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Detection and Thermal Properties of 1,4-Difluorobenzene-Naphthoquinone Biplanemer: a New Longicyclic π System

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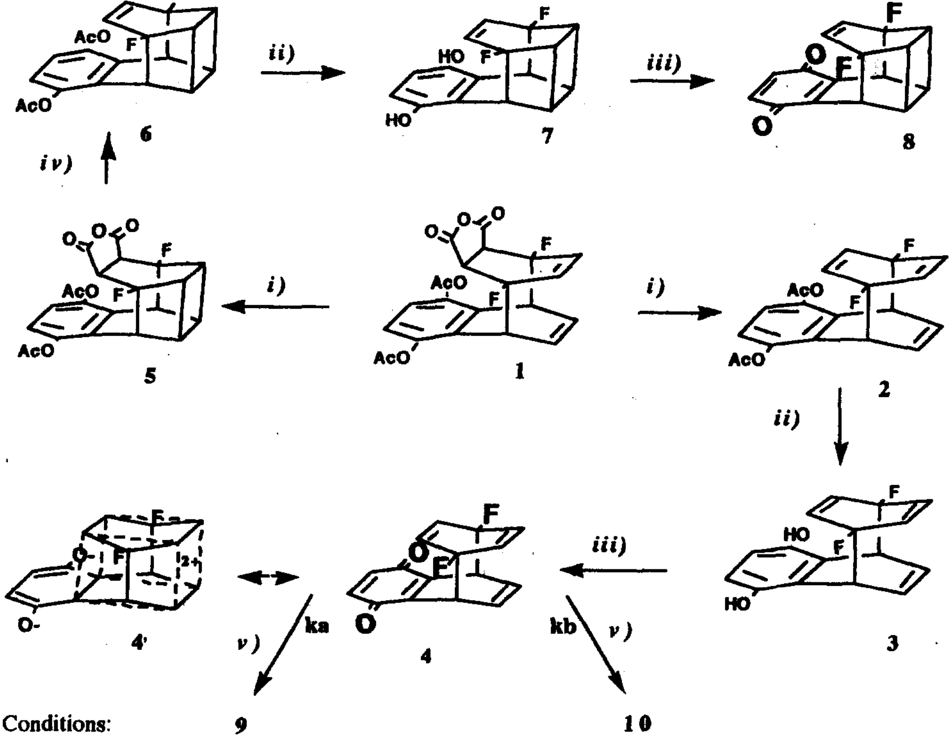
Abstract: 9,10-difluorotetracyclo[6.4.$2^{1,8}$.$2^{9,12}$.$0^{2,7}$]hexadeca-2,4,6,10,13,15-hexaene-3,6-dione is thermally labile and shows a notably clear, long wave-length CT absorption.

Longicyclic conjugation is an interesting concept of π topology because of its unique electronic character and its potential to open new chemical possibilities. Among the possibilities, longicyclic conjugated π systems may provide a new type of efficient electron donor. According to the Hoffman and Goldstein classification, a longicyclic [2.2.2.2] system is classified as the least stable in the four-ribon longicyclics, but there has not been experimental evaluation of its stability. In this report, we present the new compound possessing a quinone moiety (an electron acceptor) and the longicyclic π system (an electron donor): 9,10-difluorotetracyclo[6.4.$2^{1,8}$.$2^{9,12}$.$0^{2,7}$]hexadeca-2,4,6,10,13,15-hexaene-3,6-dione (1,4-Difluorobenzene-naphthoquinone biplanemer) **4**. We report the first detection of **4** and the preparation of **8**, and discuss the spectroscopic and themal properties of **4** in comparison with those of **8** in which the longi-cyclic conjugation is absent.

Compound **4** was prepared by the following three successive steps; [4+4]-photocycloaddition of 3,6-difluoro-1,2-dihydrophthalic anhydride and 1,4-diacetoxy-naphthalene giving **1**, followed by a Kolbe decarboxylation of **1** giving **2**, and hydrolysis of **2** providing **3** as a precursor to the title compound **4**. The introduction of fluorine atoms at the bridgehead is important for these energy rich compounds to be durable under these reaction conditions.[2,3] We prepared also the related compound **8**, starting from a common intermediate **1**, which has a double bond placed over a quinone moiety.

