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### ARTICLE



# Kinetics and thermochemistry of the $[2\pi+2\sigma+2\sigma]$ -cycloaddition of quadricyclane with 2,3-dicyano-1,4-benzoquinone

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#### Abstract

Two-stage  $[2\pi+2\sigma]$ -cycloaddition of quadricyclane (2) with 2,3-dicyano-1,4benzoquinone (1) with a huge difference in the activity of two reaction centers has been studied. In the first stage (kinetic control), the cycloaddition of 2 takes place on the activated  $C_2=C_3$  bond of 1 to form the monoadduct 3, and in the second stage the cycloaddition of 2 on the  $C_5=C_6$  bond of the monoadduct 3 occurs by 6 orders of magnitude lower with the formation of bisadduct 4. The structures of adducts 3 and 4 have been proved by NMR data and the X-Ray method, respectively. The kinetics of the first and second stages, the enthalpy of dissolution of 1 in the  $\pi$ -donor solvents, and the enthalpy of the reaction  $1+2\rightarrow 3$  have been measured.

#### **KEYWORDS**

 $[2\pi+2\sigma+2\sigma]$ -cycloaddition, quadricyclane,2,3-dicyano-1,4-benzoquinone, rate constant, reaction heat

# **1 | INTRODUCTION**

The unusual combination of the high strain energy (328  $kJ \cdot mol^{-11})^1$  of quadricyclane (2) (tetracyclo[3.2.0.0<sup>2,7</sup>0<sup>4,6</sup>]heptane) and its high thermal stability ( $k_{\text{dec.}} = 9.6 \times 10^{-6}$  $s^{-1}$  at  $140^{\circ}C^{2})^{2}$  has attracted the attention of researchers. A large amount of data on the synthesis of  $[2\pi+2\sigma+2\sigma]$ adducts of quadricyclane with a wide range of dienophiles have been accumulated,<sup>3-7</sup> but only few quantitative kinetic and thermochemical measurements were carried out for the reactions involving 2 and no data were available for the reactions involving 1. Quadricyclane has a low ionization potential (7.40 eV),<sup>8</sup> which promotes the fast formation of adducts with strong  $\pi$ -acceptor dienophiles in the cycloaddition reactions.<sup>9,10</sup> For 2,3-dicyano-1,4-benzoquinone, a high  $\pi$ -acceptor property should be expected. A huge difference in the enthalpy of C7H8 isomers formation, quadricyclane (339.1), norbornadiene (247.6), and cycloheptatriene (183.7 kJ·mol<sup>-1</sup>)<sup>7</sup>, indicate an increased strain energy in quadricyclane, which should be released significantly by opening of two cyclopropane moieties in 2 during the adduct formation. This is the reason of a record enthalpy of the reactions of 2 with tetracyanoethylene (5) (-236.1) and with 4-phenyl1,2,4-triazoline-3,5-dione (8)  $(-255.1 \text{ kJ} \cdot \text{mol}^{-1})$  in comparison with all known cycloaddition reactions.<sup>9,10</sup> So we can expect a sufficiently high stability of monoadduct 3 in the reaction  $1+2\rightarrow 3$ .

In this paper, we have established that the cycloaddition of quadricyclane (2) to 2,3-dicyanobenzoquinone (1) is a twostage process: in the first stage, the cycloaddition  $1+2\rightarrow 3$  proceeds very fast at  $C_2=C_3$  reaction center of dienophile 1. Further, very slow addition of 2 at inactivated  $C_5=C_6$  bond of monoadduct,  $3+2\rightarrow 4$ , takes place (Scheme 1). The structures of adducts 3 and 4 have been proved by NMR data and the X-Ray method, respectively. The kinetic data of the first and second stages, the enthalpy of reaction  $1+2\rightarrow 3$ , and  $\pi$ -acceptor properties of 1 have been studied.

