Thermoreversible Photo Valence Isomerization of 9-t-Butylanthracene to its 9,10-Dewar-Isomer

H. Dreeskamp, B. Jahn, and J. Pabst

Lehrstuhl B für Physikalische Chemie der TU Braunschweig

On excitation the first excited singlet state (^1L_a), 9-t-butylanthracene (1) reacts in dilute ($10^{-6}-10^{-3}$ mole $\cdot$ l^{-1}) heptane solution with a quantum yield of $\Phi = 0.016 \pm 0.002$ to its valence isomer 1-t-butyl-dibenzo-2,5-bicyclo-(2,2,0)-hexadiene (9-t-butyl-9,10-Dewar-anthracene) (2). UV-spectroscopic and ^{1}H-NMR-data of educt and product confirm the proposed isomerization. The reaction is thermoreversible. The first order rate constant of the back reaction was determined in the temperature range of 293 K to 343 K and yielded the activation enthalpy $\Delta H^* = 91 \pm 3$ [kJ $\cdot$ mole^{-1}] and the activation entropie $\Delta S^* = -25 \pm 8$ [J $\cdot$ mole$^{-1} \cdot$ K^{-1}] in heptane and 94 ± 3 [kJ $\cdot$ mole^{-1}] and -17 ± 8 [J $\cdot$ mole$^{-1} \cdot$ K^{-1}] in ethanole.

Introduction

The reversible photochemical formation of the three valence isomers of benzene, i. e. Dewar-benzene, benzvalene and prismane is well known [1]. The tendency to form stable Dewar-products is greatly increased by substitution of t-butyl groups [2], thereby introducing severe strain into the aromatic system. In analogy to these results, tri- and tetra-t-butylnaphthalene react upon irradiation to their Dewar-isomers [3]. Dewar-isomers of substituted anthracenes have been obtained in three cases: for the highly strained deca-methylanthracene it is formed photochemically [4], in the case of 1,2,3,4-tetrachloro-9,10-Dewar-anthracene it was prepared by an elaborate synthetic route [5] and recently a report on the photochemical reaction of 9-t-butylanthracene has been given [6].

While investigating the fluorescence properties of meso-substituted anthracenes [7] we observed a remarkable photochemical desactivation pathway in the case of 9-t-butylanthracene (1) which led to a photoproduct (2) which at moderate temperatures decomposes and reforms the educt (1) [8]. In striking contrast to other meso-substituted anthracenes the fluorescence quantum yield φ_F of (1) is extremely low at 293 K ($\varphi_F = 0.013$ in heptane). Furthermore, Güsten et al. [9] were unable to detect any population of the triplet-state of (1) with a μsec-flash apparatus in contrast to other meso-substituted anthracenes.

Reprint requests to Prof. Dr. H. Dreeskamp, Lehrstuhl B für Physikalische Chemie der Technischen Universität Braunschweig, Hans-Sommer-Straße 10, D-3300 Braunschweig.

Experimental

A sample of (1) was prepared [10] and kindly given to us by Schoof and Güsten * in context with our previous work [7]. The solvents were distilled along a 50 cm column to UV-spectroscopic purity. They did not show any fluorescence up to 220 nm. UV- and fluorescence spectra were recorded in heptane and ethanole in 1 mm or 10 mm cuvettes at concentrations of 10^{-6} to 10^{-3} mole l^{-1} using a Perkin Elmer 550 UV-VIS-spectrophotometer and a MPF-44 fluorescence spectrophotometer. Irradiations were carried out using a 150 W high-pressure Xe-lamp and grating monochromator. Excitation wavelength was 360 nm with a half width of up to 20 nm. The photochemical quantum yield was determined relative to the ferrioxalate actinometer [11]. Fluorescence decay times were measured by the mono photon technique using a monochromator in the excitation path.

The thermal back reaction was investigated by observing the absorbance of the educt using thermostated sample holders. 250 MHz ^{1}H-NMR spectra of (1) and (2) in degassed d$_4$-methanole solutions were measured with the Bruker WM-250 spectrometer. The assignment of NMR-transitions of proton 1 was possible with the aid of a strong and selective Overhauser-effect between the t-butyl groups and proton 1 both in the educt and product. Spectra in which small long-range couplings in the order of $0-0.3$ Hz to the protons of the t-butyl group or in position 10 were removed by double resonance were analysed by the iterative program PANIC 80 as a 4 spin system.

* Drs. S. Schoof and H. Güsten, Karlsruhe.

