

## Features of the Diels–Alder Reaction between 9,10-Diphenylanthracene and 4-Phenyl-1,2,4-triazoline-3,5-dione

V. D. Kiselev<sup>a</sup>, D. A. Kornilov<sup>a</sup>, E. A. Kashaeva<sup>a</sup>, L. N. Potapova<sup>a</sup>,  
D. B. Krivolapov<sup>b</sup>, I. A. Litvinov<sup>b</sup>, and A. I. Konovalov<sup>b</sup>

<sup>a</sup> Butlerov Institute of Chemistry, Kazan Federal University, 420008 Russia

<sup>b</sup> Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, 420088 Russia

e-mail: vkiselev.ksu@gmail.com

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**Abstract**—The Diels–Alder reaction between substituted anthracenes **1a–1j** and 4-phenyl-1,2,4-triazoline-3,5 (**2**) is studied. In all cases except one, the reaction proceeds on the most active 9,10-atoms of substituted anthracenes. The orthogonality of the two phenyl groups at the 9,10-position of diene **1a** is found to shield 9,10-reactive centers. No dienophiles with C=C bonds are shown to participate in the Diels–Alder reaction with **1a**; however, the reaction **1a** + **2** proceeds with the very active dienophile 2,4-phenyl-1,2,4-triazoline-3,5-dione. It is shown that attachment occurs on the less active but sterically accessible 1,4-reactive center of diene **1a**. The structure of adduct **3a** is proved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and X-ray diffraction analysis. The following parameters are obtained for reaction **1a** + **2** ⇌ **3a** in toluene at 25°C:  $K_{\text{eq}} = 2120 \text{ M}^{-1}$ ,  $\Delta H_{\text{f}}^{\ddagger} = 58.6 \text{ kJ/mol}$ ,  $\Delta S_{\text{f}}^{\ddagger} = -97 \text{ J/(mol K)}$ ,  $\Delta V_{\text{f}}^{\ddagger} = -17.2 \text{ cm}^3/\text{mol}$ ,  $\Delta H_{\text{b}}^{\ddagger} = 108.8 \text{ kJ/mol}$ ,  $\Delta S_{\text{b}}^{\ddagger} = 7.3 \text{ J/(mol K)}$ ,  $\Delta V_{\text{b}}^{\ddagger} = -0.8 \text{ cm}^3/\text{mol}$ ,  $\Delta H_{\text{r-n}} = -50.2 \text{ kJ/mol}$ ,  $\Delta S_{\text{r-n}} = -104.3 \text{ J/(mol K)}$ ,  $\Delta V_{\text{r-n}} = -15.6 \text{ cm}^3/\text{mol}$ . It is concluded that the values of equilibrium constants of the reactions **1a–1j** + **2** ⇌ **3a–3j** vary within  $4 \times 10^1$ – $10^{11} \text{ M}^{-1}$ .

**Keywords:** 9,10-diphenylanthracene, 4-phenyl-1,2,4-triazoline-3,5-dione, Diels–Alder reaction, regioselectivity, high pressure

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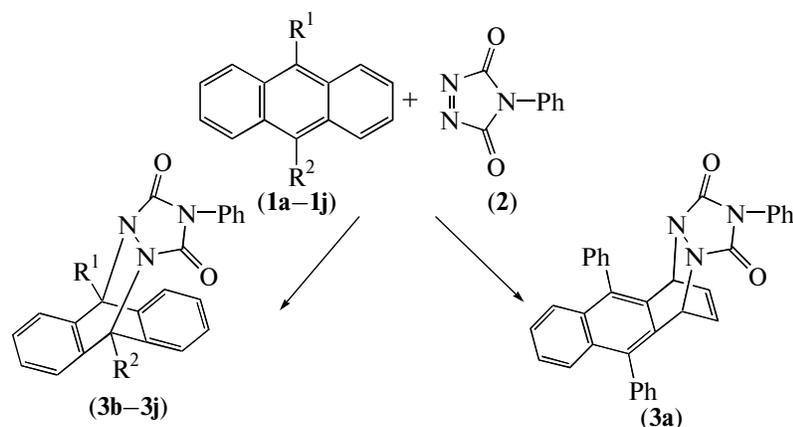
### INTRODUCTION

All dienophiles attach themselves to 9,10-reactive centers of substituted anthracenes in the Diels–Alder reaction. The overlapping of the 1,8-hydrogen atoms of anthracene fragments and 2,6-hydrogen atoms of the phenyl group of 9-phenylanthracene **1d** results in a dihedral angle of  $\sim 60^\circ$  [1]. This creates strong shielding for the C-9 of diene **1d**. Nevertheless, the reaction with 9-phenylanthracene proceeds at the 9,10-reactive position, although it is slower than for molecules without such steric hindrances [2, 3]. The Diels–Alder reaction between substituted anthracenes **1a–1j** and 4-phenyl-1,2,4-triazoline-3,5-dione **2** is shown in Scheme 1.

An almost orthogonal positioning of the planes of both phenyl groups to anthracenes plane is observed for 9,10-diphenylanthracene **1a** [4]. This prevents a dienophile from approaching the most active 9,10-reactive center of diene **1a**. The relative activity of 9,10- and 1,4-reactive centers of anthracenes,  $k_{(9,10)}/k_{(1,4)}$ , can be estimated when there are no steric hindrances in the Diels–Alder reaction [3]. The difference between the hydrogenation energy of the 1,4-

and 9,10-atoms of anthracenes is  $65 \pm 8 \text{ kJ/mol}$  [5–7]. This allows us to estimate the ratio of reaction rate constants on the 9,10- and 1,4-reactive centers of anthracenes:  $k_{(9,10)}/k_{(1,4)} = 3200$ . Theoretical calculations for the activity of different cycles of anthracenes in the Diels–Alder reaction yield a similar ratio:  $k_{(9,10)}/k_{(1,4)} = 3500$  [8]. The Diels–Alder reaction of dienophile **2** with substituted anthracenes **1b–1j** proceed at the sterically accessible and more active 9,10-position of these dienes to produce **3b–3j** [9–13]. The <sup>1</sup>H and <sup>13</sup>C NMR spectra (see below) are in accordance with the structure of adducts **3b–3j**. The Diels–Alder reaction of diene **1a** does not proceed for any known dienophile with C=C bonds under normal conditions.

