Synthesis of New Donor–Acceptor Norbornadiene Derivatives

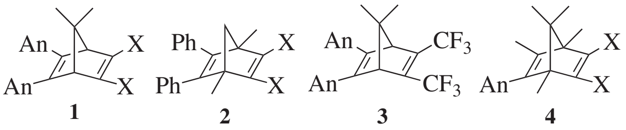
Takabumi Nagai,* Ikuko Takahashi, and Tadatomi Nishikubo†
Daikin Environmental Laboratory, Ltd., Miyukigaoka 3, Ibaraki 305-0841
†Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686

(Received May 6, 2003; CL-030382)

New donor–acceptor norbornadiene derivatives (NBDs) were synthesized from Diels–Alder reaction of methoxyphenylpentamethylcyclopendadiene with acetylene derivatives containing electron-withdrawing groups. These NBD derivatives have absorption in the visible region and photoisomerized to give thermally stable quadricyclane derivatives (QCs) with fair durability.

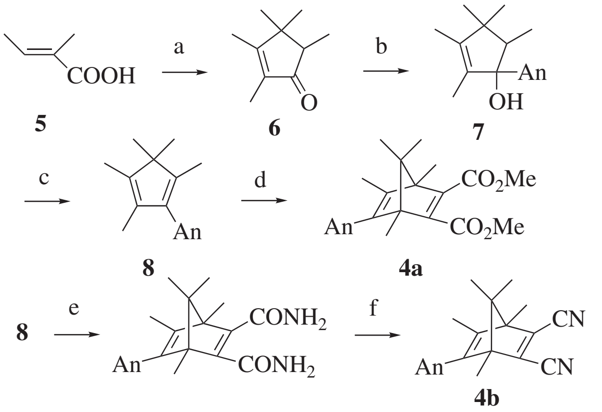
Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system,[1] because photo energy can be stored as strain energy (about 20 kcal/mol) in a QC molecule. Recently, this photochemical reaction has also been investigated as an optical wave-guide utilizing photo-induced refractive index changes[2a,2b] or as a photochromic system potentially applicable to data storage.[3a]

Taking these unique characteristics of NBD into account, many NBD derivatives[3] and photoresponsive polymers containing NBD moieties have been synthesized.[4] However, the photoreactivity and the fatigue resistance of these compounds were insufficient for practical use as advanced materials. Yoshida et al. reported that donor–acceptor (D–A) NBDs **1** absorb visible light efficiently, but thermal stability of the corresponding QCs was not high enough for practical use.[3a] To overcome these drawbacks, Nagai et al. synthesized CF$_3$-substituted D–A NBDs **3**, recently (Scheme 1).[3b] These compounds had large absorption in the visible region and gave thermally stable QCs. However, because CF$_3$-substituted NBDs contain fluorine atoms, these compounds are expensive, and, further, incur problems in the disposal of waste containing the halogen atom after use. On the other hand, Yoshida et al. also reported that D–A NBDs **2**, containing methyl groups in the 1,4-positions, gave thermally stable QCs, but they did not absorb visible light so efficiently.[3a] Furthermore we could not synthesize new derivatives of **2** which had longer wavelength absorption than that of **2**, because it was difficult to introduce more electron donative groups than a phenyl group to the donor site of **2**. Therefore, this time we report the synthesis of new D–A NBDs **4**, which have absorption in the visible region, give thermally stable QCs, and do not contain a halogen atom.

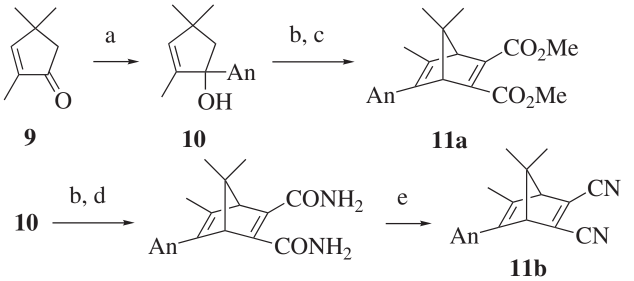


An=p-CH$_3$OC$_6$H$_5$; Ph=C$_6$H$_5$ **a**: X=COOCH$_3$; **b**: CN

Scheme 1.



Scheme 2. Synthesis of NBD derivatives **4**. Reagents and conditions: a) Ref. 5; b) p-CH$_3$OC$_6$H$_5$Li, THF, 0 °C, 1 h; c) d.HCl, room temp, 1 h, 78% from **6**; d) dimethyl acetylenedicarboxylate, toluene, reflux, 15 h, 82%; e) acetylene-dicarboxamide, DMF, 120 °C, 15 h; f) SOCl$_2$, DMF, 0 °C, 1 h, 20% from **8**.

