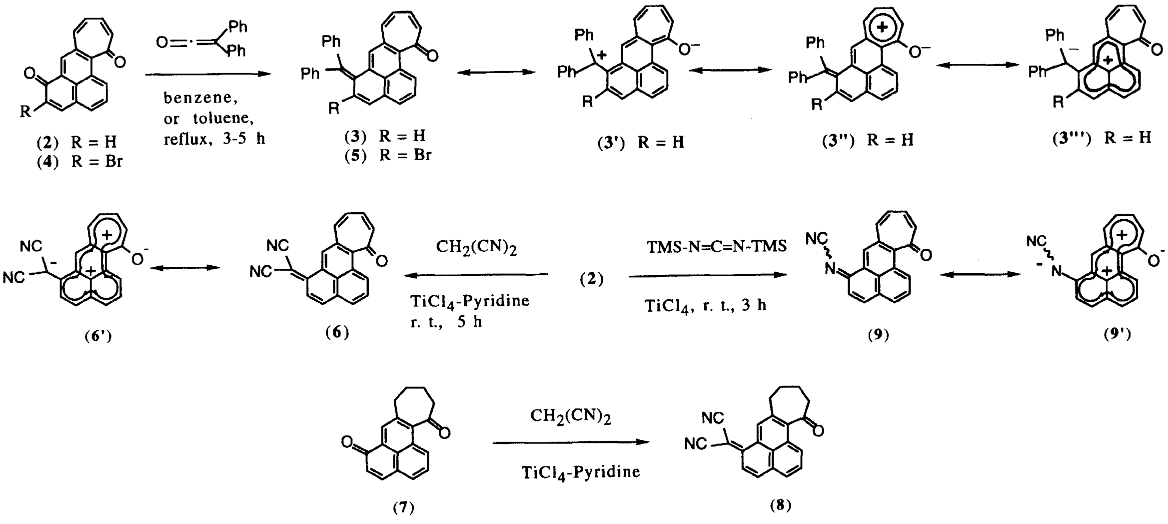

(1) (1')

Fig. 1.

The reaction of the cyclohepta[*a*]phenalene-6,12-dione (**2**) with diphenylketene in refluxing benzene for 3 h gave diphenylmethylene derivative **3** as stable yellow needles in 49% yield. Although the signals for H-4 and H-5 were overlapped with those for H-8—11 in the ^{1}H NMR spectrum of **3**, full assignments of signals for all hydrogens were done by comparing with those of 5-bromo derivative **5**, prepared similarly starting from 5-bromocyclohepta[*a*]phenalene-6,12-dione (**4**). Thus, the signals for the protons on 4- and 5-positions of **3** were assigned at $\delta=6.90$ and 6.62 respectively. And the signal resonated at $\delta=7.52$ as a singlet is assigned for the proton on the 7-position and is shifted to a higher field by 1.10 ppm more than that of the corresponding dione **2** ($\delta=8.62$), due to the anisotropic effect of phenyl group on newly introduced 6-methylene group. The signal observed at $\delta=8.48$ as a doublet of doublets is assigned to the proton on 1-position because of its similarity of observed region and the coupling constants with those of **2** ($\delta=8.67$)[6] indicating the existence of the unreacted carbonyl group on 12 position. The signals for seven-membered ring protons of **3** resonated at $\delta=6.83$ (m, H-8 and H-11) and $\delta=6.50$ (m, H-9 and H-10). The ^{13}C chemical shift of carbonyl carbon of **3** resonated at $\delta=191.4$, similar to that of carbonyl carbon at 12-position of **2**. The low frequency of the carbonyl stretching of **3** ($\nu_{\rm CO}$ 1590 cm^{-1}) similar to that of the tropone moiety of **2** in the IR spectrum indicates a large contribution of the polar structure of tropone moiety. The relatively higher ^{1}H chemical shifts of the ring protons of tropone moieties ($\delta_{\rm av}=6.67$) compared to those of corresponding **2** ($\delta_{\rm av}=7.06$), rather shifting toward those of heptafulvene (ca. $\delta=5.60$),[8] can be explained largely by the contribution of the stable cyclohepta[*a*]phenalene moiety ($\delta_{\text{av of H-8—12}}=5.72$)[9] (REPE=+0.023).[10] It due to the contribution of dipolar structure **3′**, as shown in Scheme 1, for **3**. Though the other possible dipolar structures such as **3″** or **3‴** can be excluded, because their seven-membered ring protons are expected to show rather lower chemical shifts than those of **2**. The repetitious reaction of **3** with diphenylketene gave only a gummy product instead of the expected 6,12-quinodimethane, suggesting instability of the quinodimethane compound under the conditions. The reaction of **2** with 2.5 molar amounts of malononitrile in the presence of titanium tetrachloride and pyridine[11] furnished the quinone methide, 6-dicyanomethylene derivative **6**, as sole product in 57% yield. The structure of **6** was also determined by ^{1}H NMR spectroscopy as follows. The signal observed at $\delta=9.53$ as a singlet is assigned to the proton on the 7-position, the signal at $\delta=8.74$ as a doublet of doublets is assigned to the proton at 1-position, and the signals at $\delta=7.56$ and 7.50 are assigned to the protons at 4- and 5-positions because their coupling constants are the same. These chemical shifts are lower than those of the corresponding **2** by 1.00 ppm. And the signal at $\delta=7.77$ is assigned to the protons at 3- and 8-positions, and the signals at $\delta=7.00$ as multiplet are assigned to protons at 9-, 10-, and 11-positions, as