There are a number of works dedicated to studying the behavior of 4-substituted 1,2,4-triazoline-3,5-diones in thermal and photochemical reactions [4+2]-, [3+2]-, [2+2]-cycloaddition and enone synthesis [9–21]. Studies were conducted earlier on adduct structure, reaction rate, and effect of the solvent on the [4+2]-cycloaddition of **2** to various 1,3-dienes [9–13]. 4-Phenyl-1,2,4-triazoline-3,5-dione **2**



<b>1, 3</b>	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>e</b>	<b>f</b>	<b>g</b>	<b>h</b>	<b>i</b>	<b>j</b>
R <sup>1</sup>	Ph	H	H	H	H	Me	Cl	OMe	H	H
R <sup>2</sup>	Ph	H	Cl	Ph	Me	Me	Cl	OMe	NO <sub>2</sub>	CN

Scheme 1.

have high activity in all reactions leading to attachment along N=N bonds. The lower energy of N=N bonds (418) relative to C=C bonds (611 kJ/bond) is assumed to be the main reason for the lower activation energy in all reactions along N=N bonds.

It has been shown that the reactivity of dienophile **2** is sufficiently high even at room temperature at the uncommon 1,4-reactive center in reaction **1a** + **2** → **3a** ( $k_2 = 2.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ; toluene, 25°C). The rate constants and enthalpies for the Diels–Alder reaction of 4-phenyl-1,2,4-triazoline-3,5-dione, tetracyanoethylene, and maleic anhydride with 15 cyclic and acyclic dienes were compared in [13]. It follows from these data that the activity of 4-phenyl-1,2,4-triazoline-3,5-dione in the Diels–Alder reaction is 5–6 orders of magnitude higher than that of maleic anhydride. We are now finally able to study and compare the parameters of the Diels–Alder reaction on the 9-, 10-, and 1,4-atoms of diene **1a–1j**. In this work, we studied the effect of temperature and pressure on the rate and equilibrium of the Diels–Alder reactions of 4-phenyl-1,2,4-triazoline-3,5-dione **2** with series **1a–1j** of substituted anthracenes.

## EXPERIMENTAL

All of the substituted anthracenes (Sigma Aldrich) with ≥99% purity (except for **1i** and **1j**) were used without prior purification. Dienes **1i**, **1j** (97%) were purified via column chromatography on silica gel. The eluent was benzene : hexane (1 : 2). The optical purity of the dienes was measured in the range of 390–405 nm after reacting with purified maleic anhydride of known concentration. Dienophile **2** (Aldrich, 97%) was sub-

limated prior to measurements at 100°C and a pressure of 100 Pa.  $T_m$  was 170°C (dec). The absorption of a solution of **2** in toluene did not change over long periods of time either in the closed system at room temperature or in the dark. The purity of **2** was verified via spectrophotometric titration of its solution with known concentrations of diene **1f**, which reacts rapidly with **2** ( $k_2 = 12200 \text{ M}^{-1} \text{ s}^{-1}$ ), and quantitatively ( $K_{eq} > 10^6 \text{ M}^{-1}$ ,  $\Delta H_{r-n} = -117.8 \text{ kJ/mol}$ ) at 25°C [13]. All solvents were purified and dried according to the standard procedures in [22].

Adduct **3a**, 3,10,15-triphenyl-13,15,17-triazapentacyclo-[10.5.2.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]-nonadeca-2,4(9),5,7,10,18-hexaene-14,16-dione (**3a**) decomposes at 210–220°C. Elemental analysis, %: C, 80.42, 80.52; H, 4.49, 4.43; N, 7.90, 7.84. Calc., C<sub>34</sub>H<sub>23</sub>O<sub>2</sub>N<sub>3</sub>: C, 80.78; H, 4.59; N, 8.31%. NMR <sup>1</sup>H (400 MHz), CDCl<sub>3</sub>, 25 °C,  $\delta_H$ , ppm: 5.92 (t,  $J = 3.5 \text{ Hz}$ , C<sub>(1)</sub>H, C<sub>(12)</sub>H), 6.87 (t,  $J = 3.5 \text{ Hz}$ , C<sub>(18)</sub>H, C<sub>(19)</sub>H), 7.3–8.0 (aromatics, 19H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>, 25°C) 54.73 (C<sub>(1)</sub>, C<sub>(12)</sub>), 125.26 (C<sub>(18)</sub>, C<sub>(19)</sub>), 126.73–136.11 (aromatics), 155.61 (C=O) (the numbering of atoms is similar to that in Fig. 1).

For adduct **3d**,  $\delta_H$ : 6.46 (s, C<sub>(9)</sub>H, methine group), 7.0–8.0 (m, aromatics, 18H);  $\delta_C$ : 62.70 (C<sub>(9)</sub>, methine group), 72.74 (C<sub>(10)</sub>, tert), 123.93–139.25 (aromatics), 156.61 (C=O), 157.38 (C=O) (the carbon numbering is similar to that of diene **1d**).

For adduct **3f**,  $\delta_H$ : 2.75 (s, methyl, 6H), 7.2–7.6 (m, aromatics, 13H);  $\delta_C$ : 14.74 (methyl), 63.29 (C<sub>(9)</sub>, C<sub>(10)</sub>), 121.20–140.34 (aromatics), 152.15 (C=O) (carbon numbering is similar to that of diene **1f**).

Adducts **3b**, **3f**, **3h** were synthesized in [12]. The  $^1\text{H}$  NMR spectra of **3a**, **3b**, **3e**, **3f**, and **3g** in  $\text{CDCl}_3$  in the presence of **1a**, **1b**, **1e**, **1f**, and **1g** are given in [23].