Results and Discussion

Figure 1 shows the UV-absorption spectrum of (1) in heptane. Irradiation with light of 360 nm leads to a photoreaction as observed by the decrease of the ^1L_a- or ^1B_b-band. At the same time new bands appear assigned to the photoproduct (2) with isosbestic points at 288, 273, 224 and 210 nm. The fluorescence at excitation in the 280 nm region is also given in Figure 1. It closely desembles the well known spectrum of 1,2-dimethylbenzene. On prolonged irradiation a stationary state is reached and upon standing in the dark a nearly complete reformation of (1) to within 95% is observed. This cycle could be repeated many times. The rate of product formation was proportional to the light intensity in the region of $10^{-8} - 10^{-7}$ [Einstein·cm^{-2}·s^{-1}] while the thermal back reaction was first-order in product concentration. In each case both forward and back reaction analysed with extinction – difference – diagrams according to Mauser [12] proved to be uniform reactions. Neither changing the concentration of (1) between 10^{-3} and 10^{-6} [mole·l^{-1}] nor using aerated or oxygen-free samples resulted in a change of the photochemical or thermal back reaction. The photochemical quantum yield is $\varphi = 0.016 \pm 0.002$ in heptane at 293 K. In the hydrocarbon solvent 2,2-dimethylbutane/n-pentane (8 : 3) solidified to rigid glass at 77 K no photochemical degradation is observed. Under these conditions the fluorescence quantum yield approaches one as concluded from the observation that the

measured lifetime ($\tau_F = 14.9$ ns) is equal to the natural lifetime ($\tau_0 = 14.2$ ns) as computed from the oscillator strength of the ^1L_a-transition [10] and the fluorescence spectrum shows well resolved vibrational structure in contrast to the broad band observed at room temperature (see Figure 1). In the hydrocarbon solvent paraffin of much higher viscosity even at temperatures up to 220 K no photochemical degradation of (1) is observed while the fluorescence quantum yield approaches one and the fluorescence spectrum is well resolved. The first order rate constant of the thermal back reaction was determined in the temperature range of 293 K to 343 K. The Arrhenius activation energy E_a, the preexponential factor a, the reaction enthalpy ΔH^+ and reaction entropy ΔS^+ evaluated are given in Table 1 together with some relevant kinetic data on the rearomatization of Dewar-isomers from the literature. From the observations presented above it is concluded that 9-t-butylanthracene (1) is photochemically converted to its valence isomer 1-t-butyl-dibenzo-2,5-bicyclo-(2,2,0)-hexadiene (2) (9-t-butyl-9-10-Dewar-anthracene).
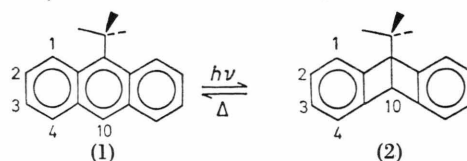
Since this reaction is not altered by excluding oxygen nor by reducing the concentration of (1) to below 10^{-5} mole·l^{-1} and since the product is of
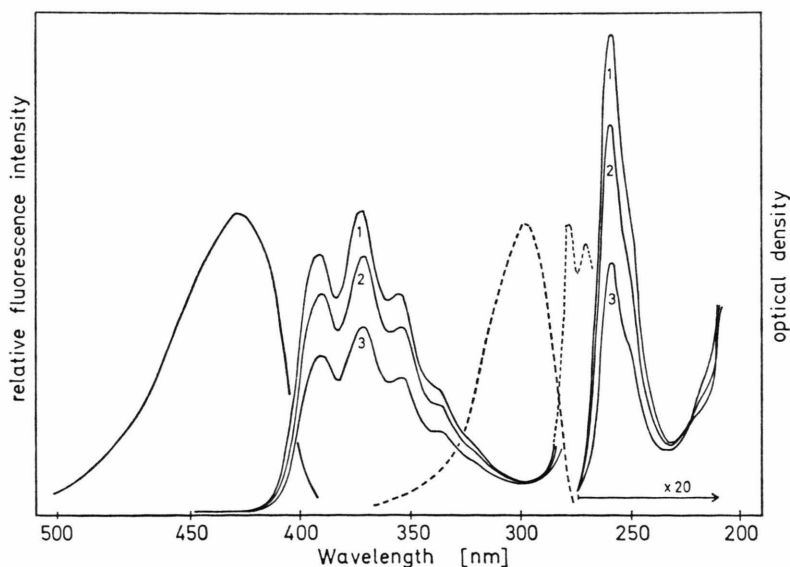
Fig. 1. Absorption and fluorescence spectra of 9-t-butylanthracene (———), the change of absorption upon irradiation at 360 nm (1—3) and the spectra of the photoproduct 9-t-butyl-9,10-Dewar-anthracene (————) in heptane at 293 K.

