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THE PHOTOCHEMICAL REACTION OF 9-CYANOANTHRACENE WITH S-CISOID 2,3-DISUBSTITUTED BUTADIENES AND THE MOLECULAR STRUCTURES OF THEIR PHOTOCHEMICAL [4+4]ADDUCTS

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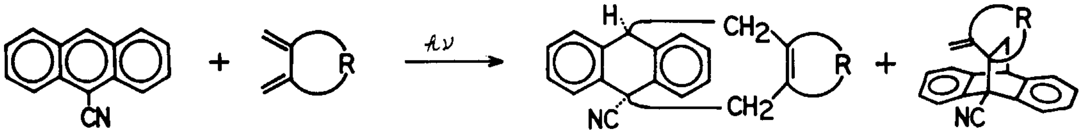
Abstract: The photochemical cycloaddition of 9-cyanoanthracene with s-cisoid 1,3-dienes (**2**–**4**) gave predominantly [4+4]cycloadducts (**5**,**6a** and **9a**). The conformational study of the adducts by the spectral and X-ray analysis confirmed that 4- or 5-membered ring condensed derivatives (**5** and **6a**) have symmetric C_{2v} type structure and those with 6-membered ring (**9a** and **10a**) are rapidly equilibrating between two equivalent folded structures.

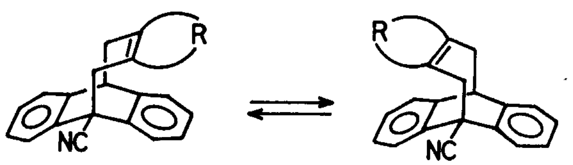
Although photochemical cycloaddition of anthracenes with various kinds of 1,3-dienes were extensively studied,1) little is known about the reactivity with s-cisoid 1,3-dienes without alkyl substituents at diene termini. We now report the first photochemical [4+4]cycloaddition of 9-cyanoanthracene (**1**) with such dienes (**2**–**4**)2) and the conformation of their [4+4]cycloadducts (**5**,**6**,**9** and **10**).



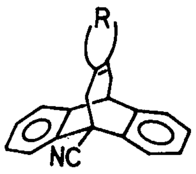
(**1**) (**2**) R=-$(CH_2)_2$- (**5**) (**7**)
(**3**) R=-$(CH_2)_3$- (**6a**) (**8**)
(**4**) R=-$CH_2CH{=}CHCH_2$- (**9a**)

Irradiation of a benzene solution of **1** and equimolar amount of the dienes (**2** and **3**) for 40-50 minutes gave the [4+4]adducts (**5** and **6a**)3) in 44 and 51% yields, respectively, along with the small amount of [4+2]adducts, **7** (9%) and **8** (10%).3) Although [4+2]cycloadduct could not be obtained in the photochemical reaction of **1** and 1,2-dimethylenecyclohex-4-ene (**4**) the yield of [4+4]cycloaddition product (**9a**) was almost the same (53%) to the above mentioned cases. Judging from the yields of these photochemical [4+4]adducts, the reactivity of these dienes are nearly equal to that of cyclic cisoid dienes.4)

In the ^1H NMR spectra of these photoadducts (**5**, **6a** and **9a**) and the tribenzo derivative (**10a**) prepared by DDQ oxidation of **9a**, the signal due to methylene protons vicinal to the cyano group appears as a sharp singlet, suggesting that their structures are either rapidly



(**A**) (**B**)



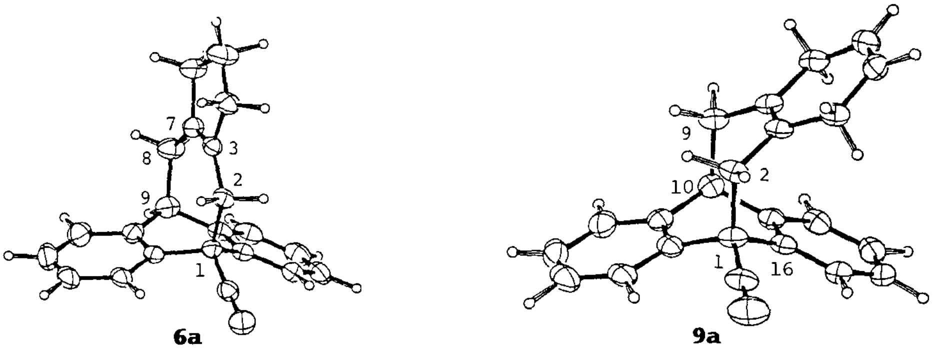
(**C**)

equilibrating between two equivalent folded structure5) (A ⇄ B) or a single symmetric C_{2v} type structure,6) in which the buteno bridge is almost perpendicular to 9,10-dihydroanthracene skeleton (C). Since it was difficult to distinguish the two possibilities only by the ^{1}H NMR spectrum,7) the X-ray analysis was then performed for **6a** and **9a**.

X-ray analysis The crystallographic data are given in Table 1 and the molecular geometries are presented in Fig. 1.8)

Table 1. Crystallographic data of **6a** and **9a**.