HITACHI U-2900 and UNICO-2800 spectrophotometers were used for kinetic measurements at atmospheric pressure. The rate of direct reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$  was studied quantitatively from the disappearance of the  $n \rightarrow \pi^*$  band of the absorption of dienophile **2** in toluene ( $\lambda_{\text{max}} = 540 \text{ nm}$ ,  $\varepsilon_{2, \text{max}} = 245 \text{ M}^{-1} \text{ cm}^{-1}$ ). For slow and equilibrium reactions  $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$ ,  $\mathbf{1g} + \mathbf{2} \rightarrow \mathbf{3g}$ ,  $\mathbf{1i} + \mathbf{2} \rightarrow \mathbf{3i}$ , and  $\mathbf{1j} + \mathbf{2} \rightarrow \mathbf{3j}$ , the initial concentrations of dienes were 15–40 times higher than that of dienophile **2** [ $(4\text{--}5) \times 10^{-3} \text{ M}$ ]. The rate of retro reaction  $\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2}$  was studied under conditions preventing equilibrium. **3a** was decomposed in the presence of *trans,trans*-1,4-diphenylbutadiene-1,3, which rapidly ( $k_2 = 6.2 \text{ M}^{-1} \text{ s}^{-1}$ ,  $30^\circ\text{C}$ ) and irreversibly ( $\Delta H_{\text{r-n}} = -142 \text{ kJ/mol}$ ) reacted with dienophile **2** forming during the decomposition of **3a** (toluene,  $25\text{--}50^\circ\text{C}$ ). The initial concentration of **3a** was  $(4\text{--}5) \times 10^{-4} \text{ M}$ ; that of 1,4-diphenylbutadiene-1,3 was  $(1\text{--}2) \times 10^{-3} \text{ M}$ . It was shown that increasing the concentration of 1,4-diphenylbutadiene-1,3 does not affect the rate of **3a** decomposition. The reaction rate was measured for the increased absorption of diene **1a** ( $D_{\text{t,1a}}$ ) at 395 nm. Observance of the Beer law had already been verified. Absorption coefficient  $\varepsilon_{\mathbf{1a}}$  in toluene at 395 nm was  $14600 \text{ M}^{-1} \text{ s}^{-1}$ . Rate coefficient  $k_1$  of the decomposition of **3a** was calculated as

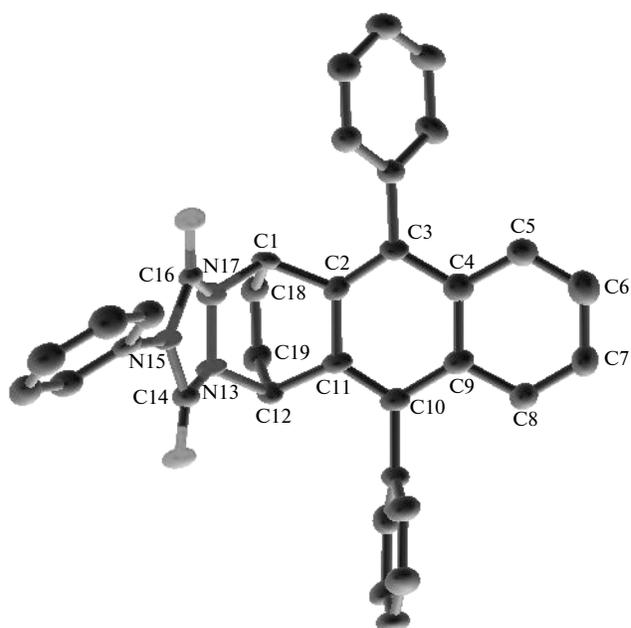
$$k_1 t = \ln[C_{0,3a}/C_{\text{t},3a}] = \ln[D_{\text{max},1a}/(D_{\text{max},1a} - D_{\text{t},1a})], \quad (1)$$

where  $D_{\text{max},1a}$  is optical density of absorption of diene **1a** after the full decomposition of **3a**;  $D_{\text{max},1a} = C_{0,3a} \varepsilon_{\mathbf{1a}}$ ; and  $D_{\text{t},1a}$  is the current absorption of diene **1a**. The reaction rate of  $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$  at high pressure was followed by changes in the optical density of dienophile **2** at 540–550 nm, where other reagents were transparent. The details of operating high pressure equipment were described in [24]. The  $C_{0,1a}/C_{0,2}$  ratio was  $\sim 10\text{--}15$ , where the initial concentration  $C_{0,2}$  was  $\sim 0.007 \text{ M}$ . The rate of  $\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2}$  decomposition at high pressure at  $45^\circ\text{C}$  in the presence 1,4-diphenylbutadiene-1,3 was measured from increasing optical density  $D_{\text{t,1a}}$  of diene **1a** at a wavelength of 395 nm over time. The bathochromic shift of the absorption band of diene **1a** occurred at a higher pressure, so the pressure dependence of the extinction coefficient of **1a** was studied to calculate the rate constant.

The apparent volume of activation  $\Delta V^\ddagger$  was calculated using the dependence of  $\ln k_p$  on  $p$ , where  $k_p$  is the reaction rate constant at pressure  $p$ . The reaction volume is normally determined from the differences between the partial molar volumes of the adducts and reagents with an error of  $\pm 1\text{--}2 \text{ cm}^3/\text{mol}$ . We used a more precise method for determining  $\Delta V_{\text{r-n}}$  [25]:

$$1/d_t = 1/d_{t=0} + C_{\text{t},3a} \Delta V_{\text{r-n}} / (1000 d_{t=0}), \quad (2)$$

where  $d_{t=0}$  and  $d_t$  are the initial and current densities of the reaction mixture;  $C_{\text{t},3a}$  is the current concentra-



**Fig. 1.** X-ray structure of (3,10,15-triphenyl-13,15,17-triazapantacyclo-[10.5.2.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]-nonadeca-2,4(9),5,7,10,18-hexaene-14,16-dione) **3a**.

tion of **3**; and  $\Delta V_{\text{r-n}}$  is the reaction volume. A DSA 5000 M vibration densitometer was used to measure the density at  $25 \pm 0.002^\circ\text{C}$ .

