

NOVEL PHOTOISOMERIZATION OF 9-TERT-BUTYL-10-CYANOANTHRACENE INVOLVING 1,2-TRANSFER OF METHYL GROUP

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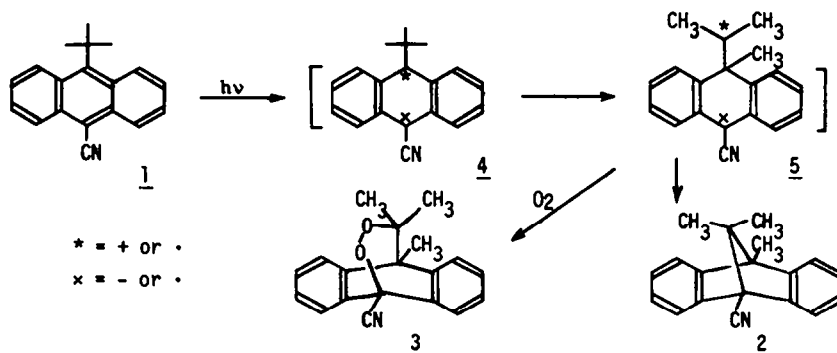
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Abstract — A novel photoisomerization of 9-tert-butyl-10-cyanoanthracene (**1**) involving the 1,2-transfer of a methyl group is described. Irradiation of **1** in acetonitrile at -20°C gave a dibenzobornadiene **2** as the sole isolable product. The structure of **2** was established by X-ray crystallography. In the solid state **1** was inert to irradiation.

The photodimerization of anthracene has drawn considerable attention¹ since its discovery by Fritzsche in 1867,² besides the photoaddition with dienes and other electron donating compounds.³ Recently it has been shown that 9-tert-butylanthracene irradiated at 0°C in isopentane isomerizes to its valence isomer, 9-tert-butyl-9,10-(Dewar-anthracene), which reverts back to the parent aromatic compound at higher temperatures.⁴ It is interesting that a tert-butyl group on aromatic rings promotes photochemical valence isomerization, namely the formation of highly strained Dewar isomers. Such a photochemical behavior of 9-tert-butyl-anthracenes is of interest because they could serve as a model system for the storage of solar energy and for a photochromic system like tert-butylated naphthalenes and anthracenes.⁵ We wish to report here novel photochemical isomerization of 9-tert-butyl-10-cyanoanthracene (**1**) to give a dibenzobornadiene **2**.



Irradiation of 1 at 0°C in acetonitrile in a nitrogen atmosphere with Pyrex-filtered UV light gave 2 in 58 % yield. The structure of 2 was assigned by its spectral data (see Experimental) and finally established by X-ray crystallography. The final parameters for the non-H atoms, bond distances between non-H atoms in angstroms and bond angles between non-H atoms in degrees are given in Table 1 and Table 2. There are three main planes in the molecule of this compound. The C11-C16, C31 and C41 atoms lie on the plane I, the C21-C26, C31 and C41 atoms on the plane II, and the C31, C41, C51, C32, C42 and N atoms on the plane III (Figure 1). The planes I, II and III intersect at a line through the C31 and C41 atoms. The dihedral angles between planes I and III as well as II and III are almost same (53.4° and 57.8°, respectively). The plane III bisects approximately the bond angle C52-C51-C53 (59.8° and 48.6°). This arrangement results from sp^3 hybrid orbitals of C31, C41 and C51.

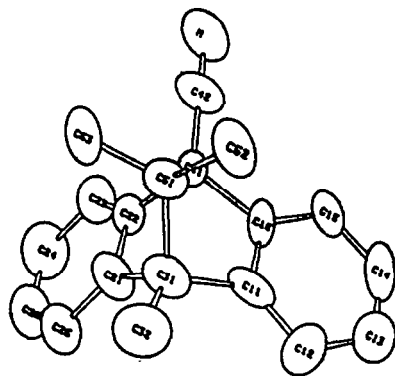
Figure 1. Stereoscopic view of 2

Table 1. Final atomic coordinates for non-hydrogen atoms.

	x	y	z
C11	0.046(1)	0.1212(9)	0.1830(8)
C12	-0.045(1)	0.076 (1)	0.102 (1)
C13	-0.121(1)	-0.022 (1)	0.127 (1)
C14	-0.093(1)	-0.060 (1)	0.225 (1)
C15	0.001(1)	-0.0132(9)	0.305 (1)
C16	0.072(1)	0.0823(9)	0.2788(9)
C21	0.304(1)	0.1861(9)	0.2123(9)
C22	0.328(1)	0.1421(9)	0.3070(8)
C23	0.460(1)	0.097 (1)	0.354 (1)
C24	0.577(1)	0.098 (1)	0.296 (1)
C25	0.552(1)	0.138 (1)	0.200 (1)
C26	0.417(1)	0.185 (1)	0.154 (1)
C31	0.141(1)	0.227 (1)	0.1866(9)
C41	0.176(1)	0.155 (1)	0.3440(9)
C51	0.127(1)	0.2668(9)	0.2989(8)
C52	-0.040(1)	0.295 (1)	0.308 (1)
C53	0.226(1)	0.361 (1)	0.342 (1)
C32	0.107(1)	0.303 (1)	0.102 (1)
C42	0.185(1)	0.149 (1)	0.4531(9)
N	0.197(1)	0.138 (1)	0.5379(8)

Table 2. Bond lengths (Å) and angles (°) of 2 with estimated standard deviations in parenthesis.