## 2 | EXPERIMENTAL

#### 2.1 | Materials

Quadricyclane **2** was synthesized from norbornadiene by the known method,<sup>11</sup> dried with metallic sodium and distilled twice under reduced pressure (600 Pa). Its purity was



SCHEME 1 Two stage reaction of quadricyclane (2) with 2,3-dicyanobenzoquione (1) with the formation of mono- (3) and bisadduct (4)

determined at the titration by known concentration of a red solution of tetracyanoethylene (**5**) in toluene. The rate constant of norbornadiene as the possible admixture in reaction with tetracyanoethylene  $(1.3 \times 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})^{12}$  is 7 orders of magnitude lower than the rate constant of reaction (**2**+**5**) (104.4 L·mol<sup>-1</sup>·s<sup>-1</sup>),<sup>10</sup> therefore only quadricyclane participates in titration. The purity of **2** was 97 ± 0.5%. 2,3-Dicyano-1,4-benzoquinone (**1**) was obtained by oxidation of 2,3-dicyanohydroquinone (98%; Sigma-Aldrich, Steinheim, Germany) with nitrogen oxide at 0°C. Quinone **1**, m.p. 181–183°C (182–183°C),<sup>13</sup> was sublimed (110°C, 10 Pa) before the measurements. All solvents were purified by known methods.<sup>14</sup>

Monoadduct **3**, 4,7-dioxotetracyclo[ $8.2.1^{7,10}0^{2,9}0^{3,8}$ ]tridecene-3,8-dicarbonitrile, was obtained as white crystals from benzene, m.p. 242–243°C (with decomposition). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a spectrometer Bruker Avance 400. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C),  $\delta$ , ppm: 1.84 (d, <sup>2</sup>J<sub>HH</sub> = 11.6 Hz, 1H); 2.38 (s, 2H); 2.47 (d, <sup>2</sup>J<sub>HH</sub> = 11.6 Hz, 1H); 3.33 (s, 2H); 6.16 (br s, 2H); 7.01 (s, 2H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 25°C),  $\delta$ , ppm: 42.19; 43.62; 44.42; 45.99; 112.83; 136.76; 139.95; 185.04.

Bisadduct 4, 4,13-dioxoheptacyclo[14.2.1.1<sup>7,10</sup>0<sup>2,15</sup>0<sup>3,14</sup> 0<sup>5,12</sup>0<sup>6,11</sup> icosa-8,17-diene-3,14-dicarbonitrile, was obtained as colorless crystals from benzene, m.p. 330°C (with decomposition). The X-ray diffraction data of adduct 4 were collected on a Bruker Kappa Apex II CCD diffractometer in the  $\omega$  and  $\varphi$ -scan modes using graphite monochromated Mo  $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation at 100(2) K. Data were corrected for the absorption effect using the SADABS program.<sup>15</sup> The structure was solved by the direct method and refined by the full matrix least-squares using SHELXTL<sup>16</sup> and WinGX<sup>17</sup> programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at calculated positions and refined using a "riding" model. Data collections: images were indexed, integrated, and scaled using the APEX2<sup>18</sup> data reduction package. Analysis of the intermolecular interactions was performed using the program PLATON<sup>19</sup>. Mercury program<sup>20</sup> package was used for figures' preparation.

Crystallographic data for compound **4**:  $C_{22}H_{18}N_2O_2$ , \*0.5( $C_2H_4Cl_2$ ), ( $C_{23}H_{20}ClN_2O_2$ ), colorless prism, size 0.07

× 0.47 × 0.67 mm<sup>3</sup>, M = 391.86, monoclinic, a = 6.5182(5)Å, b = 23.8420(18) Å, c = 11.7391(9) Å,  $\beta = 94.061(5)^{\circ}$ , V = 1819.8(2) Å<sup>3</sup>, T = 100(2) K, space group  $P2_1/n$ , Z = 4,  $\mu$ (Mo K<sub> $\alpha$ </sub>) = 0.233 mm<sup>-1</sup>,  $\rho_{calc} = 1.430$  g·cm<sup>-3</sup>, F(000) = 820, theta range for data collection 3.42–27.09°, 23,372 reflections measured, 3815 independent reflections ( $R_{int} = 0.0772$ ), 259 parameters, two restraints. Final indices:  $R_1 = 0.0444$ ,  $wR_2 =$ 0.0895 (2284 reflections with  $I > 2\sigma_I$ ),  $R_1 = 0.0999$ ,  $wR_2 =$ 0.1097 (all data), GoF = 0.986, largest difference in peak and hole (0.255 and -0.267 eÅ<sup>-3</sup>).