The X-ray data of crystal **3a** were obtained on a Bruker Smart Apex II CCD diffractometer at  $20^\circ\text{C}$  using  $\text{MoK}_\alpha$  radiation ( $0.71073 \text{ \AA}$ ) with graphite monochromator. Crystals of **3a**,  $\text{C}_{34}\text{H}_{23}\text{O}_2\text{N}_3$ , are monoclinic:  $a = 11.139(5) \text{ \AA}$ ,  $b = 22.304(8) \text{ \AA}$ ,  $c = 11.564(4) \text{ \AA}$ ,  $\beta = 119.93^\circ(3)$ ;  $V = 2489.9(17) \text{ \AA}^3$ ;  $Z = 4$ ;  $d_{\text{cryst}} = 1.349 \text{ g/cm}^3$ ; space group,  $P21/c$ . The parameters of a cell and the intensity of 5989 independent reflections, 2442 of which had  $I \geq 2\sigma$ , were measured in the  $\omega$  scanning regime of  $\theta \leq 28.00^\circ$  ( $R_{\text{int}} = 0.1720$ ). No adjustment was made for absorption ( $\mu_{\text{Mo}} = 0.85 \text{ cm}^{-1}$ ). Structures were resolved directly and refined with the full matrix of least squares using SHELX [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms are considered to be rigid atoms. The final differences were  $R_{\text{ob}} = 0.0869$  and  $R_{\text{wob}} = 0.1789$ . The images were indexed, integrated, and scaled using the APEX2 package for treating data [27]. All of the figures were produced with the ORTEP program [28]. The main geometric parameters were  $\text{C}_1\text{--C}_2$ ,  $1.521 \text{ \AA}$ ;  $\text{C}_2\text{--C}_3$ ,  $1.382 \text{ \AA}$ ;  $\text{C}_3\text{--C}_4$ ,  $1.445 \text{ \AA}$ ;  $\text{C}_4\text{--C}_5$ ,  $1.419 \text{ \AA}$ ;  $\text{C}_5\text{--C}_6$ ,  $1.365 \text{ \AA}$ ;  $\text{C}_6\text{--C}_7$ ,  $1.398 \text{ \AA}$ ;  $\text{C}_7\text{--C}_8$ ,  $1.354 \text{ \AA}$ ;  $\text{C}_8\text{--C}_9$ ,  $1.418 \text{ \AA}$ ;  $\text{C}_9\text{--C}_{10}$ ,  $1.440 \text{ \AA}$ ;  $\text{C}_{10}\text{--C}_{11}$ ,  $1.371 \text{ \AA}$ ;  $\text{C}_{11}\text{--C}_{12}$ ,  $1.515 \text{ \AA}$ ;  $\text{C}_{12}\text{--N}_{13}$ ,  $1.485 \text{ \AA}$ ;  $\text{N}_{13}\text{--C}_{14}$ ,  $1.367 \text{ \AA}$ ;  $\text{C}_{14}\text{--O}_{14}$ ,  $1.217 \text{ \AA}$ ;  $\text{C}_{14}\text{--N}_{15}$ ,  $1.398 \text{ \AA}$ ;  $\text{N}_{15}\text{--C}_{16}$ ,  $1.401 \text{ \AA}$ ;  $\text{C}_{16}\text{--O}_{16}$ ,  $1.219 \text{ \AA}$ ;  $\text{C}_{16}\text{--N}_{17}$ ,  $1.357 \text{ \AA}$ ;  $\text{N}_{17}\text{--C}_1$ ,  $1.480 \text{ \AA}$ ;  $\text{C}_1\text{--C}_{18}$ ,  $1.517 \text{ \AA}$ ;  $\text{C}_{18}\text{--C}_{19}$ ,  $1.320 \text{ \AA}$ ;  $\text{C}_{12}\text{--C}_{19}$ ,  $1.520 \text{ \AA}$ ;  $\text{C}_2\text{C}_1\text{C}_{18}$ ,  $106.16^\circ$ ;

$N_{17}C_1C_{18}$ , 104.98°;  $C_1N_{17}C_{16}$ , 128.37°;  $C_{11}C_{12}C_{19}$ , 107.00°;  $N_{13}C_{12}C_{19}$ , 103.84°;  $C_{12}N_{13}C_{14}$ , 127.67°.

## RESULTS AND DISCUSSIONS

The reaction rate constant for **2** and 9,10-diphenylanthracene **1a** + **2** → **3a** in toluene at 25°C ( $2.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ; Table 1) was considerably lower than the ones for the reactions of **2** and 9,10-diphenylanthracene **1f** (12200), 9-methylanthracene **1e** (84.0), anthracenes **1b** (0.33), and 9-phenylanthracene ( $0.40 \text{ M}^{-1} \text{ s}^{-1}$ ) [13]. The ratio of the rate constants ( $12200/2.7 \times 10^{-3}$ ) was  $4.5 \times 10^6$  at equal ionization potentials of 9,10-dimethylanthracene **1f** (7.11 eV) and 9,10-diphenylanthracene **1a** (7.10 eV) [29]. This indicates that the phenyl substituents in **1a** can partially shield even 1,4-reactive centers. As was shown above, reducing the activity due to steric hindrances by more than a factor of 3200–3500 should change the regioselectivity of reaction **1a** + **2** → **3a**. A similar comparison allows us to predict 1,4-additions during the reaction of 9,10-diphenylanthracene and maleic anhydride, and to estimate the constant of this reaction rate at 25°C with  $10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ , making it impossible to study at room temperature.