	6a	**9a**
Crystal system	Monoclinic	Monoclinic
M. F.	$C_{22}H_{19}N$	$C_{23}H_{19}N$
M. W.	297	309
Space group	$P2_1/n$	$P2_1/a$
a	18.076(5)Å	18.753(3)Å
b	16.037(4)	13.389(2)
c	11.237(2)	14.516(2)
β	101.61(2)°	111.62(1)°
Z	8	8
Reflections	4097	4373
R	0.053	0.076



6a **9a**

Fig. 1 ORTEP drawing of **6a** and **9a**.

As is clearly shown in the figure the cyclopentene condensed derivative (**6a**) has perpendicular structure and has remarkably wide sp^2 [137.3° (C2-C3=C7) and 135.9° (C3=C7-C8)] and sp^3 angles [122.1° (C1-C2-C3) and 120.5° (C7-C8-C9)].6) On the other hand, the cyclohexadiene condensed derivative (**9a**) has the folded structure in which the cyclohexadiene ring is almost planar and tilts at an angle of 57° from the C1-C2-C9-C10 plane. Bond angles of this molecule are rather normal even around the C=C double bond of the buteno bridge.

UV spectra To examine the conformation of these adducts in solution, the UV spectra were measured and given in Fig. 2 together with those of some reference compounds. The spectra of **5** and **6a** are very similar to each other, suggesting that they have the same conformation in solution. The lack of the transannular interaction between the p-orbitals of the buteno bridge and benzene rings in **5** and **6a** was confirmed by the fact that these

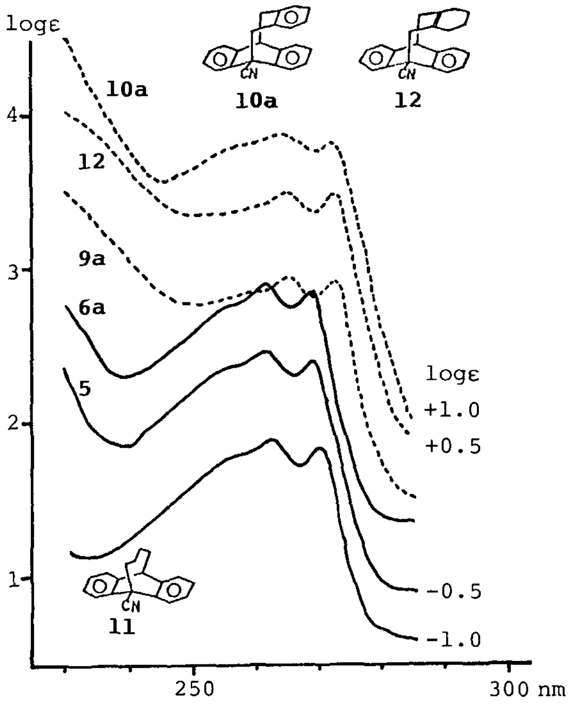
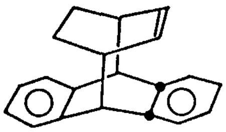


Fig. 2 UV spectra of the adducts in EtOH.

spectra are very similar to that of the butano bridged compounds (**11**), in which there is no double bond to interact with benzene rings. From this result, we can conclude that both **5** and **6a** have perpendicular conformation in solution.9)

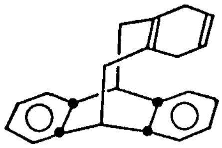
All the compounds which have six-membered carbocycles condensed onto the buteno bridge (**10a**, **9a**, and its dihydro derivative **12**), however, showed the small bathochromic shift (3-4 nm) of these bands. These spectral changes together with the disappearance of the valley around 240 nm observed in **5**, **6a**, and **11**, apparently suggested the presence of the sizable transannular interaction between the buteno bridge and the 9,10-dihydroanthracene, and hence the folded structure in every cases as in the crystals. These results were further confirmed by NMR spectra.

NMR spectra The ^{13}C NMR spectra of the decyano derivatives10) (**6b**, **9b**, and **10b**) are very informative. The quaternary carbon of the benzene ring in the rigid folded compound (**13**)4a) appeared at a low field (144.9 ppm) owing to the p-orbital compression effect11) by the double bonds of the buteno bridge, while that of **6b** having the perpendicular structure appeared at a normal position of 9,10-dihydroanthracene (140.7 ppm).



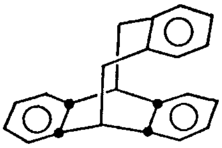
144.9 ppm

(**13**)



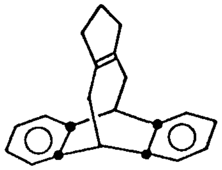
142.2

(**9b**)



142.8

(**10b**)



140.7

(**6b**)

In comparison with these values, the corresponding signals of **9b** and **10b** appeared around the midpoint (142.2 and 142.8 ppm, respectively). Since these compounds have folded structure even in solution, the quaternary benzene carbons should have an intermediate chemical shift between the normal and the sterically compressed values (∼141 ppm and ∼145 ppm, respectively), if the flipping of the buteno bridge occurs rapidly (A ⇄ B, *vide supra*). From the above mentioned chemical shift, the flipping of the buteno bridge is proven to be operative both in **9b** and **10b** at room temperature.

