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Direct Valence Isomerization of Newly Synthesized Norbornadiene Aromatic Derivatives. A Kinetic and Photophysical Study

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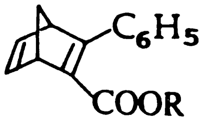
Four norbornadiene aromatic derivatives, potentially useful for light energy photochemical storage, were synthesized. Their photophysical properties and the kinetics of the valence photoisomerization reaction into quadricyclanes were investigated. Overall first-order rate constants of photoisomerization were found to be very fast and to vary markedly with the polarity of the solvent.

Valence photoisomerization of norbornadiene (NBD) derivatives into quadricyclanes (QC) has received recently much attention from the view point of the reaction mechanism,1) and also because of possible applications to solar energy photochemical storage.2) In order to increase the efficiency of solar energy storage process and to shift the absorbtion band towards the solar radiation main region ($\lambda > 300$ nm), several authors have proposed to introduce various chromophores in the norbornadiene molecule and/or to use sensitizers.2) However, the photoreactivity of these systems has been scarcely investigated, and no study of the fluorescence of aromatic norbornadienes or quadricyclanes has yet been undertaken, in spite of the mechanistic interest of fluorescence quenching and photochemical kinetics. In this paper, we report the synthesis, the photophysical properties and the photoisomerization kinetics of aromatic norbornadienes.

Compounds **1a-d** were prepared by a Diels-Alder reaction with cyclopentadiene, followed by a substitution reaction of the potassium carboxylate NBD compounds with the convenient chloride or bromide derivative.



a. R = H
b. R = $CH_2C_6H_5$
c. R = $CH_2C_6H_5$*p*-OCH_3
d. R = $(CH_2)_6OC_6H_4$*p*-OCH_3

The reaction conditions and yields are shown in Table 1. It can be seen that the use of phase transfer catalysis (PTC) allowed to prepare **1b-d** in satisfactory conditions. The yields obtained compare favorably with the ones of the literature for compounds **1a** and **1b**, and are satisfactory for new compounds **1c** and **1d**.[3)]

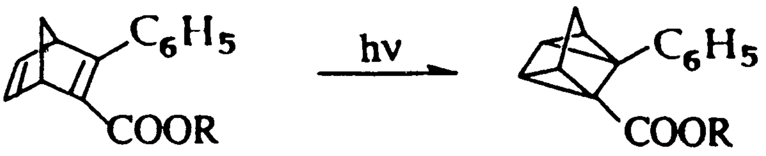
Table 1. Synthesis conditions and yields of norbornadiene aromatic derivatives

Compounds	Conditions	Yield/%	M_p/°C
1a	DA[a)],reflux,1 h	50[b)]	135[b)]
1b	PTC[c)],DMF,50°C,24 h	70[d)]	68[d)]
1c	PTC[c)],DMF,50°C,36 h	72	58
1d	PTC[c)],H_2O-CH_2Cl_2,20°C,36 h	40	liq.

a)DA: Diels-Alder reaction. b)Lit.(5): 53%, 136°C. c)PTC: Phase transfer catalysis method. d) Lit.(5): 88%, 69°C.

The UV absorption and fluorescence spectral properties of NBD aromatic derivatives in ethanol are summarized in Table 2.[4)] The shortest-wavelength maxima absorption bands located in the 200-240 nm region (Log ϵ= 3.8-4.4), can be attributed to a contribution of the NBD intramolecular charge transfer[6)] and of the benzene π,π^* ^1B transition, whereas the longest-wavelength bands appearing in the 275-295 nm (Log ϵ= 3.6-4.0) region are ascribed to the aromatic π,π^* ^1L_a and ^1L_b transitions. Compounds **1b-d** were found to be fluorescent. To the best of our knowledge, this is the first time that fluorescence properties of norbornadiene derivatives are reported. Fluorescence emission bands occurring in the 314-350 nm region are due to the phenylester group π,π^* transition. The fluorescence relative intensity increases significantly in the order:**1b** < **1c** < **1d**, suggesting that the introduction of electron-donor alkoxy group(s) in the aromatic ring enhances the probability of the radiative desactivation of the norbornadiene excited singlet-state.

Irradiation of compounds **1a-d**, performed with a filtered 284-nm Osram high-pressure mercury arc lamp, resulted in the formation of the corresponding QCs.



