

New Donor–Acceptor 2-Aryl-3-(4-pyridyl)-2,5-norbornadienes as Thermally Reversible Photochromic Systems¹

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New donor–acceptor 2,3-diarylnorbornadienes (**1N–4N**) showing high quantum yields for the blue light induced valence isomerization from the norbornadienes into quadricyclanes and the latter's thermal reversion are studied in comparison with their protonated counterparts.

Valence isomerization of norbornadiene (NBD) to quadricyclane (QC) has been one of the most promising systems for solar energy storage.^{2–4} Mechanistic studies have revealed that triplet sensitization of NBD generates the triplet state which undergoes adiabatic isomerization to form triplet QC which in turn decays rapidly to its ground state.^{5–7} The introduction of various chromophores into the NBD system can result in achieving higher quantum efficiency⁸ or shifting the absorption to the visible region.^{9,10} Recently, the NBD system has been used as a new switching system for data storage.¹¹

We report here a new series of donor–acceptor system based on norbornadiene (**1N–4N** Scheme 1) synthesized by the Diels–Alder reaction of the corresponding aryl-4-pyridylethyne with 1,3-cyclopentadiene.¹² Quantum yields for the blue light induced valence isomerization from the norbornadienes (**1N–4N**) into the respective quadricyclanes (**1Q–4Q**) were measured (0.3–0.6) in acetonitrile. Protonated forms of **1N–4N** were also studied for comparison. **1Q–4Q** could be thermally converted back to **1N–4N**.

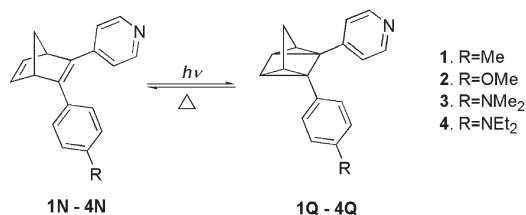
Table 1 summarizes the synthesis of the NBDs. The synthesis of the starting aryl-4-pyridylethyne has been already reported by us and others.¹³

Since the parent norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, $\lambda_{\max} < 300$ nm) can not absorb in the visible region, tremendous amount of effort has been invested in increasing the long-wavelength limit of absorption.^{4,14} Any attempt in this direction has resulted in increase in molecular weight and reduction in quantum yields.¹⁵ The NBD–QC systems reported here appear to address and solve this problem. Further, the photovalence isomerization of all the systems reported here takes place without the need to add sensitizers. This is advantageous in that the use of sensitizers may affect the isomerization by forming addition products with the NBDs, may even catalyze polymerization of the NBDs or reduce switching cycle.² Isomerization without the use of sensitizers may follow singlet route rather than triplet route.

Donor and acceptor moieties when substituted on one double bond of NBD (i.e., 2,3-diaryl), although increase molecular weight, have not reduced the quantum yields. The NBD systems reported here have high quantum yields of valence isomerization and have the long-wavelength absorption limit extended close to 500 nm. This may be due to better intramolecular charge transfer from the donor to acceptor supported by greater degree of copla-

narity of the donor and acceptor with the double bond.¹⁶

The absorption characteristics and photoconversion of the NBDs into QCs are summarized in Table 2. It can be seen that the quantum yields for the NBD–QC conversion of protonated systems, especially NMe₂ and NEt₂ substituted NBDs, are very low.



Scheme 1. Thermally reversible photoisomerization of **1–4**.

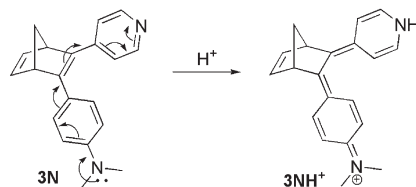
Table 1. Synthesis of NBDs (**N**)^a and conversion into QCs(**Q**)^b

Entry	Ethyne	N	Yield /%	Q	Yield /% ^c	Q→N ^{c,d} Δ /°C (t /min)
1		1N	35	1Q	100	≈ 70 (90)
2		2N	43	2Q	85	≈ 70 (90)
3		3N	45	3Q	100	≈ 50 (420)
4		4N	33	4Q	95	≈ 70 (90)

^aConditions: The ethyne (1 mmol) was heated at 220 °C, 24 h with freshly distilled 1,3-cyclopentadiene (1.2 equiv.) in toluene (10 mL) in a PTFE screw-capped thick wall 20-mL glass tube.

^bConditions: 5 mg of the NBD was dissolved in CD₃CN (0.4 mL) in NMR tube, degassed and irradiated in a 419 nm Rayonet Photoreactor 1–2 h. ^cBased on ¹H NMR (cf. Figure 1.)

^d100% on heating the same tube on hot water bath.



