Why can the Diels–Alder reaction of 9,10-diphenylanthracene with 4-phenyl-1,2,4-triazoline-3.5-dione pass by an abnormal way?

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9,10-Diphenylanthracene reacts with dienophile by 1,4-positions rather than 9,10-ones of trivial anthracenes, that has been justified with estimation of kinetic and thermodynamic parameters of the process.

4-Phenyl-1,2,4-triazoline-3,5-dione exhibits the highest reactivity in the Diels–Alder reaction with dienes, as compared with other dienophiles.[1–3] For fifteen dienes, the rate constants and enthalpies of reactions with 4-phenyl-1,2,4-triazoline-3,5-dione, tetracyano-ethylene and maleic anhydride were compared.[4] From these data, it follows that the activity of 4-phenyl-1,2,4-triazoline-3,5-dione is higher than that of maleic anhydride by five or six orders of magnitude.

We studied the reaction rate of a very inactive diene, 9,10-diphenylanthracene **1a**, with the most active dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione **2**, in a toluene solution at 5–45 °C and 1–2126 bar (Scheme 1). The enthalpy, entropy, activation volume, reaction volume and the structure of adduct **3a** were determined.
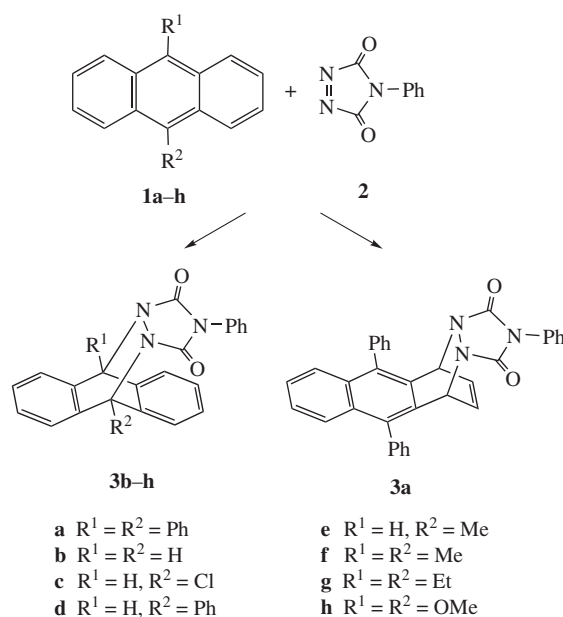
The overlapping of the 1,8-hydrogen atoms of the anthracene moiety and 2,6-hydrogen atoms of the phenyl group in 9-phenyl-anthracene **1d** leads to a dihedral angle of about 60° between these fragments.[5] For 9,10-diphenylantracene **1a**, the almost orthogonal planes of phenyl groups to the anthracene plane were observed.[6] The rate constant of the Diels–Alder reaction with the C=C bonds can be estimated[7] from the equation

$$\log k_2 = -28.81 + 316.3/(IP - EA) - 0.699 R_{C(1)-C(4)}/(IP - EA) - 0.054\Delta_r H, \quad r = 0.972 \quad (1)$$

Here the value of k_2 is in $dm^3\ mol^{-1}\ s^{-1}$, the ionization potential (*IP*) and electron affinity (*EA*) are in eV, $R_{C(1)-C(4)}$ is in pm, the enthalpy of reaction, $\Delta_r H$, is in $kJ\ mol^{-1}$, and *r* is the correlation coefficient.

The rate of reaction of 9-phenylanthracene **1d** with maleic anhydride in toluene at 25 °C ($3.6\times10^{-7}\ dm^3\ mol^{-1}\ s^{-1}$) is 2.5 orders of magnitude lower than that predicted from equation (1).[7] In the absence of steric hindrances, the relative activity of the cycloaddition reaction on 9,10- and 1,4-atoms of anthracene can be estimated using equation (1). The required parameters are available in the literature.[8–10]

From these data, it follows that the difference in the heats of hydrogenation of 9,10- and 1,4-anthracene atoms is $-65\pm8\ kJ\ mol^{-1}$. This corresponds [equation (1)] to a $k_{(9,10)}/k_{(1,4)}$ ratio of 3200. For a series of linear acenes, the activity of different cycles in the Diels–Alder reaction with acetylene has been calculated,[11] which implies the ratio $k_{(9,10)}/k_{(1,4)} = 3500$. The reaction of substituted anthracenes **1b–h** with dienophile **2** runs at the most active *meso*-position of the diene to form adducts **3b–h**.[1–4] It is clear that, for a sterically shielded and inaccessible 9,10-reaction centre of diene **1a**, the Diels–Alder reaction is impossible regardless of

a R^1 = R^2 = Ph   **e** R^1 = H, R^2 = Me
b R^1 = R^2 = H   **f** R^1 = R^2 = Me
c R^1 = H, R^2 = Cl   **g** R^1 = R^2 = Et
d R^1 = H, R^2 = Ph   **h** R^1 = R^2 = OMe