When DDQ (1 equiv.) was added into a CD_3CN solution of **3** at ambient tempeature in an NMR tube, very complicated proton resonances immediately appeared between 3.5 and 8.5 ppm instead of the expected five resonance peaks for **4** in the 500 MHz ^{1}HMR spectrum. These resonances completely disappeared by standing the mixture over night and new assignable resonances appeared at 6.98 (s), 7.12 (triplet, 1,4-difluorobenzene), 7.80 (A_2B_2, naphthoquinone), 8.04 (A_2B_2, naphthoquinone), and 8.30 ppm (broad, DDHQ). This spectrum is identical with that of a 1:1:1 mixture of 1,4-difluorobenzene, naphthoquinone and DDHQ. As these observations suggest that **4** should be thermally unsatable at ambient temperature, low temperature measurment is required to confirm the expected formation of **4**. Therefore, ^{1}HMR measurement was performed at -10 °C. It showed a spectrum of a fairly pure new product accompanied with tiny peaks arising from the successive thermal reactions. The structure of the new product was elucidated to be 1,4-difluorobenzene- naphthoquinone biplanemer based on both the FAB mass spectrum [m/z 273$(M+1)^+$] and ^{1}HMR analysis of chemical shifts (Table 1) and coupling patterns of the signals. This reaction was also monitored by UV spectroscopy at -15 °C, and a new weak broad absorption was observed around 750 nm which might be affected by the presence of the DDQH formed. In order to avoid the influence of DDQH, PbO_2 instead of DDQ was used for the oxidation. This new band also emerged in 5 min after the addition of PbO_2 at -5 °C as shown in Fig 1.[4,5] The electronic spectra of **4** and **8** were analyzed by CNDO/S calculation. The characteristic

Scheme



Conditions:

i) Electrolysis
80% Py aq.
TEA 2.0 equiv.

ii) 0.1M KOH
80% EtOH aq.

iii) DDQ / CD_3CN

iv) *hv* / Benzene

v) heat / CD_3CN

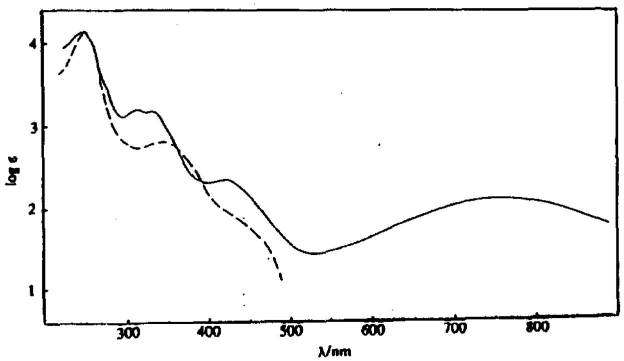


Fig. 1 UV spectra of 4(—) in CH_3CN and 8(--) in EtOH.

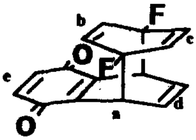
absorption band around 750 nm (38.1 kcal/mol) of **4** is attributed to CT absorption between the quinone moiety (an electron acceptor) and the longicyclic π system (an electron donor). The corresponding CT band of cage compound **8** shifts toward shorter wavelength around 450 nm (63.6 kcal/mol); however, there is a considerable wavelength difference bewteen the calculation and the observation.[6] As Cookson et al. showed that the intramolecular charge transfer transition from the cyclohexene moiety to the p-benzoquinone moiety in 1,4-dihydro-1,4- methanonaphthalene should occur at 308 nm (92.9 kcal/mol) consistent with the value for benzene-p-benzoquinone intermolecular charge-transfer at 305 nm,[7] the large bathochromic shift is attributed to efficient electron donating effect of the longicyclic conjugated π system in **4**. Thus, the longicyclic[2.2.2.2] system appears to be a very efficient donor as the four-ribon longicyclics.

The thermal reaction of 4 was examined to clarify the unique property of the longicyclic π system. Thermal rearrangement of **4** was monitored by the ^{1}HMR spectroscopy in CD_3CN at -10 °C . Within 30 min it gave rise to a mixture of **9** and **10** in a 3:1

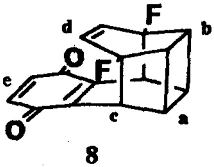
Table 1. ^{1}HMR data for **4**, **8**, **9** and **10**.

