

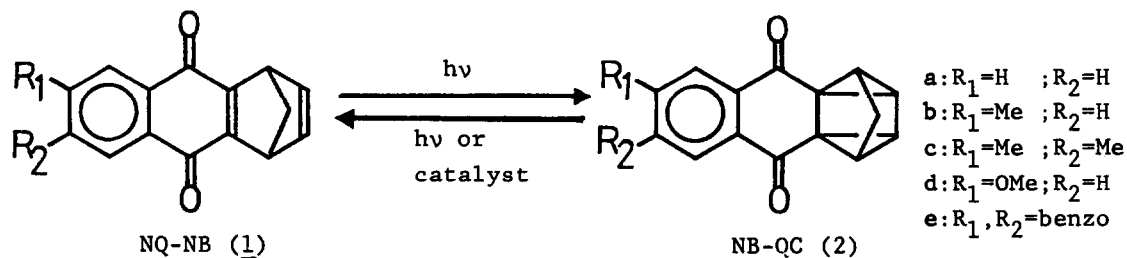
PHOTOCYCLIZATION OF NORBORNADIENES FUSED WITH QUINONE UNITS

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Summary: On irradiation with visible light, norbornadienes fused with naphthoquinone units (1) isomerized to the corresponding quadricyclanes (2) quantitatively. Methyl or methoxy substituents in the quinone unit do not affect the quantum yields ($\Phi \sim 0.2$) for the isomerization, but increase the absorbance in the visible region. The photoproducts 2 undergo easy one-electron oxidation and reduction.

Photocyclization of norbornadiene (NB) to quadricyclane (QC) is of interest from the view point of solar energy storage.¹ Since NB itself does not absorb visible light and the reaction efficiency is pretty low,² many investigations have been undertaken in order to elongate the absorption of NB to the visible region as well as increase the reaction efficiency.^{3,4} In this connection, norbornadienes fused with quinone moieties are intriguing from the following points of view. First, they may absorb visible light for the presence of quinone chromophores. Charge-transfer interactions between the quinone moieties and olefinic part resulting in red-shifts of absorbance are also expected. Secondly, since the photocyclization of NB proceeds via the excited triplet state,⁵ the reaction efficiency may be increased by the fast intersystem crossing due to the two carbonyl groups. Thirdly, these compounds can be easily prepared in high yields from readily available quinone derivatives and cyclopentadiene. However, several attempts to undergo the photocyclization of these types of norbornadienes have been failed so far.^{3,6} We report here the photocyclization of norbornadienes fused with naphthoquinones [NQ-NB (1)] as the first examples giving the corresponding quadricyclanes.



Compound (1a) was prepared according to the literature.⁷ Substituted derivatives of NQ-NB (1b)-(1d) and the benzologue (1e) were analogously prepared in 60-73% yields from the corresponding naphthoquinones (3) by Diels-Alder reaction with cyclopentadiene followed by base-catalyzed isomerization to quinols and successive oxidation with ferric chloride. The UV spectra⁸ of (1) are essentially the same with those of the corresponding quinones except for the elongated end absorption and the new maxima around 280 nm which are attributed to the interactions between the quinone moieties and the olefinic part.⁶ It is noteworthy that (1d) and (1e) shows the absorption maxima in the visible region⁸. When the dichloromethane solutions containing 10^{-4} - 10^{-5} mol dm^{-3} of (1) were irradiated with an 150 W Xe lamp ($\lambda = 410 \pm 10$ nm), the UV spectra changed gradually with several isobestic points indicating that (1) isomerized simply to another species. The photoproducts proved to be the corresponding quadricyclanes [NQ-QC (2)], which were confirmed by the ¹H-NMR spectra.⁸ They could be isolated by evaporating the solvent, followed by recrystallization from dichloromethane - hexane.⁹ As shown in Table 1, the chemical yields for (2a) - (2d) are nearly quantitative, while that for the benzologue (2e) is limited to 87% which may be attributed to slow decomposition of (2e) under the reaction conditions. The conversions of (1a) - (1c) increase in the order of (1a), (1b), and (1c), indicating that methyl substituents in the quinone unit accelerate the photocyclization. This effect is remarkable for the methoxy group since (1d) isomerized completely by the irradiation with longer wavelength light for the same period. The quantum yields at 405 nm for this reaction are independent on the substitution of methyl or methoxy groups. However, these substituents increase the absorbance in the visible region as seen from the comparison of ϵ at 460 nm, where nearly the same values of quantum yields were obtained. These results show that NQ-NB (1a) - (1d) undergo facile and quantitative photocyclization by the irradiation with visible light, which is accelerated by the methyl or methoxy substituents in the quinone unit for the increase of absorbance in the visible region. On the other hand, when the NQ-NB (1a) solutions (3.8×10^{-5} mol dm^{-3} in dichloromethane) were irradiated with UV light ($\lambda = 370 \pm 10$; 350 ± 10 nm with an 150 W Xe lamp), photostationary states were obtained whose molar ratios of (1a) : (2a) were determined to be 80 : 20 and 75 : 25, respectively, on the basis of UV spectra. Since nearly the same photostationary states [(1a) : (2a) = 79 : 21 at 370 nm; 74 : 26 at 350 nm] were obtained by the irradiation of NQ-QC (2a) solutions, this valence isomerization is photochemically reversible. The efficiency of cycloreversion is four times larger than that for the cyclization since the absorbance of (1a) and (2a) are nearly the same at 370 nm and the molar ratio is 4 : 1 in the photostationary state at 370 nm. Cycloreversion was also caused by a catalyst. Thus, treatment of a dichloromethane solution of NQ-QC (2a) with 0.05 equivalent of Co(II)tetraphenylporphyrin in the dark resulted in the complete isomerization to NQ-NB (1a) in quantitative yield.