Scheme 1.

shown in Fig. 2. It is noteworthy that in both cases the reaction gave only one of the possible quinonemethide compounds, that is, the reaction took place selectively at the carbonyl group of 6-position (phenalenone moiety). Steric and electronic factors were perhaps responsible for this regioselectivity. The former factor could be eliminated by the facts from the following experiments. The same kind of reaction for cyclohepta[*a*]phenalene-6,10-dione,[6] an isomer of **2** having a sterically less hindered carbonyl group at 10-position, gave exclusively a 6-methylene derivative, not a 10-methylene one.[12] We failed in the attempt to introduce a cyanoimino group, considered to be a less hindered substituent than diphenylmethylene and dicyanomethylene groups, to 12-position by the reaction of **2** with bis(trimethylsilyl)carbodiimide and TiCl$_4$[13] at r. t. for 5 h; only 6-cyanoimino derivative **9** was obtained in 24% yield. The structure of **9** was confirmed in a similar manner. The ^{1}H NMR assignments of protons are shown in the experimental section. The detailed explanation by the latter one remains ambiguous. To examine the effects of the introduced electron-withdrawing group, such as dicyanomethylene or cyanoimino group, compared with the carbonyl group, on the contribution of the dipolar structure in the phenalene moiety, 8,9,10,11-tetrahydro derivative **8** as reference compound was prepared from tetrahydro derivative **7**. The average chemical shift of **8** is a little lower than that of **7**, only by 0.12 ppm. Thus, the average chemical shifts of all ring protons of **6** ($\delta_{av}=7.74$) and **9** ($\delta_{av}=7.73$) are a little lower than that of dione **2** ($\delta_{av}=7.51$). These results indicate that the contribution of the dicationic structures of **6′** and **9′** is important for **6** and **9**, in contrast with that of **3**.

Although the compound **2** is composed of tropone and phenalenone moieties as mentioned above, these results suggest that these quinonemethides **3**, **5**, and **6** are not merely composed of tropone and phenafulvene moieties. Thus, all conjugated π-electrons should be taken into account in the determination of electronic states of these compounds.

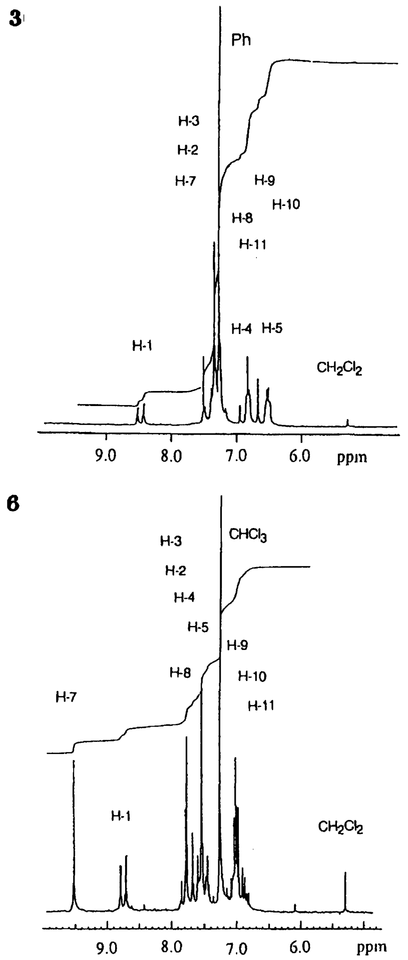


Fig. 2. ^{1}H NMR spectra of **3** (above) and **6** (below) in CDCl$_3$ at 90 MHz.