C11-C12	1.382(13)	C11-C16	1.368(12)	C11-C31	1.566(12)
C12-C13	1.457(15)	C13-C14	1.389(15)	C14-C15	1.394(14)
C15-C16	1.421(12)	C16-C41	1.521(11)	C21-C22	1.378(11)
C21-C26	1.395(11)	C51-C52	1.587(10)	C42-N	1.162(11)
C21-C31	1.551(11)	C22-C23	1.388(11)	C22-C41	1.574(10)
C23-C24	1.427(13)	C24-C25	1.382(15)	C25-C26	1.410(14)
C31-C51	1.622(12)	C31-C32	1.484(13)	C41-C51	1.573(11)
C41-C42	1.414(13)	C51-C53	1.528(12)		
C12-C11-C16	126. (1)	C12-C11-C31	129. (1)		
C16-C11-C31	105. (1)	C11-C12-C13	114. (1)		
C12-C13-C14	119. (1)	C13-C14-C15	126. (1)		
C14-C15-C16	114. (1)	C11-C16-C15	121. (1)		
C11-C16-C41	111.6(9)	C15-C16-C41	127. (1)		
C22-C21-C26	119.9(9)	C22-C21-C31	109.9(8)		
C26-C21-C31	130. (1)	C21-C22-C23	125.9(8)		
C21-C22-C41	105.7(8)	C23-C22-C41	128.5(9)		
C22-C23-C24	114. (1)	C41-C42-N	176. (1)		
C22-C41-C51	98.4(7)	C51-C41-C42	116.0(8)		
C31-C51-C53	117.5(8)	C41-C51-C52	112.1(7)		
C41-C51-C53	113.7(8)	C52-C51-C53	108.3(8)		
C31-C51-C41	93.8(7)	C31-C51-C52	110.9(8)		
C23-C24-C25	120. (1)	C24-C25-C26	124. (1)		
C21-C26-C25	116. (1)	C11-C31-C21	103.7(8)		
C11-C31-C51	99.3(8)	C11-C31-C32	118.1(9)		
C21-C31-C51	95.9(8)	C21-C31-C32	116.8(8)		
C51-C31-C32	119.3(8)	C16-C41-C22	102.7(7)		
C16-C41-C51	99.0(7)	C16-C41-C42	120.7(8)		
C22-C41-C42	116.3(8)				

The photochemical reaction of 1 was carried out under various conditions. The results are summarized in Table 3. There was no temperature dependence for the formation of 2 (Run 1

and Run 2). Irradiation of 1 in a hexane solution under bubbling nitrogen for a longer time gave only a low yield of a product which was tentatively assigned as an endoperoxide 3. In our recent study on the time resolved fluorescence decay of 1 in poly(methyl methacrylate), it has been suggested that a nonradiative process competing with the fluorescence exists above -120°C .⁶ This process probably corresponds to the formation of 2. Involvement of a triplet state for the formation of 2 is improbable, since the benzophenone sensitized reaction of 1 resulted in no formation of 2. On irradiation in the solid state at 0°C , 1 was completely recovered (Run 4). The photostability of 1 in the solid state is most probably due to the restriction of a spatial movement of the skeletal atoms of 1 to 2 in its crystal lattice, according to the general topochemical rule for solid state photochemistry.⁷

The photoisomerization of 1 to 2 may occur via a biradical or a zwitterionic intermediate 4 which undergoes the intramolecular 1,2-shift of a methyl group to give 5. The homolytic 1,2-shift of aryl and alkyl groups has been well documented.⁸ However, a finding that the disappearance rate of 1 was much slower in a nonpolar solvent (Run 3) seems to be a support for an ionic mechanism.

Table 3. Photoreaction of 1 under various conditions.

Run	Temperature ($^{\circ}\text{C}$)	Medium	Irrad. time (h)	Atmosphere	Yield of <u>2</u> (%)
1	0	Acetonitrile	43	N_2	52
2	-20	Acetonitrile	40	N_2	58
3	0	n-hexane	200	N_2 (bubbling)	0 ^a
4	0	Solid state	40	N_2	0

^a A product tentatively assigned as peroxide 3 was isolated in 22 % yield. The peroxide formation is ascribable to oxygen present as impurity in commercial nitrogen.

