Trifluoromethyl-substituted Norbornadiene, Useful Solar Energy Material

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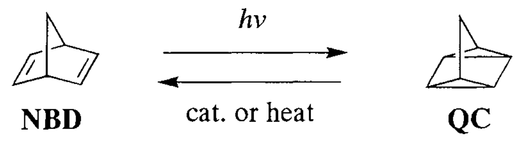
Trifluoromethyl (CF_3)-substituted NBD derivatives, which not only produce thermally stable QC derivatives but also absorb visible light efficiently, were synthesized. These NBD derivatives exhibited efficient fatigue resistance.

Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storange system,[1] because photoenergy can be stored as strain energy (about 20 kcal / mol) in a QC molecule (Scheme 1). Recently, this photochemical reaction has also been investigated as a new switching system in the optoelectronic field or as a photochromic system potentially applicable to data storage.[2]



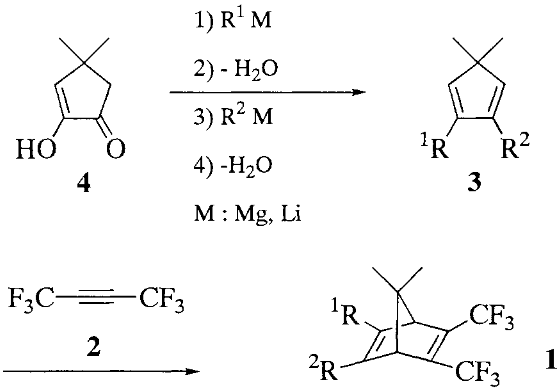
NBD **QC**

Scheme 1.

However, the photochemical reaction of NBD does not ordinarily occur upon irradiation with sunlight, because NBD does not efficiently absorb visible light. To solve this problem, there are two different methods used. One is the use of photosensitizers such as benzophenone derivatives in the NBD reaction system. However, there are no suitable photosensitizers with high stability and high efficiency for practical use. The other is the introduction of suitable chromophores into the NBD molecule to extend the absorption to the longer wavelength. To this end, many NBD derivatives have been synthesized. Yoshida *et al.* have found that donor-acceptor (D-A) NBDs have C-T absorption in a visible region and cyclize to give QCs in high quantum yield.[3] However, these NBDs do not absorb visible light efficiently (low ε ~1000) and the corresponding QCs are not stable enough, namely, they revert to the starting NBDs rapidly at room temperature.

It is known that a perfluoroalkyl group often serves to produce a stable valence isomer of aromatic compounds.[4] As in the case of NBDs, introduction of a CF_3 group would be expected to give the corresponding QCs with increased stability. Therefore, we synthesized new NBDs (**1**) containing a CF_3 group on the C-T acceptor site and found that these NBDs not only produce the expected thermally stable QCs but also absorb visible light efficiently.

NBDs (**1**) were synthesized in fair to good yields by Diels-Alder reaction of hexafluoro-2-butyn (**2**) with the appropriate cyclopentadiene derivatives (**3**) obtained from cyclopentanedione (**4**) (Scheme 2 and Table 1).[5] This NBD synthesis strategy involves the facile introduction of a variety of substituents into the 2,3 positions of the NBD framework. Absorption spectra of the NBDs in the UV-visible region are shown in Figure 1. Thus, CF_3-substituted NBDs have quite large absorption coefficient (ε value) in a visible region as compared with those of NBDs having other groups such as COOMe (**5**) or CN (**6**).[7] The absorption maxima of NBDs tend to red shift (**1a** < **c** < **d** < **b** < **e** < **f**) with the electron-donating ability of the donor group. Especially, **1f** having 2-benzofuran as a donor group, has log ε 4.30 at 414 nm and the absorption cut-off of **1e** reaches 580 nm (Scheme 2 and Figure 1).



Scheme 2. Synthesis of new NBD derivatives

Table 1.

1	R1	R2	λ_{max}nm [a] (log ε)	λ_{AE} nm [a]	Yield/% from **4**
a	p-MeOC$_6$H$_4$	p-MeOC$_6$H$_4$	346 (3.71)	440	- Ref.6
b	p-Me$_2$NC$_6$H$_4$	p-Me$_2$NC$_6$H$_4$	390 (3.93)	510	14
c	p-Me$_2$NC$_6$H$_4$	p-MeOC$_6$H$_4$	374 (3.93)	500	9.5
d	p-Me$_2$NC$_6$H$_4$	2-Thiophenyl	385 (3.89)	520	8.5
e	p-Me$_2$NC$_6$H$_4$	2-Benzofuryl	407 (4.11)	580	39
f	2-Benzofuryl	2-Benzofuryl	414 (4.30)	480	27.3