Crystallographic data for the structure **4** has been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1878601. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44(0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

#### 2.2 | Kinetic measurements

The rate of the fast reaction  $1+2\rightarrow 3$  was measured by the stopped flow method (spectrophotometer Cary 50 Bio with RX 2000 attachment) in 1,2-dichloroethane at 25.0 and 44.4°C. The reaction was monitored by a change in absorption of 2,3-dicyano-1,4-benzoquinone (1) at 440 nm, where compounds 2 and 3 are optically transparent. The initial concentrations of 1 and 2 were  $2.57 \times 10^{-2}$  and  $4.47 \times 10^{-2}$ mol·L<sup>-1</sup>, respectively. The slow reaction rate of  $2+3\rightarrow 4$  was measured in 1,2-dichloroethane at 25 and 45°C (spectrophotometer Hitachi U-2900). The course of the reaction was monitored by the change of monoadduct 3 absorption at 368 nm, where the compounds 2 and 4 are optically transparent. The initial concentrations of 2 and 3 were 2.0 and 0.075 mol·L<sup>-1</sup>, respectively. The relative standard errors of the rate constants did not exceed 3%.

#### **2.3** | Calorimetric measurements

To estimate the  $\pi$ -acceptor properties of **1**, the enthalpies of dissolution of **1** were determined at 25°C in  $\pi$ -donor solvents, chlorobenzene, benzene, toluene, and *o*-xylene using a differential calorimeter as described earlier.<sup>21</sup> The sample of **1** was placed in a small stainless steel cylinder, the base and top of



**FIGURE 1** Two projections of bisadduct **4** molecule in the crystal with a partial atomic numbering scheme. Non-hydrogen atoms are represented by thermal vibration ellipsoids (p = 50%), hydrogen atoms are spheres of arbitrary radius (A) and (B) omitted for clarity. Some of bond lengths in the molecule: C21 N21 1.150(3), C22 N22 1.144(3), C4 O4 1.204(3), C13 O13 1.207(3), C2 C15 1.554(3), C2 C3 1.574(3), C3 C21 1.455(3), C3 C4 1.540(3), C4 C5 1.500(3), C5 C6 1.547(3), C6 C7 1.547(3), C7 C8 1.521(3), C7 C20 1.545(3), C8 C9 1.326(3) Å. [Color figure can be viewed at wileyonlinelibrary.com]

which were closed with the thin (0.1 mm) round Teflon gaskets and tightly screwed onto the lid. After achieving thermal equilibrium, the Teflon films were cut out with a razor blade. Three measurements of enthalpy of dissolution were made for each solvent. The relative error of the dissolution enthalpy was less than  $1.0 \text{ kJ} \cdot \text{mol}^{-1}$ .

The heat of reaction  $1+2\rightarrow 3$  was determined by adding crystals of 1 to a solution of excess 2 in toluene. The enthalpy of the reaction in toluene ( $-182.2 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ ) was determined taking into account the dissolution enthalpy of 1 in toluene ( $6.3 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ ).

#### **3 | RESULTS AND DISCUSSION**

#### 3.1 | X-Ray diffraction data

The structure of 4,13-dioxoheptacyclo[14.2.1.1<sup>7,10</sup>0<sup>2,15</sup>0<sup>3,14</sup> 0<sup>5,12</sup>0<sup>6,11</sup> licosa-8,17-diene-3,14-dicarbonitrile 4 was unambiguously confirmed by the single-crystal X-ray experiments. According to the data obtained, the molecule 4 is symmetric and has its own plane of symmetry, but loses it in the crystal and is in the general position of the monoclinic unit cell (Figure 1). On the contrary, solvated dichloroethane molecule is located at the center of symmetry, so that in the independent part of the unit cell one bisadduct 4 molecule and half of the dichloroethane molecule are located. Bond lengths in the molecule 4 are in the range of standard values of bond lengths, and no significant deviations from them are observed, with the exception, perhaps, of three C-C bonds: C6-C11, C5-C12, and C3-C14, the values of which are 1.567(3), 1.580(3), and 1.607(3)Å—this is noticeably higher than the standard C–C single bond for sp3-hybridized atoms. One of the reasons for the observed values can be a rather stressed state of atoms in the rigid carbon frame formed. A bisadduct 4 molecule formally possesses 12 chiral centers, and the analysis of their relative configuration by the PLATON program led to the following configuration of the molecule: C1 - S, C2 - R, C3 - S, C5 - S, C6 - R, C7 - S, C10 - R, C11 - S, C12 - R, C14 - R, C15 - S, and C16 - R. Given that the compound 4 crystallizes in the centrosymmetric space group *P21/n*, it should be borne in mind that the crystal also contains the molecules with reverse configuration of chiral centers.