EXPERIMENTAL

Melting points are uncorrected. ¹H- and ¹³C-NMR spectra were measured on a Varian T-60 and a JOEL TNM-GX 400 spectrometers, respectively, with tetramethylsilane as internal standard. Infrared spectra were measured on a JASCO IRA-1 spectrometer. Thin layer chromatography was carried out on a Merck TLC plastic sheet precoated with silica gel 60 F₂₅₄ for analytical purpose and on a Merck kiesel gel 60 PF₂₅₄ for preparative purpose. 9-tert-Butyl-10-cyanoanthracene (1) was prepared according to the literature procedure.⁹

Irradiation of 9-tert-butyl-10-cyanoanthracene (1)

In acetonitrile solution. A solution of 1 (60 mg) in acetonitrile (250 ml) was bubbled with nitrogen and irradiated at 0°C in a closed vessel in an nitrogen atmosphere with a 400 W high-pressure mercury lamp having a Pyrex cooling jacket surrounded by an evacuated glass tube for 43 h. After the removal of the solvent under reduced pressure, the residue was separated by preparative TLC (silica gel; 1 : 1 n-hexane-benzene) to give 2 (31 mg; 52 %), m.p. $100-103^{\circ}\text{C}$ (from n-hexane); IR (nujol) 2260 cm^{-1} (CN); ¹H-NMR (CDCl_3) δ 0.93 (s, 6H, gem. CH_3), 1.58 (s, 3H, CH_3), 6.80-7.43 (m, 8H, arom. H); ¹³C-NMR (CDCl_3) δ 149.6 & 145.6 (bridge-head arom. C), 126.5, 125.6, 121.0 & 120.9 (arom. C), 117.0 (CN), 82.4, 77.5 & 59.9 (quaternary C), 18.6 (gem. CH_3), 7.7 (CH_3); Mass spectrum m/z 259(M⁺). Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}$: C, 87.99; H, 6.90; N, 5.40 %. Found: C, 87.70; H, 6.90; N, 5.17 %.

In hexane solution. A hexane solution of 1 was irradiated at 0°C under bubbling nitrogen with a high-pressure mercury lamp for 200 h. After the removal of the solvent, the residue

was separated by preparative TLC as above to give an unstable peroxide **3** as a solid (22 %). $^1\text{H-NMR}$ (CDCl_3) δ 1.37 (s, 6H, gem. CH_3), 1.70 (s, 3H, CH_3), 6.97–7.30 (m, 6H, arom. H), 7.33–7.70 (m, 2H, arom. H); Mass spectrum m/e 291 (M^+).

In the solid state. Crystals of **1** were ground to a fine powder in a mortar. The powder (60 mg) was placed between two Pyrex glass plates and irradiated in a nitrogen atmosphere for 30 h at 0°C using a 400 W high-pressure mercury lamp. The starting material was quantitatively recovered (NMR and TLC).

Benzophenone sensitization. A solution of **1** (15 mg) and benzophenone (100 mg) in acetonitrile (20 ml) was irradiated at 0°C with a 400 W high-pressure mercury lamp under bubbling nitrogen for 8 h. After the removal of the solvent, the residue was analyzed by TLC and $^1\text{H-NMR}$. Only a small amount of **2** and benzopinacol was detected on TLC.

X-ray crystallography.

Pale yellow crystals of **2** were obtained by slow evaporation from a n-hexane solution. The crystal structure was determined on a $\text{ENRAF-NONTUS CAD 4}$ diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal belongs to monoclinic system, space group $\text{P2}_1/\text{n}$. Its unit cell parameters are $a = 9.10(1)$, $b = 12.422(3)$, $c = 13.53(5) \text{ \AA}$, $\beta = 99.32(2)^\circ$, $Z = 4$, $D_{\text{calc.}} = 1.14 \text{ g/cm}^3$. Unique reflections of 2908 were collected in the range of $2^\circ < \theta < 25^\circ$ using $w-2\theta$ scan mode, in which 623 reflections with $I > 3\sigma(I)$ were considered to be observed. The intensities of the reflections were reduced to the amplitudes of structure factors and LP correction and absorption correction were applied. The structure was solved by direct method (MULTAN 82). Most of non-hydrogen atoms were located from E-map. The remaining non-hydrogen atoms were found in the succeeding difference Fourier syntheses. The coordinates of hydrogen atoms were calculated. In the final structure refinement by the full matrix least-square method, the anisotropic thermal parameters and coordinates of non-hydrogen atoms and the isothermal parameters of hydrogen atom were refined. The final R factors are $R = 0.058$ and $\text{RW} = 0.064$. The maximum residual electron density peak on the final difference Fourier map is $0.28\text{e}/\text{\AA}^3$.

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