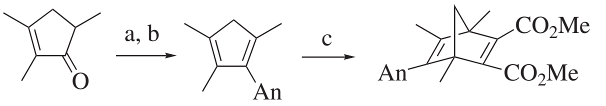


Scheme 3. Synthesis of NBD derivatives **11**. Reagents and conditions: a) p-CH$_3$OC$_6$H$_5$MgBr, THF, room temp, 2 h; b) d.HCl, room temp, 1 h; c) dimethyl acetylene-dicarboxylate, toluene, reflux, 15 h, 73% from **9**; d) acetylene-dicarboxamide, DMF, 120 °C, 15 h; e) SOCl$_2$, DMF, 0 °C, 1 h, 16% from **9**.

These NBDs **4** were synthesized from Diels–Alder reaction of methoxyphenylpentamethylcyclopentadiene derivative **8** with acetylene derivatives containing electron-withdrawing groups as shown in Scheme 2. Cyclopentadiene **8** was synthesized from the addition of an aryl lithium reagent to cyclopentenone **6** obtained from *trans*-dimethylacrylic acid **5**,[5] followed by dehydration catalyzed by p-toluene sulphonic acid. We also synthesized NBDs **11** and **14** as shown in Schemes 3 and 4. Cyclopentenones **9**[6] and **12**[7] were synthesized according to the literature. Structures of the new compounds were confirmed by MS, IR, and NMR spectra.

The data of the absorption spectra of NBDs are shown in Table 1. These NBDs had absorption in the visible region. The absorption maxima of **4b** was 380 nm and the absorption edge reached 500 nm.

Next, we examined the thermal stability of QCs at room



12 **13** **14**

Scheme 4. Synthesis of NBD derivatives **14**. Reagents and conditions: a) p-$CH_3OC_6H_5MgBr$, THF, room temp, 2 h; b) d.HCl, room temp, 1 h, 67% from **12**; c) dimethyl acetylenedicarboxylate, toluene, 80 °C, 1 h, 100%.

temperature (20 °C) in a PMMA solid film. These QCs samples were prepared from photoisomerization of the corresponding NBDs contained in PMMA solid film by irradiation with a xenon lamp. As shown in Table 1, it was found that **4b** not only had longer wavelength of absorption maxima and absorption edge but also produced far more stable QCs than **1a**, **2b**, **11a**, and **11b**. It seems that QCs obtained from NBDs which have methyl groups in the C-1 and C-4 positions are more stable than QCs obtained from NBDs which have H in the C-1 and C-4 positions, although NBDs which have H in the C-1 and C-4 positions have longer wavelength of absorption maxima and absorption edge than NBDs which have methyl groups in the C-1 and C-4 positions.

The stored thermal energy in the QCs obtained from **4a** and **4b** was measured on DSC. As shown in Table 2, the irradiated **4a** and **4b** released 64 kJ/mol of thermal energy, respectively.[8] These compounds have a smaller capacity of heat storage per molecule than that reported (80–90 kJ/mol) for other QCs.[3b,9] However, **4b** has a larger capacity of heat storage per weight than **3**, since the molecular weight of **4** is lower than that of **3**. It seems that the stored thermal energy in the QCs which have substituents in the C-1 and C-4 positions is lower than that of QCs which have H in the C-1 and C-4 positions, since the strain contained in the QC framework is partly released by introduction of substituents into the C-1 and C-4 positions of the QC molecule. Therefore, QCs which have methyl groups in the C-1 and C-4 positions are more stable than QCs with H in the C-1 and C-4 positions.

We also examined the ability of the NBDs to turn over the cycles of photoisomerization (NBDs→QCs) and thermal reversion (QCs→NBDs).[3] As shown in Figure 1, **3** showed better durability than **4**. While **4a** and **4b** having methyl groups in the C-7 positions showed fair durability, **14** having H in the C-7 position showed very low durability. The reason why the substituent in the C-7 position affects the durability is not clear. More work on examination of the relationship between the structure and durability of NBDs is necessary. Furthermore, it is apparent that 2,6-di-*tert*-butylphenol,[11] a radical scavenger, improves the durability of NBDs, since the radical scavenger suppresses the formation of byproducts caused by the polymerization of the NBDs and QCs.

Table 1. Absorption spectra of NBDs and thermal stability of QCs

No. of NBDs	Absorption spectra of NBDs[b]		$T_{1/2}$ of QCs (at 20 °C)
	λ_{max}/nm	λ_{AE}/nm[c]	
1a[a]	355	480	6.5 h
1b[a]	395	550	11 min
2b[d]	350[d]	454[d]	10 h[d,e]
4a	313	414	stable
4b	380	500	170 h
11a	329	460	21.8 h
11b	378	490	16 min
14	317	430	stable

[a]**1a** and **1b** were synthesized according to Ref. 3a. [b]1×10^{-4} mol dm^{-3} solution in acetonitrile. [c]$\varepsilon = 10$. [d]Ref. 3a. [e]$T_{1/2}$ at 45 °C.