Table 1. Kinetic parameters of the thermal rearomatization of various Dewar-compounds. (a) This work.

Dewar compound	E_a [kJ · mole^{-1}]	$\log a$ [sec^{-1}]	$\Delta H^{\neq}$ [kJ · mole^{-1}]	$\Delta S^{\neq}$ [J · K^{-1} · mole^{-1}]	Solvent	Ref.
9-t-butyl-9,10-Dewar-anthracene	93.3 ± 2.9	11.9 ± 0.8	90.8 ± 2.9	− 25.1 ± 8.4	n-heptane	(a)
	96.2 ± 2.9	12.5 ± 0.8	93.7 ± 2.9	− 17.2 ± 8.4	ethanole	
1,2,3,4-tetrachloro-9,10-Dewar-anthracene	102.4 ± 3.5	14.0 ± 0.5	99.5 ± 3.4		hexane	[5]
hemi-Dewar-naphthaline	99.1 ± 2.6	12.3 ± 0.4	96.3 ± 2.5	− 18.4 ± 7.7	n-heptane	[13]
1,3,7,9-tetra-t-butyl-Dewar-naphthaline	100.4 ± 4.2	11.3 ± 0.8			cyclohexane/hexane	[3]
Dewar-benzene			96.2 ± 8.4	− 20.9 ± 14.6	tetrachloro-ethylene	[14]

	$\delta(C(CH_3)_3)$	$\delta(1)$	$\delta(2)$	$\delta(3)$	$\delta(4)$	$\delta(10)$
1	1.92	8.58	7.35	7.37	7.96	8.28
2	1.16	7.27	7.13	7.12	7.18	4.83
	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
1	+ 9.08	+ 1.04	+ 0.78	+ 6.46	+ 1.48	+ 8.48
2	+ 7.35	+ 0.94	+ 1.09	+ 7.75	+ 0.96	+ 7.30

Table 2. NMR-parameters of 10^{-2} [mole · l^{-1}] 9-t-butylanthracene (**1**) and 9-t-butyl-9,10-Dewar-anthracene (**2**) in d$_4$-methanole. Chemical shifts relative to $\delta(CHD_2OD) = 3.33$. Chemical shifts ± 0.005, coupling constants ± 0.03 Hz.

equal solubility in methanole down to 220 K as the educt a conceivable 9,10-photooxidation or 9,10-dimerisation is excluded. Furthermore, since the reaction is thermoreversible it may be postulated to be a monomolecular valence isomerization without a drastic alteration in the carbon sceleton. This is supported by the UV-absorption and fluorescence spectra which clearly show that the extensive conjugation of the anthracene is reduced to that of a benzene ring. The final proof is taken from the ^{1}H-NMR-data as given in Table 2: The central symmetry plane is retained in (**2**), the large down-field shift of the aromatic protons 1, 4, 5 and 8 due to the large ring current in (**1**) is reduced to values of a substituted benzene in (**2**). Finally proton 10 is shifted from $\delta = 8.28$ in (**1**) to $\delta = 4.83$ in (**2**). Taking into account the effect on the chemical shift by the two ring currents δ in (**2**) is in excellent agreement with the values of the chemical shift of the methine protons in Dewar-benzene $(\delta = 3.2)$ [2] and hemi-Dewar-naphthalene $(\delta = 3.97)$, [3]. The much smaller variation in the three vicinal coupling constants $(J_{1,2}, J_{2,3}, J_{3,4})$ in (**2**) compared to (**1**) confirm the ortho-di-substituted benzene sub-unit in (**2**).

As shown in Table 1 the activation parameters for the rearomatization reaction $(2) \to (1)$ compare very well with thermal valence isomerization reactions of Dewar-isomers. In particular it appears from these data that the activation entropy $\Delta S^{\neq}$ is hardly affected in going from Dewar-benzene to Dewar-anthracene nor by introducing bulky t-butyl groups.

The strong viscosity dependence of the fluorescence properties and valence isomerization of 9-t-butylanthracene appear to be related: Since the high quantum yield of fluorescence and strong vibrational structure of the fluorescence spectrum in rigid solvents is lost in fluid solutions the equilibrium geometries of the ground and first excited singlet state in (**1**) will be different. Conceivably this is caused by a steric interaction between the bulky t-butyl group and the anthracene sceleton. In the case of 9-isopropylanthracene a rotational barrier of $\Delta G^{\neq} = 56.9$ [kJ · mole^{-1}] has been obtained by ^{13}C-NMR [15].

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