The rates of photoisomerisation of NBD aromatic derivative solutions (5.10^{-5} M) were determined at 293 K by measuring the decrease, with

Table 2. UV absorption and fluorescence properties of NBD aromatic derivatives in ethanol[a)]

Compounds	Absorption λ_{max}/nm ($\log\epsilon$)[b)]	Fluorescence λ_{ex}/nm	λ_{em}/nm[c)]	I_F[d)]
1a	205(4.55),288(3.85)	-[e)]	-[e)]	-[e)]
1b	205(4.35),293(3.74)	284	316,350	1.0
1c	203(4.38),280(3.88)	232,274	298,314	2.5
1d	203(4.11),290(3.40)	231,291	326	8.2

a)Concentrations: $5\cdot10^{-5}$ M. b)Molar absorption coefficients are expressed in $M^{-1}.cm^{-1}$. c) Maxima are underlined. d) relative fluorescence intensity corrected for the solvent signal and normalized to 1.0. e) Compound not fluorescent.

irradiation time, of the absorption peak at 275-295 nm. The isobestic points observed at about 230 nm and 250 nm in the UV spectra indicate that the photoreaction is very clean, proceeding without side reactions (Fig.1). The photoisomerization rates obeyed first-order kinetics.

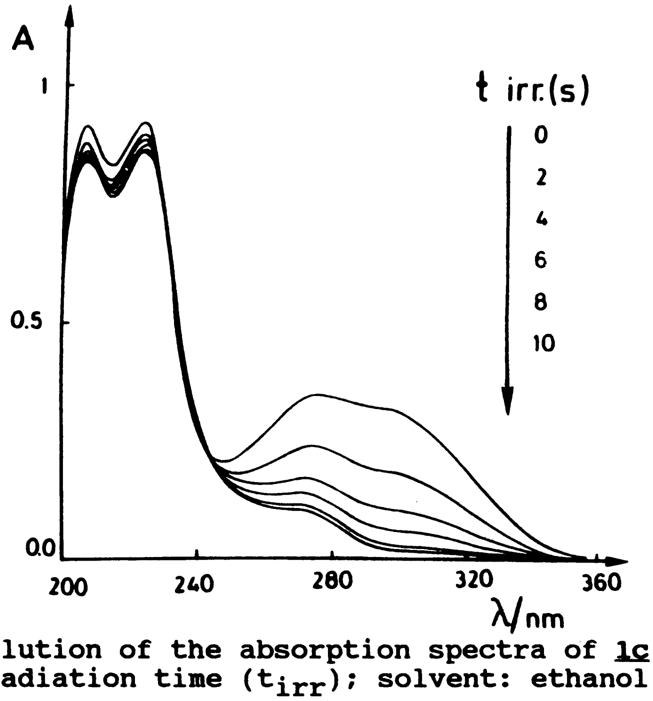


Fig.1. Evolution of the absorption spectra of **1c** with irradiation time (t_{irr}); solvent: ethanol.

The overall first-order rate constants (k_1) (Table 3) between $1.2.10^{-1}$ and $3.2.10^{-1}$ s^{-1}, showing that the photoisomerization rates of these NBD aromatic derivatives are very fast and depend on the polarity of the solvent. Indeed, our k_1 values were much larger than those obtained by Iizawa et al[7)] for several (*p*-substituted phenyl) carbamoyl NBD derivatives in methylene chloride. These very high photochemical reactivities demonstrate the advantage of using such a NBD derivative system for a rapid, efficient light energy storage.

Table 3. Photoisomerization first-order rate constants (k_1x10, s^{-1}) of norbornadiene aromatic derivatives in several solvents[a)]

Compounds	DMSO	CH_3CN	C_2H_5OH	CH_2Cl_2	THF	$CHCl_3$
1a	2.66	1.46	1.82	1.67	1.45	1.49
1b	1.19	1.23	1.47	1.66	1.68	1.99
1c	3.25	2.35	2.82	2.29	2.01	2.36
1d	2.03	1.79	1.94	-[b)]	1.74	2.20

a) Determined with the Guggenheim method. Correlation coefficients were $\geq$ 0.98 and relative errors were $\leq$ 10%. b) No first-order kinetic plot.

The photophysical behaviour of the NBD aromatic derivatives is characterized by a rapid increase of their fluorescence signal upon UV irradiation. This feature may be due to the progressive reduction of the fluorescence quenching of the aromatic cycle by the NBD moiety, during the photoisomerization reaction of the NBD into the QC derivatives. Work is now in progress in our laboratory for determining the inter and/or intramolecular nature of this quenching.

References

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