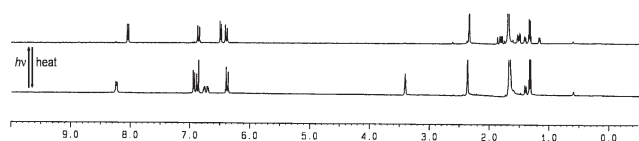
Scheme 2. Protonation and charge transfer in **3N**.

This may be due to the formation of, for example, **3NH**⁺ cation, which effectively retards cycloisomerization (Scheme 2), although the protonation further extends the long-wavelength limit. Hence the free base NBDs can be considered as superior candidates for the valence isomerization applications

Table 2. Absorption spectral characteristics of **N** and **Q** and the quantum yields for the formation of **Q**

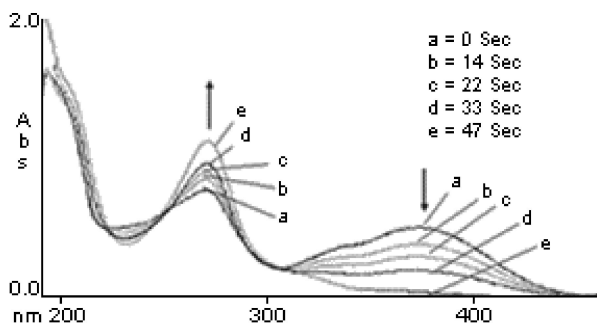
Entry	N ^a	UV maxima/nm, (ϵ , $\times 10^4/\text{M}^{-1}\text{cm}^{-1}$)	Q ^b	UV maxima/nm	ϕ^c
1	1N	196, 225, 301 (1.39)	1Q	196, 222	0.6
2	1NH⁺	196, 254, 381 (0.76)	1QH⁺	196, 255	0.53
3	2N	195, 237, 311 (2.56)	2Q	251, 261	0.31
4	2NH⁺	199, 233, 388 (0.15)	2QH⁺	198, 233	0.27
5	3N	206, 260, 366 (5.57)	3Q	251, 333	0.34
6	3NH⁺	331, 373, 485 (2.96)	3QH⁺	196, 268, 485	0.008
7	4N	195, 270, 373 (7.33)	4Q	201, 270	0.36
8	4NH⁺	200, 280, 497 (0.93)	4QH⁺	200, 280, 497	0.01

^aSolvent: Deaerated CH₃CN. ^bWavelength used for the conversion of **N** → **Q** = 419 nm; **3QH⁺** and **4QH⁺** cannot be considered as having been formed and remain as **3NH⁺** and **4NH⁺**. ^cQuantum yields for **N** → **Q** photoconversion arrived at using ferric oxalate actinometry.¹⁷

**Figure 1.** ¹H NMR spectra of **3N** (bottom) and **3Q** (top) in CD₃CN in the same NMR tube during a valence isomerization cycle.

(such as optical data storage and photochromic systems) to the protonated ones. Stronger donors such as NMe₂ and NEt₂ groups increase the long-wavelength absorption limit largely than poor donors like CH₃ and OCH₃ groups.

Figure 1 shows the ¹H NMR spectral profile of **3N** during valence isomerization cycle. As the compound transforms from **NBD** into **QC** new peaks corresponding to unsymmetrical **QC** at the alkyl region appear between 1.5 and 2.5 ppm while the signals due to olefinic double bond CH at 6.75 ppm (two symmetric multiplets) disappear as also the peak at 3.4 ppm corresponding to the bridge junction (C-1, C-4) CH. This trend has been observed for all the systems studied here and the interconversion has been quantitative.

**Figure 2.** UV-vis absorption changes during valence isomerization **4N** to **4Q** λ_{irr} = 419 nm.

The photovalence isomerization of **4N** as studied by UV-vis spectral changes is depicted in Figure 2. Curve a is that of **4N** in CH₃CN (1×10^{-3} M) whose longer wavelength band at 373 nm slowly decreases with respect to time and finally flattens (curve e) which is nothing but that of **4Q**. This behavior occurs without employing a sensitizer. Further it was noticed that the interconversion is concentration dependent: faster at low concentrations and slower at higher concentrations.

The calculated ground state energy of formation¹⁸ of **3Q** is

129.9 kJ mol⁻¹ (or 451 J g⁻¹) more than that of **3N** and the activation barrier for conversion of **QC** back to **NBD** lies at 130 kJ mol⁻¹. These values are beneficially far higher than ordinarily expected of molecular systems that can be applied for solar energy storage.² Further, the systems reported here have good fatigue resistance as observed from the NMR behavior (as in Figure 1) even after 20 cycles.

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References and Notes

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