The NMR spectrum of adduct **3a** (see above) differs considerably from the spectra of **3d** and **3f**. The presence of protons on the saturated tertial carbon atoms and in the ethylene fragment corresponds to the formation of 1,4-adduct **3a**. These signals are missing from the reactions with the accessible 9,10-reactive centers; e.g., **1f** + **2** → **3f**. X-ray diffraction analysis of crystal **3a** corresponds to the formation of an *exo*-conformation of adduct **3a** (Fig. 1).

The kinetic data for direct reaction **1a** + **2** → **3a** and retro reaction **3a** → **1a** + **2** allow us to calculate equilibrium constants ( $K_{\text{eq}}$ ), enthalpies ( $\Delta H^\ddagger$ ), entropies ( $\Delta S^\ddagger$ ) of activation and reaction ( $\Delta H_{\text{r-n}}$ ,  $\Delta S_{\text{r-n}}$ ).

Electron-acceptor substituents dramatically reduce the activity of dienes **1g**, **1i**, **1j** and the stability of their adducts (Table 1).

As was shown in [25], the adjusted value of activation volume  $\Delta V_{\text{corr}}^\ddagger$  requires that we consider the correction for solution compression,

$$\Delta V_{\text{corr}}^\ddagger = -RT \partial \ln(k_p) / \partial P + (n-1)RT\beta_T, \quad (3)$$

where  $k_p$  is the rate constant under pressure, calculated without adjusting for concentration ( $m$ ,  $c$ ,  $x$ ) under pressure  $p$ ,  $(n-1)RT\beta_T$  is a correction for compressibility, where  $n$  is the order of the reaction and  $\beta_T = \partial \ln(d) / \partial p$  is the coefficient of solvent compressibility. Data on the effect pressure has on the rate constants of direct reaction **1a** + **2** → **3a** and retro reaction **3a** → **1a** + **2** are presented in Table 2 and in Fig. 2.

The pressure dependence of the reaction rate (Fig. 2) is described by second order polynomial and logarithmic equations

$$\begin{aligned} \ln(k_{2,p}/k_{2,p=1}) &= -0.0040 \\ &= 7.84 \times 10^{-4} p - 9.10 \times 10^{-8} p^2, \quad R = 0.9990, \end{aligned} \quad (4)$$

$$\begin{aligned} \ln(k_p/k_{p=1}) & \\ &= 2.070 \ln[(2540 + p)/2540]; \quad R = 0.9980. \end{aligned} \quad (5)$$

According to (4), the experimental value of activation volume  $\Delta V_{\text{app}}^\ddagger$  is  $-19.4 \pm 1.2 \text{ cm}^3/\text{mol}$ . The adjusted value of  $\Delta V_{\text{corr}}^\ddagger$  was calculated using Eq. (3) and toluene compressibility coefficient  $\beta_T = 90 \times 10^{-6} \text{ bar}^{-1}$  [30]:  $-17.2 \pm 1.2 \text{ cm}^3/\text{mol}$ . From Eq. (5), we find that  $\Delta V_{\text{app}}^\ddagger$  and  $\Delta V_{\text{corr}}^\ddagger$  are  $-20.1 \pm 1.2$  and  $-17.9 \pm 1.2 \text{ cm}^3/\text{mol}$ , respectively. Ratio (4) has better correlation coefficient than (5). Nevertheless, Eq. (4), in contrast to (5), assumes there is a false peak at  $p = 4300 \text{ bar}$ , so reaction rate [ $\ln(k_p/k_{p=1})$ ] at higher pressures cannot be predicted. It should be noted that the difference between the two values of  $\Delta V^\ddagger$  at  $p = 1$  lies within the experimental error. Equation (5) can be used to determine the activation volume at any pressure, and to predict the reaction rate under pressure. The effect pressure has on the rate of decomposition **3a** → **1a** + **2** is minimal (Table 2, Fig. 2):

$$\begin{aligned} \ln(k_{1,p}/k_{1,p=1}) & \\ &= 0.00046 + 3.1 \times 10^{-5} p - 2.80 \times 10^{-8} p^2, \end{aligned} \quad (6)$$

where correction member  $(n-1)RT\beta_T$  is equal to 0 ( $n = 1$ ), so  $\Delta V_{\text{exp}}^\ddagger = \Delta V_{\text{corr}}^\ddagger = -0.8 \pm 0.8 \text{ cm}^3/\text{mol}$ . The difference between activation volumes  $\{\Delta V_{\text{corr}}^\ddagger(\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}) - \Delta V_{\text{corr}}^\ddagger(\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2})\} = -16.4 \pm 2.0 \text{ cm}^3/\text{mol}$  should be equal to the value of reaction volume  $\Delta V_{\text{r-n}}$ . This value ( $-15.6 \pm 0.3 \text{ cm}^3/\text{mol}$ , Fig. 3) is also determined ((2), Fig. 3) from three independent measurements and agrees with the difference between the activation volumes ( $-16.4 \pm 2.0 \text{ cm}^3/\text{mol}$ ) of the direct (**1a** + **2** → **3a**) and retro (**3a** → **1a** + **2**) processes.

Ratio  $\Delta V_{\text{corr}}^\ddagger / \Delta V_{\text{r-n}}$  is  $1.10 \pm 0.10$ . The resulting values for the enthalpy, entropy, and activation and reaction volumes of **1a** + **2** → **3a** with 1,4-atoms of diene were compared to the parameters of several reactions with 9,10-atoms of substituted anthracenes **1f** and **1d** and maleic anhydride (Table 3). The close values of the entropy and activation and reaction volumes of both the 1,4- and 9,10-atoms of anthracenes are remarkable.