The electronic absorption of **3** in CH$_2$Cl$_2$ exhibits the longest absorption maximum at 462 nm; this is greater than that of **2** (400 nm). But the absorption in ethanol is tailing at more than 700 nm as shown in Fig. 3. In concd H_2SO_4, the longest absorption maximum of **3** was observed at 640 nm, which was greater than that of **2** (540 nm sh) in the same conditions, indicating the formation of the cationic species. However, attempts to detect it by measurement of ^{1}H NMR spectrum in CH_3COOD under various conditions were unsuccessful and no recovery of **3** from the solution by addition of a large excess of water was attained. This might be attributed to polymerization of the formed cationic species.[13)]

The cyclic voltammogram of **3** showed three reversible half-wave reduction potentials, indicating the formation of stable radical anions, dianions and radical trianions, as shown in Table 1. The first half-wave reduction potential ($^1E_{1/2}=-0.59$) is considerably more positive than those of dione **2** ($^1E_{1/2}=-0.83$)[5)] and 2,6-di-*t*-butyl-4-diphenylmethylene-2,5-cyclohexadien-1-one ($^1E_{1/2}=-0.78$).[2)] This feasible electron reduction of **3** may also be attributable to the great contribution of the polar structure in quinonemethide **3** and to the stability of cyclohepta[*a*]phenalene moiety, as shown in the spectroscopic interpretation of the ^{1}H NMR results. Since the first reduction potentials of cyanoimino derivative **9** are more positive than those of **3** and **6**, the $^1E_{1/2}$ values of these compounds increase in the order of **2**, **6**, **3**, and **9**. Furthermore, judging from this first reduction potential, we can utilize these compounds as a good probase.

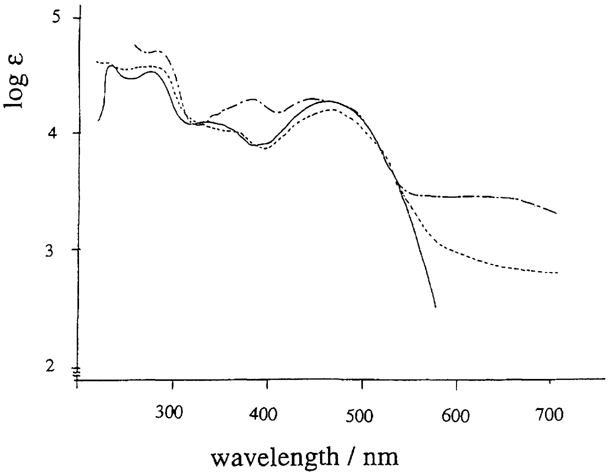


Fig. 3. UV-vis absorption spectra of **3** in CH_2Cl_2 (—), EtOH (- - -), and concd H_2SO_4 (–••–).

Table 1. The Cycic Voltammogram of New Quinonemethides **3**, **6**, **9** and Known Related Quinone **2**

Quinone methides and quinones	$^1E_{1/2}$	$^2E_{1/2}$	$^3E_{1/2}$
(**2**)	−0.83	−1.12	
(**3**)	−0.59	−0.83	−1.17
(**6**)	−0.73	−1.30	
(**9**)	−0.44	−1.01	

Experimental

All the melting points were uncorrected. The IR spectra were taken on a Hitachi IR-810 spectrometer; the UV-vis spectra were taken on a UV-265FS and UV-2100S. The ^{1}H NMR spectra were taken on a Hitachi R24 (60 MHz) and on a JEOL-FX90 (90 MHz) spectrometers, in chloroform-*d* (TMS as an internal standard). ^{13}C NMR spectra were taken on a JEOLFX90 (23 MHz) spectrometer, in chloroform-*d* (TMS as an internal standard). The mass spectra were taken on a JEOL-OISG-2 mass spectrometer. The cyclic voltammetric measurements were performed on a Yanako P-1100. A standard three-electrode cell configuration was employed using a glassy carbon disk working electrode, a Pt wire auxiliary electrode, and an Ag wire as an Ag/Ag^+ quasi-reference electrode. The reference electrode was calibrated at the completion of each measurement on a saturated calomel electrode (SCE). Solvent and supporting electrode were purified before use. Reduction potentials of quinones were measured by cyclic voltammetry, using dimethyl sulfoxide containing tetrabutylammonium perchlorate (0.1 mol dm^{-1}) as solvent.