In the absence of classical hydrogen bonds, the main types of the structure-forming interactions in the crystal of **4** are presented by the intermolecular C–H···O and C–H···N hydrogen bonds, the combined effect of which leads to the formation of two-dimensional supramolecular structures—corrugated H-layers of molecules lying in the crystallographic plane Oac (Figure 2A). Parallel stacking of such two-dimensional structures along the crystallographic direction Ob is carried out in such a way that only Van der Waals interactions are carried out between them (Figure 2B). Solvate molecules of dichloroethane are located in the linear pseudocavities, formed of fragments of four neighboring bisadduct **4** molecules in a checkerboard pattern (Figure 2C), with the distances 4.1 Å between centers of Cl atoms of neighboring solvate molecules.

With such mutual packing of the molecules in the crystal, there are practically no voids potentially accessible for the solvent, and calculated packing index of the molecules, equal to 0.727, approaches to the upper limit of the range characteristic of crystals of organic compounds (0.65–0.75).<sup>22</sup> We emphasize that the structure-forming interactions lead to the formation of two-dimensional layer structures located along the two shortest distances of the unit cell. The absence of significant interactions along the third direction seems to imply the least stable direction in the crystal, along which we should expect the destruction of the crystal at the initial stages of this process.



**FIGURE 2** Three projections of the crystal packing in 4: (A) H-layers, view along  $\partial b$ , solvent molecules omitted for clarity, C–H···O, C–H···N interactions are shown by dashed lines; (B) crystal packing view along  $\partial c$  axis; (C) view along  $\partial a$  axis. Solvent molecules are shown in the "space-fill" model. Some of bisadduct 4 molecules, belonging to the same H-layers, are shown in "ball-and-stick" or "space-fill" model styles. [Color figure can be viewed at wileyonlinelibrary.com]

в



**SCHEME 2**  $\pi$ -Acceptors used in the calorimetric analysis

A

**TABLE 1** Comparison of the enthalpy of dissolution ( $\Delta H_{\text{dissol}}$ , kJ·mol<sup>-1</sup>) of some  $\pi$ -acceptors in  $\pi$ -donor solvents at 25°C

<i>π</i> -Acceptor	o-Xylene	Toluene	Benzene	Chlorobenzene
Tetracyanoethylene (5)	1.4	9.7	14.9	23.0
2,3-Dicyano-1,4-benzoquinone (1) <sup>a</sup>	2.1	6.3	10.3	15.7
Tetrachloro-1,4-benzoquinone (6)	9.2	12.6	16.7	18.0
1,3,5-Trinitrobenzene (7)	5.9	7.5	9.6	10.9
4-Phenyl-1,2,4-triazoline-3,5-dione (8)	18.0	18.3	20.6	21.8
Maleic anhydride (9)	15.1	16.4	16.9	18.4
1,4-Benzoquinone (10)	16.3	16.4	17.1	17.6

<sup>a</sup>Data of this work, the others from Ref. 23.

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#### 3.2 | Calorimetric data

Very high reactivity of tetracyanoethylene (5) in the cycloaddition reactions<sup>12,23–26</sup> can be explained by the high  $\pi$ acceptor value of 5 (EA = 2.88 eV [Ref. 27]). The  $\pi$ -acceptor properties of dienophiles can be estimated by the difference of the charge transfer energy of  $\pi$ , $\pi$ -complexes with a convenient  $\pi$ -donor, such as hexamethylbenzene<sup>28</sup> or by the difference of interaction energy with  $\pi$ -donors, obtained from the dissolution heat of dienophiles in  $\pi$ -donor aromatic solvents.<sup>23</sup> The observed value of a maxima of the charge transfer absorption bands of the hexamethylbenzene complex with 2,3-dicyano-1,4-benzoquinone (1) is  $\lambda_{\text{max}}$  575 nm,  $E_{\text{c.t.}}$  2.15 eV, and with tetracyanoethylene (5) is  $\lambda_{\text{max}}$  538 nm,  $E_{\text{c.t.}}$  2.30 eV, both in 1,2-dichloroethane. These data predict the greater  $\pi$ -acceptor property and activity of dienophile 1. The difference in the interaction energy of  $\pi$ , $\pi$ -complexes can be determined independently. The obtained values of dissolution enthalpy of  $\pi$ -acceptors 1, 5–10 (Scheme 2) are presented in Table 1.