Scheme 1

the potential dienophile activity. Under normal conditions, the reaction between diene **1a** and all known dienophiles with C=C bonds does not take place, whereas in case of dienophile **2** it occurs even at room temperature ($k_2 = 2.7\times10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$, toluene, 25 °C). From the obtained values of $k_{(9,10)}/k_{(1,4)}$ it follows that when the investment of energy required for the flattening of diene **1a** is more than 20 kJ mol^{-1}, the direction of cycloaddition can be changed to less active but sterically accessible 1,4-atoms of anthracene.

The ^{1}H NMR spectrum (Figure 1) of adduct **3a** {400 MHz, CDCl$_3$, 25 °C, δ: 5.92 [t, C(1)H, C(12)H], 6.87 [t, =C(18)H, =C(19)H], atom numeration as in Figure 2} is very different from the spectra of adducts **3b–h**. The presence of two protons at the saturated carbon atoms C(1) and C(12) and the ethylene fragment =C(18)H, =C(19)H is consistent with the formation of 1,4-adduct **3a**, which is not observed in the spectrum of adduct **3f** (Figure 1). Additionally, X-ray analysis (Figure 2)† confirms the formation of the *exo*-conformation of adduct **3a** – 3,10,15-triphenyl-13,15,17-triazapentacyclo[10.5.2.0^{2,11}.0^{4,9}.0^{13,17}]-nonadeca-2,4(9),5,7,10,18-hexaene-14,16-dione. The formation of *endo*-isomer may inhibit 9,10-phenyl substituents.

Note that the ^{1}H NMR spectrum of **3a** is identical to that reported elsewhere,[12] but the possible formation of such adduct was not considered.

Table 1 Enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$), activation volume ($\Delta V^{\neq}_{corr}$) and the volume of reactions (ΔV_r) in toluene at 25 °C.

Reaction (reaction centre)	$\Delta H^{\neq}$/kJ mol^{-1}	$-\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta V^{\neq}_{corr}$/cm^3 mol^{-1}	ΔV_r/cm^3 mol^{-1}	$\Delta V^{\neq}_{corr}/\Delta V_r$
9,10-Diphenylanthracene + **2** (1,4)^a	58.8	97	−17.2	−15.5	1.11
9,10-Dimethylanthracene + MA (9,10)^b	40.2	150	−21.7	−18.9	1.15
9-Phenylanthracene + MA (9,10)^b	68.0	140	−23.2^c	−27.3	0.85
2-Methyl-1,3-butadiene + MA^d	59.0	149	−34.8^e	−34.5	1.0

^{a} This work. ^{b} From ref. 4. ^{c} At 60 °C. ^{d} From ref. 13. ^{e} At 35 °C.
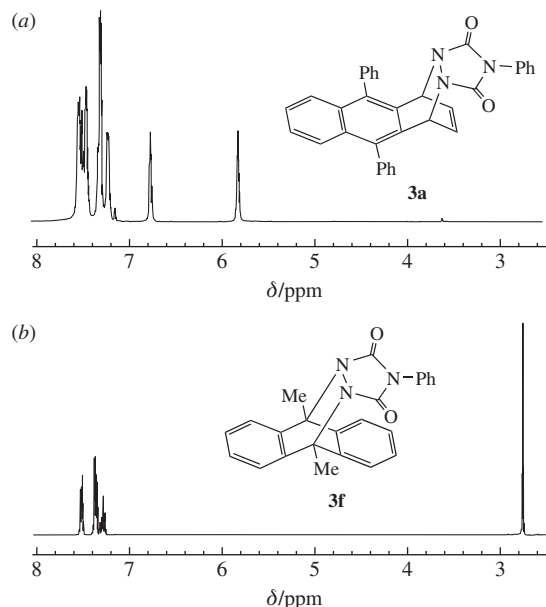
Figure 1 ^{1}H NMR spectra of adducts (*a*) **3a** and (*b*) **3f** (0.162 mol dm^{-3}) in CDCl$_3$ at 25 °C. The ratio of the peak areas of the aromatic protons (7.1–7.8 ppm) and the peaks at 6.87 and 5.92 ppm in the adduct **3a** is 19.5 : 2 : 2.
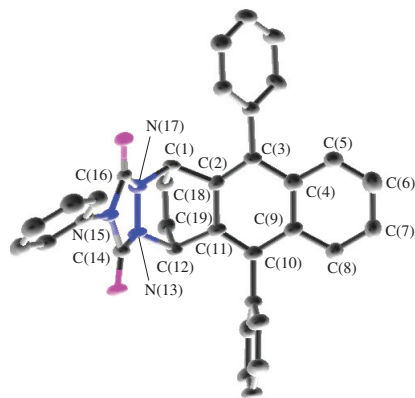
Figure 2 ORTEP structure of *exo*-adduct **3a**.