Variable temperature ^{1}H NMR spectra of **10a** were then examined in order to find the activation energy of this dynamic process, paying the attention to the two sharp signals due to methylene hydrogens of the buteno bridge. By lowering the temperature the signals gradually became broad and at -126°C they reached to a so-called coalescence state (Fig. 3). From these spectral changes, the activation energy of this conformational equilibrium was estimated to be 6.7±0.3 kcal/mol.12)

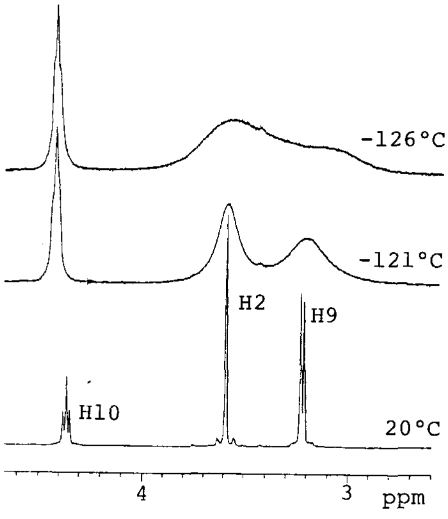


Fig.3 VT-NMR of **10a**.

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3) All new compounds gave satisfactory elemental analyses. Some of their physical properties are as follows (^{1}H NMR in CCl_4).
5: m.p. 181–183°C; δ 1.92(4H,bs), 2.68(2H,m), 3.03(2H,bs), 4.11(1H,t,J=4 Hz), 7.20–7.50 (6H,m), 7.70–7.90(2H,m).
6a: m.p. 205–207°C; δ 1.30–1.70(2H,m), 1.90–2.25(4H,m), 2.69(2H,m), 3.01(2H,bs), 4.09 (1H,t,J=4), 6.90–7.40(6H,m), 7.65–7.90(2H,m).
9a: m.p. 167–168°C; δ 2.30(4H,s), 2.45(2H,d,J=6.5), 2.80(2H,s), 4.10(1H,t,J=6.5), 5.26 (2H,s), 7.10–7.30(6H,m), 7.55–7.80(2H,m).
10a: m.p. 194–195°C; δ 3.20(2H,d,J=6.5), 3.58(2H,s), 4.31(1H,t,J=6.5), 6.65–6.90(4H,m), 7.00–7.30(6H,m), 7.55–7.80(2H,m).

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5) K. Sisido, Y. Udo and H. Nozaki, J. Org. Chem., **26**, 584 (1961); K. Sisido, R. Noyori, and H. Nozaki, J. Am. Chem. Soc., **84**, 3562 (1962); K. Sisido, R. Noyori, N. Kozaki, and H. Nozaki, Tetrahedron, **19**, 1185 (1963).

6) The similar C_{2v} conformation was reported in 2,2,5,5-tetramethyl-7,8,9,10-dibenzobicyclo-[4.2.2]deca-3,7,9-triene. [O. Ermer, Angew. Chem. Int. Ed. Engl., **16**, 658 (1977)].

7) D. M. Wieland and C. G. McCarty, J. Org. Chem., **37**, 4285 (1972).

8) All computations were carried out using the UNICS3 program system [T.Sakurai and K. Kobayashi, Rep. Inst. Phys. & Chem. Res., **55**, 69 (1979)]; Final crystallographic coordinates have been deposited in the Cambridge Crystallographic Data Center.

9) The reason for these peculiar perpendicular structures can be obtained by the molecular mechanics calculation. While the perpendicular structure have unfavorable widened bond angle (**6a**, calcd.;θ_{1-2-3}=122.3°, θ_{2-3-7}=135.5°) in the buteno bridge, the folded structures have eclipsing interaction in $C_{Ar}-C_1-C_2-C_3$ (**10b**, calcd.; $\phi_{16-1-2-3}$=8.0°). Since the external bond angle of the normal cyclobutene or cyclopentene is wider than the usual sp^2 angle, the destabilization energy for widening the angles in the perpendicular structure is well compensated by the stabilization due to the release from the unfavorable eclipsing interaction in the bridge.

10) The reductive decyanation was performed using potassium on alumina. [D. Savoia, E. Tagliavini, C. Trombini and A. U-Ronchi, J. Org. Chem., **45**, 3227 (1980)].

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12) Since the chemical shift difference between the two nonequivalent methylene hydrogens of the frozen structure could not be obtained, the value (31 Hz) found in the low temperature spectrum of the compound having a tropone ring condensed on the buteno bridge(13) was used.

13) Y. Fukazawa, T. Fujihara, T. Okajima, and S. Usui to be published.

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