С

The change in the heat of dissolution of  $\pi$ -acceptors in the studied series of  $\pi$ -donor solvents corresponds to the difference in enthalpies of the  $\pi,\pi$ -complexes in the following



**FIGURE 3** Correlations of the relative enthalpy of the tetracyanoethylene (5) solvation  $[\delta H_{solv}(5) = \Delta H_{solut.}(5)/S_i - \Delta H_{solut.}(5)/o$ -xylene] with that of 2,3-dicyano-1,4-benzoquinone (1), tetrachloro-1,4-benzoquinone (6), 1,3,5-trinitrobenzene (7), 4-phenyl-1,2,4-triazoline-3,5-dione (8), maleic anhydride (9), and 1,4-benzoquinone (10). [Color figure can be viewed at wileyonlinelibrary.com]

order (Figure 3): tetracyanoethylene (5), blank, 100%, correlation coefficient, r = 1; 2,3-dicyano-1,4-benzoquinone (1), 64%, r = 0.997; tetrachloro-1,4-benzoquinone (6), 43%, r = 0.970; 1,3,5-trinitrobenzene (7), 24%, r = 0.986; 4-phenyl-

1,2,4-triazoline-3,5-dione (8), 19%, r = 0.942; maleic anhydride (9), 15%, r = 0.995; 1,4-benzoquinone (10), 6%, r = 0.948.

# **3.2** | Rate constants of $[2\pi+2\sigma+2\sigma]$ -cycloaddition

The values of the rate constants of some fast and very slow reactions are presented in Table 2.

The reaction rate constants (ln  $k_2$ ) of a quadricyclane (2) with tetracyanoethylene (2+5) (4.65), 2,3-dicyano-1,4benzoquinone (2+1) (3.61), 4-phenyl-1,2,4-triazoline-3,5dione (2+8) (-1.27), and with 1,4-benzoquinone (2+10) (-12.6) change in the same order of  $\pi$ -acceptor properties that follows from the data in Figure 3 (100, 64, 19, and 6%).

The rate constant of the reaction  $1+2\rightarrow 3$  at the 2,3-reaction center is  $2.7 \times 10^6$  times higher than that of **2** with the monoadduct **3**. This corresponds to a much higher electrophilicity of  $C_2=C_3$  carbon atoms in dienophile **1** compared to  $C_5=C_6$ . Note, that **2** reacts only 20 times faster with monoadduct **3** compared with 1,4-benzoquinone (**10**). The stronger donor-acceptor pair, 9,10-dimethylanthracene (**11**) (IP = 7.04 eV)<sup>29</sup> and tetracyanoethylene (**5**) (EA = 2.88 eV)<sup>27</sup> reacts faster than **2** (IP = 7.40 eV<sup>8</sup>)<sup>8</sup> with **5** despite the huge loss in the enthalpy of reaction (148 kJ·mol<sup>-1</sup>, Table 2). It can be noted that the enthalpy and entropy of activations of the reactions  $[2\pi+2\sigma+2\sigma]$ - (**1+2**) and  $[4\pi+2\pi]$ -cycloaddition (**1+11**) are very close (Table 2).

#### 3.3 | Enthalpies of $[2\pi+2\sigma+2\sigma]$ -cycloaddition

Highly exothermic reactions often, but not always,<sup>29</sup> go faster. Typically, the enthalpies of the Diels–Alder reac-

**TABLE 2** The rate constants  $(k_2, L \cdot mol^{-1} \cdot s^{-1})$ , enthalpy  $(\Delta H^{\neq}, kJ \cdot mol^{-1})$  and entropy activation  $(\Delta S^{\neq}, J \cdot mol^{-1} \cdot K^{-1})$ , and enthalpy  $(\Delta H_{r-n}, kJ \cdot mol^{-1})$  of some cycloaddition reactions

Reaction	$k_2 (T/ {}^{o}C)$ , solvent	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$-\Delta H_{\rm r-n}$
(1+2)	36.9 (25), S1 50.8 (44.4), S1	$10.5 \pm 1.2$	$179.7 \pm 4.0$	$182.2 \pm 0.8,$ S2
(3+2)	$1.35 \times 10^{-5}$ (25.0), S1 7.11 × 10 <sup>-5</sup> (45.0), S1	$63.0 \pm 2.0$	$126.7 \pm 6.7$	a
(10+2)	$3.41 \times 10^{-6}$ (45.0), S1	-	-	а
(1+11) <sup>b</sup>	235.0 (25.0), S1 304.1 (317.75 K), S1	$7.9 \pm 1.3$	$172.9 \pm 4.3$	-
(5+2) <sup>c</sup>	104.4 (293.15 K), S2	18.0 ± 1.1	$145.0 \pm 4.0$	236.6 ± 1.0, S3
(5+11) <sup>d</sup> (5+11) <sup>e</sup>	2810 (298.15), S2 92700 (24.9), S1	11.9 -8.7	138.0 178.8	- 88.3 <sup>f</sup>

Solvents: S1, 1,2-dichloroethane; S2, toluene; S3, 1,4-dioxane; S4, dichloromethane

<sup>a</sup>Very low rate for the measurements of the reaction heat.