Special attention was given to determining the equilibrium parameters, due to the dramatic differences between the data obtained via UV monitoring of the absorption of **2** in the reaction mixture (Table 1)

**Table 1.** Rate constants ( $k_2$ ,  $M^{-1} s^{-1}$ ), enthalpies ( $\Delta H^\ddagger$ , kJ/mol), entropy ( $\Delta S^\ddagger$ , kJ/mol/K) of activation, equilibrium constants ( $K_{eq}$ ,  $M^{-1}$ ), enthalpies ( $\Delta H_{r-n}$ , kJ/mol), and volumes ( $\Delta V_{r-n}$ ,  $cm^3/mol$ ) for the Diels–Alder reactions of substituted anthracenes **1a–1j** with dienophile **2** in toluene

$k_2$	$K_{eq}$	$\Delta H$	$\Delta S$	$\Delta V_{r-n}$	$\Delta H_{r-n}$
<b>1a + 2 → 3a</b>					
0.00110 (15°C)	2120 (25°C)	58.6	–97	–15.9 <sup>b</sup>	–50.2 <sup>d</sup>
0.00272 (25°C)	[57 (25°C)] <sup>a</sup>			–15.5 <sup>b</sup>	[–16.7] <sup>a</sup>
0.00276 (25°C)	1410 (30°C)			–14.9 <sup>c</sup>	
0.00573 (35°C)	1120 (35°C)			–15.2 <sup>c</sup>	
0.0125 (45°C)	776 (40°C)			–15.4	
	534 (45°C)				
	443 (50°C)				
<b>3a → 1a + 2</b>					
$1.29 \times 10^{-6}$ (25°C)		108.8	7.3	15.4	50.2
$2.81 \times 10^{-6}$ (30°C)					
$5.12 \times 10^{-6}$ (35°C)					
$1.11 \times 10^{-5}$ (40°C)					
$2.34 \times 10^{-5}$ (45°C)					
$4.02 \times 10^{-5}$ (50°C)					
<b>1b + 2 → 3b</b>					
0.33 (25°C) <sup>e</sup>	$10^6$ – $10^9$ (25°C)	–	–	–	–96.7 <sup>e</sup>
	[328 (25°C)] <sup>a</sup>				[–44.0] <sup>a</sup>
<b>1c + 2 → 3c</b>					
0.0645 (15°C)	$1.5 \times 10^5$ (25°C)	47.3	–99.6	–18.5 <sup>c</sup>	–83.1 <sup>d</sup>
0.130 (25°C)	51800 (35°C)			–19.0 <sup>b</sup>	
0.185 (30°C)	11200 (50°C)			–18.6 <sup>b</sup>	
	4160 (60°C)			–18.7	
<b>1d + 2 → 3d</b>					
0.218 (15°C)	$6.3 \times 10^4$ (25°C)	41.4	–113.8	–21.2 <sup>b</sup>	–73.2 <sup>f</sup>
0.291 (20°C)				–22.1 <sup>b</sup>	–70.8 <sup>f</sup>
0.297 (20°C)				–20.8 <sup>b</sup>	–72.5 <sup>f</sup>
0.402 (25°C)				–21.4 <sup>b</sup>	–72.2
0.397 (25°C)				–21.4	
<b>1e + 2 → 3e</b>					
84 (25°C) <sup>e</sup>	$10^6$ – $10^{10}$ (25°C)	–	–	–	–101.9 <sup>e</sup>
	[115 (25°C)] <sup>a</sup>				[–52.9] <sup>a</sup>
<b>1f + 2 → 3f</b>					
12180 (25°C) <sup>e</sup>	$10^6$ – $10^{12}$ (25°C)	–	–	–	–117.8 <sup>e</sup>
	[101 (25°C)] <sup>a</sup>				[–35.6] <sup>a</sup>
<b>1g + 2 → 3g</b>					
0.0031 (25°C)	40	–	–	–	–
	[28 (25°C)] <sup>a</sup>				[–40.2] <sup>a</sup>
<b>1h + 2 → 3h</b>					
13750 (25°C) <sup>e</sup>	$>10^7$	–	–	–	–87.9 <sup>f</sup> ; –91.7 <sup>g</sup>
<b>1i + 2 → 3i</b>					
$1.04 \times 10^{-4}$ (20°C)	–	58.6	–120.5	–18.6 <sup>c</sup>	–
$1.67 \times 10^{-4}$ (25°C)					
$2.53 \times 10^{-4}$ (30°C)					
$5.30 \times 10^{-4}$ (40°C)					
$2.19 \times 10^{-3}$ (60°C)					
<b>1j + 2 → 3j</b>					
$5.55 \times 10^{-4}$ (25°C)	160 (25°C)	–	–	–15.8 <sup>c</sup>	–
$5.70 \times 10^{-4}$ (25°C)				–16.1 <sup>b</sup>	
				–15.9	

<sup>a</sup> Data of [23]. <sup>b</sup> Reaction volume was determined according to Eq. (2) using adduct concentrations calculated from kinetic data. <sup>c</sup> Adduct concentrations were calculated using measurements of the absorption of dienophile **2** during the reaction. <sup>d</sup> The enthalpy of reaction was calculated from the difference between the enthalpies of activation for the direct and reverse reactions. <sup>e</sup> Data of [13]. <sup>f</sup> Data from calorimetric measurements of the reaction heat in toluene at 25°C. <sup>g</sup> Data from calorimetric measurements of the reaction heat in 1,2-dichloroethane at 25°C.