Table 2. The Capacity of Heat Storage of NBDs

No. of NBDs	Capacity of Heat Storage of NBDs[a]	
	kJ/mol	J/g
3[b]	80[b]	171[b]
4a	64	167
4b	64	201

[a]Measured by DSC. [b]Ref. 3b.

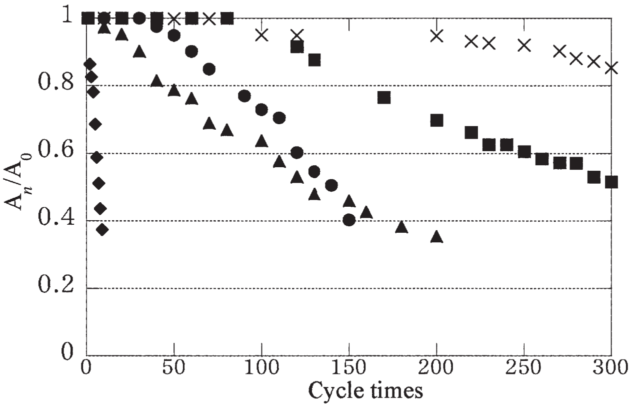


Figure 1. Durability of NBD derivatives: (X) **3**; (●) **4a**; (▲) **4b**; (■) **4a** added 0.5 wt% of 2,6-di-*tert*-butylphenol; (◆) **14**.[12]

In conclusion, our result suggests the usefulness of NBDs **4** that do not contain halogen. Namely, NBDs **4** have absorption in the visible region, to produce thermally stable QCs with fair durability.

We would like to thank Professor Sadao Miki of Kyoto Institute of Technology for helpful discussions.

References and Notes

1 R. R. Hautala, R. B. King, and C. Kutal, "Solar Energy," Hamana, Clifton, NJ (1979), p 333.

2 a) S. Morino, T. Watanabe, Y. Magaya, and K. Horie, *J. Photopolym. Sci. Technol.*, **7**, 121 (1994). b) Y. Kato, H. Muta, S. Takahashi, K. Horie, and T. Nagai, *Polym. J.*, **33**, 868 (2001), and references cited therein.

3 a) S. Miki, Y. Asako, and Z. Yoshida, *Chem. Lett.*, **1987**, 195. b) T. Nagai, K. Fujii, I. Takahashi, and M. Shimada, *Bull. Chem. Soc. Jpn.*, **74**, 1673 (2001), and references cited therein.

4 T. Nagai, M. Shimada, Y. Ono, and T. Nishikubo, *Macromolecules*, **36**, 1786 (2003), and references cited therein.

5 C. Morel-Fourrier, J.-P. Dulcere, and M. Santelli, *J. Am. Chem. Soc.*, **113**, 8062 (1991).

6 a) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970). b) J. Mathew, *J. Org. Chem.*, **56**, 713 (1991).

7 G. Gowda and T. B. H. McMurry, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 274.

8 a) A. Ikeda, A. Kameyama, T. Nishikubo, and T. Nagai, *Macromolecules*, **34**, 1786 (2001). b) Y. Konno, A. Kameyama, T. Nishikubo, and T. Nagai, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 2683 (2001).

9 A. Tsubata, T. Uchiyama, A. Kameyama, and T. Nishikubo, *Macromolecules*, **30**, 5649 (1997), and references cited therein.

10 Preparation of PMMA solid film: A solution of NBDs (10 mg) and PMMA (250 mg) in chloroform (2 mL) was cast on a quartz plate. Then, the quartz plate-cast film was dried in vacuo at 80 °C for 15 h. Examination of the durability: The experiment was performed under argon atmosphere. Initially, the polymer film was irradiated by a 500-W xenon lamp (Ushio Electric Co., UI-502Q) until the disappearance of the absorbance of the absorption maxima. Then, the film containing the corresponding QC moieties was heated on a hot plate until the reversion of the absorbance of the NBD moieties (**4** or **14**: irradiated for 10 min, then heated at 120 °C for 30 min; **3**: irradiated for 10 min, then heated at 130 °C for 40 min.).

11 H. Taoda, K. Hayakawa, and K. Kawase, *J. Chem. Eng. Jpn.*, **20**, 335 (1987).

12 A_0 and A_n are the differences in the absorbance values between NBDs and QCs at λ_{max} of the NBDs on the 1st and nth cycles of reactions, respectively.

Published on the web (Advance View) July 21, 2003; DOI 10.1246/cl.2003.754