<sup>b</sup>Reaction of **1** with 9,10-dimethylanthracene (**11**).

<sup>c</sup>From Ref. 10.

<sup>d</sup>From Ref. 29.

<sup>e</sup>From Ref. 26.

<sup>f</sup>From Refs. 24 and 29.

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**TABLE 3** The enthalpy of reactions  $(\Delta H_{r-n}, kJ \cdot mol^{-1})$  of 2,3-dicyano-1,4-benzoquinone (1), tetracyanoethylene (5) and 4-phenyl-1,2,4-triazoline-3,5-dione (8) with quadricyclane (2), 9,10-dimethylanthracene (11) and cyclopentadiene (12)

	$-\Delta H_{\rm r-n}$		
$\pi$ -Donor reagents	1	5	8
2	182.2	236.6 <sup>a</sup>	255.1ª
11	$(\sim 50 \pm 5)^{b}$	88.3 <sup>c</sup>	117.8 <sup>c</sup>
12	$(\sim 60 \pm 5)^{b}$	113 <sup>c</sup>	134 <sup>c</sup>

<sup>a</sup>From Ref. 10.

<sup>b</sup>Estimated values.

<sup>c</sup>From Ref. 23.

tion lie in the range from -50 to  $-200 \text{ kJ} \cdot \text{mol}^{-1} \cdot 2^{23,29}$  It is useful to compare the enthalpy of the reactions of 2,3-dicyano-1,4-benzoquinone (1), tetracyanoethylene (5), and 4-phenyl-1,2,4-triazoline-3,5-dione (8) with the quadricyclane (2), 9,10-dimethylanthracene (11), and cyclopentadiene (12) (Table 3).

Since the difference in the reaction enthalpy of dienophiles with common diene depends little on the nature of the diene,<sup>23,30</sup> we can estimate the reactions enthalpy of 2,3-dicyano-1,4-benzoquinone with 9,10-dimethylanthracene (1+11) (~-50 ± 5) and with cyclopentadiene (1+12) (~- $60 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ ). The exothermicity of the reaction (2+1) is 54 kJ·mol<sup>-1</sup> lower than that of reaction (2+5) and 72.9 kJ·mol<sup>-1</sup> than that of reaction (2+8). So, the kinetic activity and thermodynamic stability of the reaction (1+2→3) change in opposite directions. Calorimetric measurements of the reaction (2+3→4) failed to be carried out because of the very low reaction rate.

## 4 | CONCLUSION

The difference in the energy of the charge transfer band in  $\pi,\pi$ -complexes of hexamethylbenzene with 1 ( $\lambda_{max}$  575 nm,  $E_{\rm c.t.}$  2.15 eV) and with 5 ( $\lambda_{\rm max}$  538 nm,  $E_{\rm c.t.}$  2.30 eV) in 1,2-dichloroethane corresponds to a lower level of LUMO in 2,3-dicyano-1,4-benzoquinone than in tetracyanoethylene. However, from the difference in the heat of dissolution in  $\pi$ donor solvents, it is necessary to conclude that 2,3-dicyano-1,4-benzoquinone is inferior to tetracyanoethylene in the specific interaction with  $\pi$ -donors. This fact is confirmed by the values of the rate constants of the reactions of tetracyanoethylene and 2.3-dicyano-1,4-benzoquinone with strong electron donors quadricyclane and 9,10-dimethylanthracene. The data obtained make it possible to recommend quadricyclane for carrying out the Diels-Alder reactions with C=C bonds of the low-active and very high conjugated dienophiles. Similarly, to conduct the reactions with the low-active and high conjugated dienes, the most convenient partner should be 4-phenyl-1,2,4triazoline-3,5-dione.

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#### **CONFLICT OF INTEREST**

The authors hereby confirm they have no conflicts of interest.

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