6-(Diphenylmethylene)cyclohepta[*a*]phenalen-12-(6*H*)-one (3). To a solution of **2** (2.23 g, 8.6 mmol) and triethylamine (4.80 g, 47.5 mmol) in dry benzene (30 mL) was added diphenylacetyl chloride (7.20 g, 31.3 mmol) at refluxing during a time period of 30 min; this refluxing was continued for 5 h. After being cooled, the solution was concentrated by evaporation under reduced pressure. The residue was column chromatographed on silica gel to give 1.73 g (49%) of **3** from benzene elution.

3: Pale yellow needles; mp 144.5—145.5 °C (CH_2Cl_2–hexane); IR (KBr) 3020w, 1639s, 1590s, 838s, 762s cm^{-1}; ^{1}H NMR $\delta=8.48$ (dd, $J=1.3$ & 8.4 Hz, H-1), 7.52 (s, H-7), 7.40 (m, 2H), 7.36 (m, 4H), 7.28 (m, 6H), 6.90 (d, $J=10.1$ Hz, H-4), 6.83 (m, H-8 & H-11), 6.62 (d, $J=10.1$ Hz, H-5), 6.50 (m, 2H, H-9 & H-10); ^{13}C NMR $\delta=191.4$, 145.3, 144.2, 143.4, 137.7, 135.5, 135.1, 134.9, 132.7, 131.9, 131.7, 130.7, 130.4, 130.2, 129.5, 128.5, 127.9, 127.8, 127.6, 127.0, 125.4, 125.2; ES $\lambda_{\max}$ (CH_2Cl_2) 462 ($\log\varepsilon=4.26$), 335 (4.09), 276 (4.54), 232 nm (4.59); (cH_2SO_4) 620 ($\log\varepsilon=3.45$), 478 (4.24), 446 (4.28), 382 (4.29), 257 nm (4.82); (EtOH) 466 ($\log\varepsilon=4.19$), 339 (4.10), 275 (4.67), 228 nm (4.16); MS *m/z* 408 (M^+, 100%), 380 (M^+-CO, 97%), 303 ($M^+-C_6H_5$, 53%). Found: C, 91.08; H, 4.87%. Calcd for $C_{31}H_{20}O$: C, 91.18; H, 4.90%.

The half-wave reduction potentials for all compounds, obtained by measuring the CV spectra, are listed in Table 1.

5-Bromo-6-(diphenylmethylene)cyclohepta[*a*]phenalen-12(6*H*)-one (5). In a similar manner to the above reaction, the bromo derivative was obtained in 4% yield, however toluene was used as a solvent in place of benzene.

5: Orange needles, mp 235.5—237.5 °C (CH_2Cl_2–hexane); IR (KBr) 3020w, 1640s, 1605s, 770s cm^{-1}; ^{1}H NMR $\delta=8.55$ (dd, $J=1.3$ & 9.0 Hz, H-1), 7.42 (m, 14H), 6.85 (m, H-8 & H-11), 6.55 (m, H-9 & H-10); ES $\lambda_{\max}$ (CH_2Cl_2) 504 ($\log\varepsilon=3.77$), 407 (4.06), 344 (4.09), 286 (4.31), 256 nm (4.43); MS *m/z* 488 & 486 (M^+, 67 & 82%), 407 (M^+-Br, 65%), 330 ($M^+-C_6H_5$, 31%). Found: C, 76.52; H, 3.92%. Calcd for $C_{31}H_{19}BrO$: C, 76.39; H, 3.90%. Many attempts to measure the ^{13}C NMR spectrum of **5** and also of the following compounds **6** and **9** failed because of their low solubility in many solvents.

6- (Dicyanomethylene)cyclohepta[*a*]phenalen- 12-(6*H*)-one (6). To a solution of **2** (3.24 g, 12.6 mmol) and malononitrile (1.86 g, 28.2 mmol) in dichloromethane (50 mL) was added $TiCl_4$ (5.79 g, 30.5 mmol) in dry CH_2Cl_2 (30 mL) dropwise for 30 min at r. t., followed by dropwise addition of pyridine (3.56 g, 45.1 mmol) for 30 min at r. t. The reaction mixture was stirred overnight. The resulting mixture was poured into 1 L of 3 M HCl–ice and extracted with CH_2Cl_2 twice. The combined organic layer was washed with brine twice and dried over anhydr. $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on silica gel to give 2.20 g (57%) of **6**.