[a] 1×10^{-4} mol dm^{-3} solution in acetonitrile

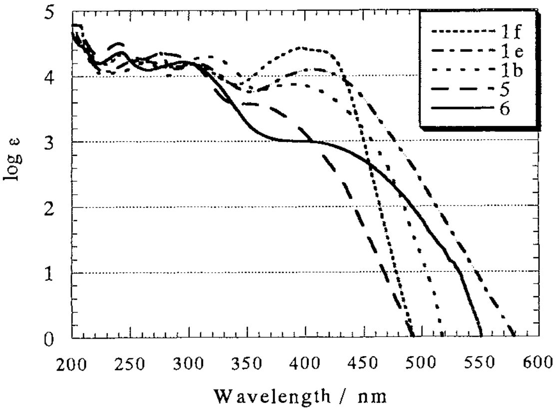


Figure 1. Absorption spectra of NBD derivatives. (1×10^{-4} mol dm^{-3} solution in acetonitrile.)

Next, we examined the thermal stability of QCs at room temperature (20 °C) in a PMMA solid film (Table 2).[8] As shown in Table 2, the CF_3 group increased the thermal stability of QCs. In particular, **1b**, **e**, and **f** not only have larger absorption in the visible region but also produce far more stable QCs than **5** and **6**.

Table 2. Thermal stability of QC derivatives at room temperature in the dark

No. of NBD derivatives	$T_{1/2}$ of QC derivatives (at 20 °C)
5	6.5 h
6	11 min
1a	stable
1b	1 year
1c	stable
1e	25 h
1f	26 h

We also examined the ability of the CF_3-substituted NBDs to turn over the cycles of photochemical valence isomerization (NBDs -> QCs) and thermal reversion isomerization (QCs -> NBDs).[9] Few studies concerning the reversibility of NBD compounds have been reported so far.[3a, 10] Fatigue resistance of NBDs **1a**, **1c**, and **1f** in PMMA solid film is shown in Figure 2.[11] While **1c** having a *p*-dimethylaminophenyl group showed fair fatigue resistance to result in ca 30% loss in extinction after $3.5x10^2$ cycles, **1a** and **1f** having *p*-methoxyphenyl groups and 2-benzofuryl groups, respectively, showed excellent fatigue resistance. After 10^3 times of the cycle, the loss in extinction was 30% and 3% for **1a** and **1f**, respectively. These results possibly indicate that the dimethylaminophenyl group seems to be more labile for photo or thermal degradation than methoxylphenyl and benzofuryl groups. We are continuing to investigate the effect of some light stabilizers so as to improve the photochemical fatigue resistance of NBDs.

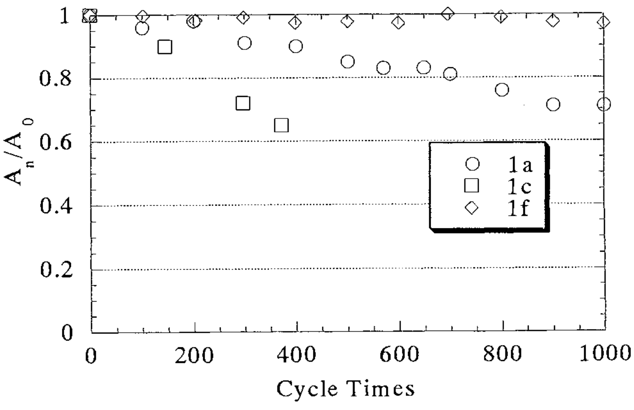


Figure 2. Durability of CF_3-NBD derivatives.[11]

In conclusion, our result suggests the usefulness of CF_3-substituted NBDs for advanced materials. Namely, these NBDs that have absorption in the visible region, produce thermally stable QCs with efficient fatigue resistance.

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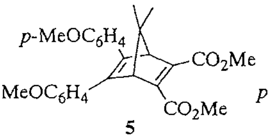
6 **1a** was synthesized in 91% yield by hexafluoro-2-butyn with 2,3-bis-(*p*-methoxyphenyl)-5,5-dimethylcyclopenta-1,3-diene, which was prepared according to the literature: K. Hirao, A. Yamashita, A. Ando, H. Yamamoto, H. Iijima, T. Hamada, and O. Yonemitsu, *J. Chem. Res.*, **1987**, (*M*), 1401.
7 Compounds **5**, **6** were synthesized according to Ref.3b.



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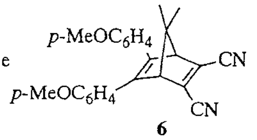

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8 The PMMA solid film doped with **1** was prepared according to Ref.3b.
9 A typical procedure for photochemical isomerization and thermal reversion of solid film is as follows. The experiment was performed under argon atmosphere. Initially, the film doped with NBDs 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 doped with the corresponding QCs was heated on a hot plate until the reversion of the absorbance of the NBDs (**1a** : irradiated for 10 min, then heated at 130°C for 40 min; **1c** : irradiated for 1min, then heated at 120°C for 20 min; **1f** : irradiated for 1min, then heated at 80°C for 15 min).
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11 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.