† *Crystallographic data for* **3a** were collected on a Bruker Smart Apex II CCD diffractometer at 20 °C using graphite monochromated MoKα radiation (0.71073 Å). Crystals of compound **3a** (C$_{34}$H$_{23}$N$_3$O$_2$) are monoclinic, space group $P2_1/c$, $a = 11.139(5)$, $b = 22.304(8)$ and $c = 11.564(4)$ Å, $\beta = 119.93(3)°$, $V = 2489.9(17)$ Å^3, $Z = 4$, $d_{calc} = 1.349$ g cm^{-3}. Intensities of 5989 independent reflections, from which 2442 with $I \geqslant 2\sigma$, were measured in the ω-scan, $\theta \leqslant 28.00°$ mode ($R_{inr} = 0.1720$). Absorption correction was not applied [μ(MoKα) = 0.85 cm^{-1}]. The structures were solved by a direct method and refined by the full-matrix least-squares using the SHELX.[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined as rigid atoms. The final residuals were $R_{ob} = 0.0869$, $R_{wob} = 0.1789$. Data collection: images were indexed, integrated and scaled using the APEX2 data reduction package.[15] All figures were made using the ORTEP program.[16]

CCDC 922287 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

We studied the rate of the reaction **1a** + **2** → **3a** in toluene at atmospheric pressure in a temperature range of 15–50 °C and in a pressure range of 1–2126 bar at 25 °C.‡ The dependence of $\ln k_2$ on P is described by the relation

$$\ln(k_{2,p}/k_{2,p=1}) = -0.004 + 7.84\times10^{-4}P - 9.10\times10^{-8}P^2.$$

The experimental activation volume $\Delta V^{\neq}_{exp}$ is −19.4±1.2 cm^3 mol^{-1}. Taking into account the change of the concentration of reactants under pressure, $(n - 1)\beta_T RT$, the corrected value of $\Delta V^{\neq}_{corr}$ is −17.2±1.2 cm^3 mol^{-1}.

Table 1 compares the values of enthalpy, entropy, activation volume and the volume of reaction **1a** + **2** → **3a** on 1,4-reaction centre with the parameters for reactions on 9,10-reaction centre of substituted anthracenes with maleic anhydride (MA). Note that the absolute values of the entropy of activation and the reaction volume on the 1,4-atoms of anthracene are much smaller than those for the reactions on 9,10-atoms.

References

1 J. Sauer and B. Schröder, *Chem. Ber.*, 1967, **100**, 678.
2 M. E. Burrage, R. C. Cookson, S. S. Gupte and D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1325.
3 A. I. Konovalov, I. P. Breus, I. A. Sharagin and V. D. Kiselev, *Zh. Org. Khim.*, 1979, **15**, 361 (in Russian).
4 V. D. Kiselev, I. I. Shakirova, D. A. Kornilov, H. A. Kashaeva, L. N. Potapova and A. I. Konovalov, *J. Phys. Org. Chem.*, 2013, **26**, 47.
5 V. Langer, J. Sieler and H.-D. Becker, *Z. Kristallogr.*, 1992, **199B**, 304.
6 J. M. Adams and S. Ramdas, *Acta Crystallogr.*, 1979, **35B**, 679.
7 V. D. Kiselev and A. I. Konovalov, *J. Phys. Org. Chem.*, 2009, **22**, 466.
8 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, New York, 1970, p. 180.
9 G. G. Iskhakova, V. D. Kiselev, E. A. Kashaeva, L. N. Potapova, E. A. Berdnikov, D. B. Krivolapov and I. A. Litvinov, *Arkivoc*, 2004, **xii**, 70.
10 S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
11 P. v. R. Schleyer, M. Manoharan, H. Jiao and F. Stahl, *Org. Lett.*, 2001, **3**, 3643.
12 N. Roy and J.-M. Lehn, *Chem. Asian J.*, 2011, **6**, 2419.
13 R. A. Grieger and C. A. Eckert, *J. Chem. Soc., Faraday Trans. 1*, 1970, **66**, 2579.
14 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
15 *APEX2 (Version 2.1), SAINTPlus. Data Reduction and Correction Program (Version 7.31A)*, Bruker Advansed X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, 2006.
16 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

‡ In kinetic measurements, the concentration of diene **1a**, 60–100 mmol dm^{-3}, was much higher than that of dienophile **2**, 4–8 mmol dm^{-3}. The reaction rate was followed by the change of the absorption of **2** at 540 nm (ε 245 mol dm^{-3} cm^{-1} in toluene), where **1a** and **3a** are transparent.