6: Reddish needles, mp 246.0—248.0 °C (CH_2Cl_2–hexane); IR (KBr) 3045w, 2202s, 1643m, 1619vs, 1570m, 1297s, 837s cm^{-1}; ^{1}H NMR $\delta=9.53$ (s, H-7), 8.74 (dd, $J=2.0$ & 7.9 Hz, H-1), 7.77 (m, 2H), 7.56 (d, $J=5.5$ Hz, H-4), 7.50 (m, 1H), 7.50 (d, $J=5.5$ Hz, H-5), 7.00 (m, 3H); ES λ_{max} (CH_2Cl_2) 512 ($\log\varepsilon=3.46$), 403 (3.63), 332sh (3.75), 278nm (3.96); MS m/z 306 (M^+, 25%), 278 (M^+-CO, 100%). Found: C, 82.07; H, 3.21; N, 8.96%. Calcd for $C_{21}H_{10}N_2O$: C, 82.34; H, 3.29; N, 9.15%.

6-(Dicyanomethylene)-8,9,10,11-tetrahydrocyclohepta[*a*]phenalen-12(6*H*)-one (8). To a solution of **7** (2.35 g, 8.97 mmol) and malononitrile (1.20 g, 18 mmol) in dichloromethane (50 mL) was added $TiCl_4$ (1.04 g, 16 mmol) in dry CH_2Cl_2 (30 mL) dropwise for 30 min at r. t., followed by addition of pyridine (3.59 g, 22 mmol) dropwise for 30 min at r. t. Then this mixture was stirred for overnight. The resulting reaction mixture was poured into 1 L of 3 M HCl–ice and extracted with CH_2Cl_2 twice. The combined organic layer was washed with brine twice and dried over anhydr. $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on silica gel to give 2.11 g (76%) of **8**.

8: Reddish needles, mp 235—237 °C (CH_2Cl_2); IR (KBr) 3045w, 2950w, 2202vs, 1678vs, 836m cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=9.20$ (s, H-7), 8.10 (dd, $J=2.1$ & 7.6 Hz, H-1), 7.75 (d, $J=6.3$ Hz, H-4), 7.66 (d, $J=6.3$ Hz, H-5), 7.50 (m, 2H), 3.08 (m, 2H), 2.83 (m, 2H), 1.94 (m, 4H); ^{13}C NMR $\delta=208.4$, 155.2, 144.1, 138.3, 137.3, 132.0, 130.3, 129.1, 129.0, 128.4, 127.9, 125.6, 116.8, 114.8, 42.7, 33.3, 25.1, 23.0; ES λ_{max} (CH_2Cl_2) 482 ($\log\varepsilon=4.29$), 280 (4.42), 229 nm (4.08); MS m/z 310 (M^+, 100%), 282 (M^+-CO, 58%). HRMS, Found: m/z 310.1092. Calcd for $C_{21}H_{14}N_2O$: M, 310.1042. Found: C, 81.25; H, 5.66; N, 9.16%. Calcd for $C_{21}H_{14}N_2O$: C, 81.29; H, 5.56; N, 9.03%.

6-(Cyanoimino)cyclohepta[*a*]phenalen-12(6*H*)-one (9). To a solution of **2** (0.50 g, 2.00 mmol) in CH_2Cl_2 was added $TiCl_4$ (2.90 g, 15 mmol); this was followed by dropwise addition of bis(trimethylsilyl)carbodiimide (5.60 g, 30 mmol) in CH_2Cl_2 (20 mL) at r. t. for 30 min. Then the reaction mixture was refluxed for 24 h. The resulting reaction mixture was filtered, and the filtrate was washed with brine twice and dried over anhydr. $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel to give 0.13 g (24%) of **9** from CH_2Cl_2 elution.

9: Orange needles (CH_2Cl_2), mp 200 °C (decomp); IR (KBr) 3030w, 2170vs, 1645m, 1618vs, 1578m, 1523vs, 839m cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=9.06$ (s, 1H, H-7), 8.78 (dd, $J=1.53$ & 8.55 Hz, 1H, H-1), 7.90 (d, $J=9.3$ Hz, H-8), 7.81 & 7.74 (m, 2H, H-2 & H-3), 7.65 (d, $J=6.30$ Hz, 1H, H-4), 7.45 (d, $J=6.30$ Hz, H-5), 7.00 (m, 3H, H-9, 10, 11); MS m/z 282 (M^+, 29%). 254 (93%), 202 (100%). HRMS, Found: m/z 282.0794. Calcd for $C_{21}H_{10}N_2O$: M, 282.0793. Found: C, 80.45; H, 3.67; N, 10.02%. Calcd for $C_{21}H_{10}N_2O$: C, 80.84; H, 3.57; N, 9.92%.

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