**Table 2.** Effect of pressure ( $P$ , bar) on the rate constants of the direct reaction ( $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$ ,  $k_2$ ,  $\text{M}^{-1} \text{s}^{-1}$ ) at  $25^\circ\text{C}$  and the reverse reaction ( $\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2}$ ,  $k_1$ ,  $\text{s}^{-1}$ ) at  $45^\circ\text{C}$  in toluene

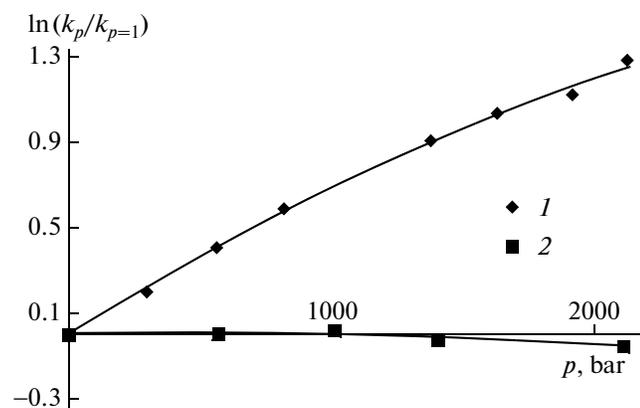
$p$	$k_{2,p}/k_{2,p=1}$	$\ln(k_{2,p}/k_{2,p=1})$	$p$	$k_{2,p}/k_{2,p=1}$	$\ln(k_{2,p}/k_{2,p=1})$
<b><math>\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}</math></b>			<b><math>\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2}</math></b>		
1	1	0	1	1	0
298	1.23	0.207	567	1.005	0.005
563	1.51	0.412	1012	1.019	0.0188
820	1.81	0.593	1402	0.975	-0.025
1381	2.48	0.908	2110	0.945	-0.056
1624	2.81	1.033			
1918	3.07	1.122			
2126	3.60	1.281			

**Table 3.** Comparison of enthalpy ( $\Delta H^\ddagger$ , kJ/mol), entropy ( $\Delta S^\ddagger$ , J/mol/K), volume of activation ( $\Delta V_{\text{corr}}^\ddagger$ ,  $\text{cm}^3/\text{mol}$ ), and volume of the series of reactions ( $\Delta V_{\text{r-n}}$ ,  $\text{cm}^3/\text{mol}$ ) in toluene at  $25^\circ\text{C}$ 

Reaction (reactive center)	$\Delta H^\ddagger$	$-\Delta S^\ddagger$	$V_{\text{corr}}^\ddagger$	$\Delta V_{\text{r-n}}$	$V_{\text{corr}}^\ddagger / \Delta V_{\text{r-n}}$
9,10-Diphenylanthracene + <b>2</b> (1,4) <sup>a</sup>	58.6	97	-17.2	-15.6	1.10
9,10-Dimethylantracene + MA (9,10) <sup>b</sup>	40.2	150	-21.7	-18.9	1.15
9-Phenylanthracene + MA (9,10) <sup>b</sup>	68.0	140	-23.2 <sup>c</sup>	-27.3	0.85
2-Methyl-1,3-butadiene + MA <sup>d</sup>	59.0	149	-34.8 <sup>e</sup>	-34.5	1.01

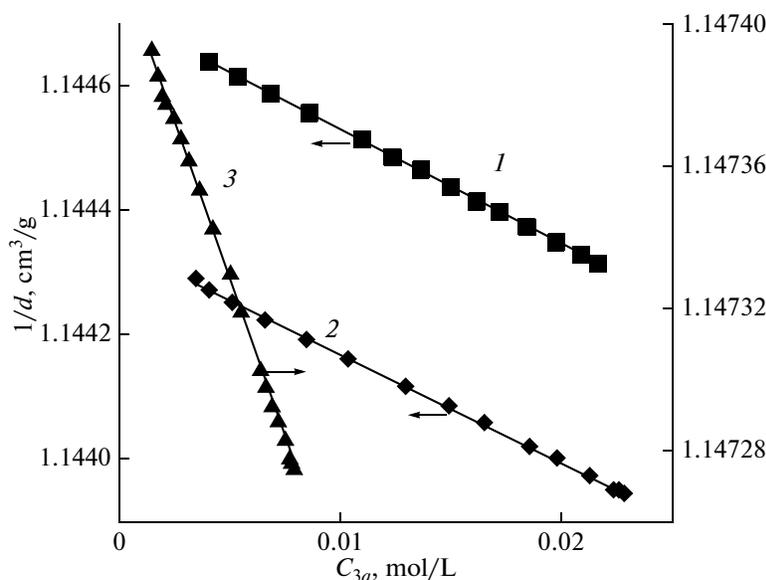
<sup>a</sup> Data of this work. <sup>b</sup> Reaction with maleic anhydride (MA) according to the data of [30]. <sup>c</sup> At  $60^\circ\text{C}$ . <sup>d</sup> According to [31]. <sup>e</sup> At  $35^\circ\text{C}$ .

and while monitoring the concentration of diene **1a** by means of  $^1\text{H}$  NMR [23]. We repeatedly studied reaction  $\mathbf{1b} + \mathbf{2} \rightleftharpoons \mathbf{3b}$  (35 mM of diene **1b** and 35 mM of dienophile **2** in chloroform at  $25^\circ\text{C}$  as in [23]) using vacuum-dried 4-phenyl-1,2,4-triazoline-3,5-dione with UV monitoring of its concentration. We calculated the values for the initial absorption of dienophile **2** ( $D_{2,\text{calc}} = 6.2$ ;  $\lambda = 540 \text{ nm}$ ;  $\varepsilon_{2,540 \text{ nm}} = 177 \text{ M}^{-1} \text{ s}^{-1}$ ) and diene **1b** ( $D_{1b,\text{calc}} = \sim 280$ ;  $\lambda = 378 \text{ nm}$ ;  $\varepsilon_{1b,378 \text{ nm}} =$

**Fig. 2.** Pressure (bar) dependence of  $\ln(k_p/k_{p=1})$  for direct reaction  $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$  (1) at  $25^\circ\text{C}$  and for reverse reaction  $\mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2}$  (2) at  $45^\circ\text{C}$  in toluene.