Since NQ-QC (2) consist of an electron-donating quadricyclane moiety and

Table 1. Photocyclization^a of NQ-NB (1) and quantum yields^b of cyclization

compound	irradiation wavelength ^c [λ/nm]	conversion of (1) [%]	yield ^d of (2) [%]	Φ at 405 ± 10 nm	Φ at 460 ± 10 nm	ϵ at 460 nm
a: R ₁ =H ; R ₂ =H	> 410	63	100	0.21	0.14	34
b: R ₁ =Me ; R ₂ =H	> 410	76	100	0.21	0.15	42
c: R ₁ =Me ; R ₂ =Me	> 410	87	100	0.22	0.19	52
d: R ₁ =OMe; R ₂ =H	> 435	100	95	0.22	0.21	480
e: R ₁ , R ₂ = benzo	> 435	63	87	-	-	

^a Dry CH₂Cl₂ solutions of (1) (2 x 10⁻² mol dm⁻³) were irradiated by a 2kW Xe lamp for 15 min at room temperature.

^b Measured in CH₂Cl₂ containing 0.8-1.2 x 10⁻² mol dm⁻³ of (1) by an 150 W Xe lamp on a Hitachi MPF-4 spectrophotometer using potassium ferrioxalate as an actinometer.

^c Toshiba glass filters of Y-44 (λ > 410 nm) and Y-46 (λ > 435 nm) were used.

^d The yields were determined on the basis of NMR spectra and calculated based on consumed (1).

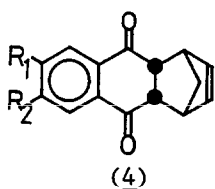
Table 2. Reduction potentials^a of NQ-QC (2), Diels-Alder adducts (4), NQ-NB (1), and Naphthoquinones (3)

compound	NQ-QC (2)	adduct (4)	NQ-NB (1)	NQ (3)
a: R ₁ =H ; R ₂ =H	-1.52 ^c (+1.31 ^c) ^b	-1.59	-0.71	-0.71
b: R ₁ =Me ; R ₂ =H	-1.55 ^c (+1.28 ^c) ^b	-1.62	-0.73	-0.73
c: R ₁ =Me ; R ₂ =Me	-1.61 ^c (+1.28 ^c) ^b	-1.67	-0.76	-0.76
d: R ₁ =OMe; R ₂ =H	-1.55 ^c (+1.23 ^c) ^b	-1.62	-0.73	-0.74
e: R ₁ , R ₂ = benzo	-1.46 ^c (+1.26 ^c) ^b	-1.64 ^c	-0.77	-0.78

^a E_{1/2}/V vs. SCE, measured in CH₃CN containing 0.1 mol dm⁻³ Et₄NClO₄, Pt wire, scan rate 100 mV s⁻¹. The oxidation potential of Ferrocene is +0.38 V.

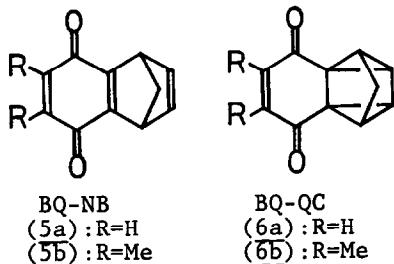
^b Oxidation potential. That for unsubstituted quadricyclane is 1.22 v^c.

^c Irreversible. E^{red} and E^{ox} are calculated as E_{pc} (cathodic peak potential) + 0.03 and E_{pa} (anodic peak potential) - 0.03, respectively.



electron-accepting diacylbenzene units, they undergo easy one-electron oxidation and reduction as shown in Table 2. Reduction potentials of NQ-NB (1), naphthoquinones (3), and Diels-Alder adducts (4) are also shown for comparisons. Although the redox waves for (2) are all irreversible, the oxidation and reduction potentials are similar values with that for unsubstituted quadricyclane and those for the corresponding Diels-Alder adducts (4), respectively. These facts indicate that the orbital coefficients of HOMO for (2) are largely located in the quadricyclane moiety while those for LUMO are in diacylbenzene units. Accordingly, the intramolecular charge-transfer interactions are expected to occur in NQ-QC (2) since the through bond interactions between cyclopropane rings and carbonyl groups may be small due to the spiro type connection. The relatively elongated end absorption down to 400 nm for the UV spectra of (2) and the down field shifts of 0.2 ppm for the ring protons in ¹H-NMR spectra of (2) compared with those of (1) or (4) are accounted for by the intramolecular charge-transfer interactions. Stronger interactions are expected for BQ-QC (6) containing an enedione unit instead of diacylbenzene, which may be obtained by the irradiation of BQ-NB (5).¹⁰ The