	Chemical Shifts (δ, ppm)[a]									
Compound	a	b	c	d	e	f	g	h	i	i'
4	3.99	6.20	6.35	6.60	6.75					
8	3.05	3.24	4.34	5.95	6.84					
9	3.88	4.48	5.03	5.92	6.00	6.10	6.14	6.64	6.76	6.79
	Jac:6.0, JaF: 28.5, Jbe:5.5, JbF:10.0, Jcg:1.2, JcF:10.0, Jdg:6.0, JeF:10.0, Jfh:6.0, Jii':9.9.									
10	3.62	4.20	4.22	5.25	5.64	6.03	6.08	6.40	6.72	6.75
	Jab:13.9, Jac:4.8, Jag:4.8, Jah:3.0, Jbd:6.0, Jbe:0.8 ,JbF:13.9, JcF:28.0, JdF:12.0,Jef:8.0,JeF:14.0,Jgh:9.9.									

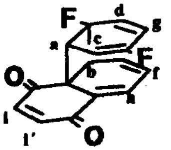
Conditions;Solvent=CD_3CN,Temp.=-10°C. a: J values are reported in hertzs.



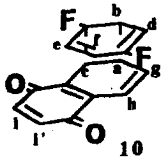
4



8



9



10

Table 2. Activation parameters of rearrangement 4 → 9 and 4 → 10.

	ΔH* (kcal/mol)	ΔS* (eu)	ΔG≠ (kcal/mol)
ka 4 → 9	17.0	- 13.2	20.9
kb 4 → 10	16.5	- 17.4	21.7

ratio due to a Cope rearrangement via a boat form transition state. The structures **9** and **10** were confirmed by the decoupling technique (Table 1). After warming to ambient temperature and standing overnight, further retro[2+2]cycloaddition of both **9** and **10** took place resulting in the formation of 1,4-difluorobenzene and naphthoquinone quantitatively. The decrease of **4** obeyed first order kinetics at three temperatures and the thermodynamic parameters are summarized in Table 2. As expected typical $\Delta S^{\neq}$ constants of thermal Cope rearrangements via a boat transition state are relatively high (-0.4 ~ -3 eu) compared with those via a chair transition state(-13 ~ -11.4 eu).[8] It is notable that -13.2 and -17.4 eu are rather small values for the Cope rearrangement via a boat transition state required from the stereochemistry of **4**. It is interesting that the rearrangement involving the quinone moiety is favorable in spite of providing a higher strained product **9** (ka =2.66×10^{-4} s^{-1} at 25 °C) than **10** (kb=2.45×10^{-5} s^{-1} at 25 °C). Although **4** was expected to be stabilzed by forming a longicyclic 6 π system **4'**, it thermally readily decomposed to give 1,4-naphthoquinone and 1,4-difluorobenzene via the rapid Cope rearrangement followed by retro[2+2]cycloaddition, but not via retro[4+4]cycloaddition which is a typical decomposition manner for other biplanemers.[2]

We thank the Okayama NMR Center for NMR spectra of **1-10**, recorded on a Varian VXR-500 spectrometer.

References and Notes

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4. The structures of all new compounds **1-8** were determined by CH analysis, ^{1}HMR, IR, and UV spectra. The selected data for **4** and **8** are as follows. **4**: Yield quantitative; UV ($CHCl_3$) λ_{max} 750 (log ε = 2.12), 425 (2.34), 332 (3.17), 314 (3.19), and 250 nm (4.14); MS (FAB, MNBA) m/e 273 $(M+1)^+$. **8**; Yield 94%; mp 126-130 °C; IR (KBr) ν_{max} 1638, and 1584cm^{-1}; UV (EtOH) λ_{max} 344 (log ε = 2.8), and 251 nm (4.12); Calcd. for $C_{16}H_{10}F_2O_2$: C,70.59; H, 3.70 %. Found: C,70.28; H, 3.69%.
5. As the UV spectrum of the reaction mixture of the oxidation using PbO_2 at -5 °C shown in Fig.1 was identical in the visible region with that of a reaction mixture (-15°C) using DDQ, the molecular absorption coefficients of **4** was calculated assuming that the yield of **4** is quantitative. The NMR spectral analysis of the reaction mixture also supports this assumption.
6. Sj and S0 transitions of **4** and **8** after configuration interaction caluculated by CNDOS/S: **4:** 529 (Oscill. Streng.= 0.0051, Absorption= CT), 524 (0.0002, nπ*), 396 (0.0150, ππ*), 313 (0.0199, ππ*, quinone part= Q), 303 (0.0590, ππ*), and 242 nm (0.9342, ππ*, Q). **8:** 550 (0.0001, nπ*), 376 (0.0075, CT), 304 (0.1723, ππ*), and 240 nm (0.6667, ππ*, Q).
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