$8000 \text{ M}^{-1} \text{ s}^{-1}$ ). Allowing for the final absorption of **2** ( $D_{2,t=\infty} = 0.010$ ,  $\sim 0.2\%$  of equilibrium dienophile **2**) and **1b** ( $D_{1b,t=\infty} = 0.216$ ,  $\sim 0.1\%$  of equilibrium diene **1b**), the equilibrium constant of reaction  $\mathbf{1b} + \mathbf{2} \rightleftharpoons \mathbf{3b}$  is more than  $10^7 \text{ M}^{-1}$ , which is considerably higher than the value ( $328 \text{ M}^{-1}$ ) given in [23]. This can be explained by the low purity of the dienophile **2** used in [23] without purification, and by lack of the signals in the  $^1\text{H}$  NMR spectrum of dienophile **2** needed to monitor it. The level of conversion for equimolar concentrations of dienes **1f**, **1b**, **1e** and dienophile **2** was found to be very high in toluene at  $25^\circ\text{C}$ , preventing us from determining the equilibrium constants with a high degree of accuracy. These evaluations were based on data for the initial ( $D_{0,2} = 1.777$ ,  $540 \text{ nm}$ ;  $\varepsilon_2 = 245 \text{ M}^{-1} \text{ s}^{-1}$ ,  $C_{0,2} = 7.253 \times 10^{-3} \text{ M}$ ) and final absorption ( $D_\infty = 0.002$ ,  $0.005$ , and  $0.002$ ) with equimolar concentrations of dienes **1f**, **1b**, **1e**, respectively. It follows that equilibrium constants  $K_{\text{eq}}$  of these reactions are higher than  $10^6 \text{ M}^{-1}$ .  $K_{\text{eq}}$  can be calculated using data on the enthalpies of these reactions in solution (Table 1) if we use an entropy of  $-150 \text{ kJ}/(\text{mol K})$ . The equilibrium constants of reactions  $\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{3}$  differ more than by 10 orders of magnitude (Table 1).

The high values of  $K_{\text{eq}}$  agree with observations of the full decoloration of equimolar concentrations of **1b** and **2** in toluene (Table 1) and dichloromethane [12], and of solutions of **1h** and **2** in benzene and 1,4-



**Fig. 3.** Reaction volume of  $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$ , determined from the dependence of specific volume  $1/d$  on adduct concentration ( $C_{t,3a}$ ) in solution: (1)  $1/d = -0.018353 C_{t,3a} + 1.144711$ ,  $R = 0.9999$ ,  $C_{0,1a} = 0.1131$  M,  $C_{0,2} = 0.02328$  M, (2)  $1/d = -0.017319 C_{t,3a} + 1.144342$ ,  $R = 0.9997$ ,  $C_{0,1a} = 0.1174$  M,  $C_{0,2} = 0.02294$  M, (3)  $1/d = -0.017909 C_{t,3a} + 1.147418$ ;  $R = 0.9995$ ;  $C_{0,1a} = 0.09873$  M;  $C_{0,2} = 0.00898$  M;  $\Delta V_{r-n} = -16.0$  (1),  $-15.1$  (2),  $-15.6$  cm<sup>3</sup>/mol (3).

dioxane at room temperature [9]. The equilibrium constants of reaction  $\mathbf{1a} + \mathbf{2} \rightleftharpoons \mathbf{3a}$  in toluene were calculated using the ratio  $K_{eq} = k_2/k_1$ . For reactions  $\mathbf{1c} + \mathbf{2} \rightleftharpoons \mathbf{3c}$ ,  $\mathbf{1g} + \mathbf{2} \rightleftharpoons \mathbf{3g}$ ,  $\mathbf{1j} + \mathbf{2} \rightleftharpoons \mathbf{3j}$ , they were calculated from the initial and equilibrium absorption of dienophile  $\mathbf{2}$ . For reactions  $\mathbf{1j} + \mathbf{2} \rightleftharpoons \mathbf{3j}$  and  $\mathbf{1k} + \mathbf{2} \rightleftharpoons \mathbf{3k}$ , time needed to attain equilibrium was  $\sim 10$ – $20$  h at  $25^\circ\text{C}$ .

## CONCLUSIONS

The reaction of 9,10-diphenylanthracene  $\mathbf{1a}$  and highly active dienophile  $\mathbf{2}$  proceeds with changing regioselectivity. The shielding of active 9,10-reactive centers of  $\mathbf{1a}$  excludes the common path of the Diels–Alder reaction with any dienophile. Only the high activity of dienophile  $\mathbf{2}$  is sufficient for reactions along the less active and more accessible 1,4-path. Direct spectrophotometric measurements of the equilibrium parameters corresponded to the high stability of adducts  $\mathbf{3b}$ – $\mathbf{3e}$  and  $\mathbf{3h}$  in the reaction of  $\mathbf{2}$  attachment on the 9,10-atoms of dienes. However, adducts  $\mathbf{3g}$ ,  $\mathbf{3j}$  with acceptor substituents in diene have low stability. The resistance to the decomposition of the adducts from Diels–Alder reactions with dienophile  $\mathbf{2}$  and maleic anhydride is comparable [13], while the reaction rate constant of  $\mathbf{1a}$  and maleic anhydride ( $10^{-9}$  M<sup>-1</sup> s<sup>-1</sup>) is too slow for the reaction to proceed under normal conditions (kinetic control). On the other hand, the reaction rates of  $\mathbf{1a}$  and dienophile  $\mathbf{2}$  and tetracyanoethylene should be comparable [13]. However, the equilibrium constant for the reaction of

$\mathbf{1a}$  and tetracyanoethylene is lower than that for the reaction of  $\mathbf{1a}$  and  $\mathbf{2}$  by a factor of  $10^3$ – $10^5$  [13]. The level of conversion for the reaction of  $\mathbf{1a}$  and tetracyanoethylene is therefore very low under ordinary conditions; i.e., it is not possible for thermodynamic reasons. The entropy and volume parameters of reaction  $\mathbf{1a} + \mathbf{2} \rightarrow \mathbf{3a}$  on the 1,4-atoms of diene do not differ appreciably from those of ordinary  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$  reactions on 9,10-reactive centers.

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Crystallographic data for the structure of  $\mathbf{3a}$  are on file at the Cambridge Crystallographic Data Centre (CCDC number 922287) and can be accessed over the internet at [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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