UV spectra of (5a) and (5b) changed gradually with several isosbestic points [240, 279, and 425 nm for (5a); 257, 292, and 422 nm for (5b)] on irradiation with visible light ($\lambda = 450 \pm 10$ nm with an 150 W Xe lamp in CH_2Cl_2), and new



maxima appeared in 300-400 nm region. The colored photoproducts were deduced to be BQ-QC (6) from the $^1\text{H-NMR}$ spectrum of (6b),¹² although they were too labile to be isolated in pure form. The newly appeared absorption maxima in near visible region belong to BQ-QC (6), which are considered to be resulted from strong intramolecular charge-transfer interactions.

References and Notes

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- UV spectra [$\lambda_{\text{max}}/\text{nm}$ in CH_2Cl_2 ($\log \epsilon$):] (1a), 248(4.19), 253(4.26), 275 (sh, 4.14), 280(4.15), 337(3.44); (1b), 253(4.24), 258(4.31), 280(4.13), 342 (3.50); (1c), 257(sh, 4.30), 262(4.37), 286(4.10), 345(3.55); (1d), 269(4.33), 287(4.04), 347(3.50), 410(3.03); (1e), 282(sh, 4.39), 288(4.39), 300(4.31), 413(3.67); (2a), 231(4.57), 252(4.17), 287(sh, 3.57), 300(sh, 3.65), 307(3.69), 353(sh, 3.22), 372(sh, 2.95); (2b), 245(4.59), 256(4.22), 262(sh, 4.18), 300 (3.68), 310(3.71), 350(sh, 3.25), 370(sh, 2.97); (2c), 243(4.63), 262(4.23), 270 (sh, 4.20), 300(sh, 3.69), 314(3.66), 350(sh, 3.25), 368(sh, 3.02); (2d), 248 (4.49), 280(4.23), 316(sh, 3.77), 325(sh, 3.73), 356(sh, 3.23), 374(sh, 2.93); (2e), 272 (4.80), 302(sh, 3.93), 347(3.59), 364(3.71). $^1\text{H-NMR}$ spectra [δ ppm in CDCl_3 (J in Hz)]: (2a), 2.42(2H, t, 1.2), 3.14(2H, dt, 4.5, 1.2), 2.96(2H, d, 4.5), 7.59-7.82(2H, m), 8.05-8.28(2H, m); (2b), 2.36(2H, tm, 1.2), 2.51(3H, s), 2.96 (2H, dm, 4.2), 3.12(2H, tdm, 1.2, 4.2), 7.51(1H, dd, 1.5, 7.5), 7.98(1H, d, 1.5), 8.09 (1H, d, 7.5); (2c), 2.37(1H, tm, 1.2), 2.38(1H, tm, 1.2), 2.40(6H, s), 2.92(2H, dm, 4.5), 3.09(2H, dddm, 1.2, 1.2, 4.5), 7.93(2H, s); (2d), 2.39(2H, dd, 1.4, 1.4), 2.92 (1H, dd, 3.6, 2.1), 2.96(1H, dd, 3.6, 2.1), 3.09(1H, td, 1.4, 3.6), 3.11(1H, td, 1.4, 3.6), 3.93(3H, s), 7.21(1H, dd, 2.7, 8.7), 7.61(1H, d, 2.7), 8.15(1H, d, 8.7); (2e), 2.45(1H, dt, 12.0, 1.5), 2.47(1H, dt, 12.0, 1.5), 3.03(2H, d, 5.0), 3.18(2H, ddd, 1.5, 1.5, 5.0), 8.76(2H, s), 7.66-7.73(2H, m), 8.07-8.13(2H, m).
- NQ-QC (2) are sensitive to nucleophiles such as methanol and also decompose on SiO_2 and Al_2O_3 . As described in the text, (2) absorb unexpected longer wavelength light near visible region, and the photocycloreversion of (2) is much faster than the photocyclization of (1). These may be the reason why the attempts to cyclize (1) or related compounds to the corresponding quadricyclanes have been failed so far.
- (5a) was prepared according to the literature, ref 11. (5b) was prepared analogously from 2,3-dimethylbenzoquinone in 34% yield. UV spectra [$\lambda_{\text{max}}/\text{nm}$ in CH_2Cl_2 ($\log \epsilon$):] (5a), 258 (4.23), 316 (sh, 2.57), 389 (2.75); (5b), 272 (sh, 4.22), 278 (4.25), 311 (2.84), 388 (2.19).
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- $^1\text{H-NMR}$ spectrum of (6b) [δ ppm in CDCl_3]: 2.03(6H, s), 2.33(2H, m), 2.75(2H, dm, 4.5Hz), 2.92(2H, dm, 4.5Hz).

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