

Cycloaddition Reactions

Theoretical and Structural Analysis of Long C–C Bonds in the Adducts of Polycyanoethylene and Anthracene Derivatives and Their Connection to the Reversibility of Diels–Alder Reactions

Anna K. H. Hirsch,^[a, c] Philippe Reutenauer,^[a] Marc Le Moignan,^[b] Sébastien Ulrich,^[a, d] Peter J. Boul,^[a] Jack M. Harrowfield,^[a] Peter D. Jarowski,^{*[b]} and Jean-Marie Lehn^{*[a]}

Abstract: X-ray structure determinations on four Diels–Alder adducts derived from the reactions of cyano- and ester-substituted alkenes with anthracene and 9,10-dimethylanthracene have shown the bonds formed in the adduction to be particularly long. Their lengths range from 1.58 to 1.62 Å, some of the longest known for Diels–Alder adducts. Formation of the four adducts is detectably reversible at ambient temperature and is associated with free energies of reaction ranging from -2.5 to -40.6 kJ mol⁻¹. The solution equilibria have been experimentally characterised by NMR spectroscopy. Density-functional-theory calculations at the MPW1K/631 + G(d,p) level with PCM solvation agree with experiment with average errors of 6 kJ mol⁻¹ in free energies of reaction and structural agreement in adduct bond lengths of 0.013 Å. To understand more fully the cause of the reversibility and its relationship to the long adduct bond lengths, naturalbond-orbital (NBO) analysis was applied to quantify donoracceptor interactions within the molecules. Both electron donation into the σ^* -anti-bonding orbital of the adduct bond and electron withdrawal from the σ -bonding orbital are found to be responsible for this bond elongation.

Introduction

Since the discovery by Diels and Alder of the pericylic reaction between maleimides and furans,^[1] which now bears their names, the scope of the Diels–Alder (DA) reaction has widened to the point that it was described in the 1970s as the most useful and powerful synthetic tool of all.^[2] The product, or DA adduct, results from the cycloaddition of a conjugated diene to an alkene in which two bonds are formed in a single operation, affording an unsaturated six-membered ring; the mechanism of this reaction has been the subject of intense scrutiny.^[3] The DA reaction has been known to be detectibly reversible

[a]	Dr. A. K. H. Hirsch, Dr. P. Reutenauer, Dr. S. Ulrich, Dr. P. J. Boul, Prof. J. M. Harrowfield, Prof. Dr. JM. Lehn
	Institut de Sciences et d'Ingénierie Supramoléculaires (ISIS)
	Université de Strasbourg, 8 allée Gaspard Monge
	67000 Strasbourg (France)
	E-mail: Lehn@unistra.fr
[b]	M. Le Moignan, Dr. P. D. Jarowski
	Department of Physics, Advanced Technology Institute
	University of Surrey, Guildford, GU2 7XH (UK)
	E-mail: p.d.jarowski@surrey.ac.uk
[c]	Dr. A. K. H. Hirsch
	Current address: Stratingh Institute for Chemistry
	University of Groningen, Nijenborgh 7, 9747 AG (The Netherlands)
[d]	Dr. S. Ulrich
	Current address: Institut des Biomolécules Max Mousseron (IBMM)
	UMR 5247, Ecole Nationale Supérieure de Chimie de Montpellier
	8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5 (France)
	Supporting information for this article is available on the WWW under
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since its discovery, but whereas the (forward) cycloaddition reaction finds wide synthetic application, the retro-Diels-Alder (rDA) reaction has attracted considerably less attention. This is presumably because it often requires elevated temperatures, a factor that reduces its synthetic utility substantially. The factors determining both the equilibrium position and the kinetics of the forward and back reactions are not completely understood and few examples of systems displaying readily monitored rDA properties have been described. The DA reaction between isodicyclopentadiene and tetracyanoethylene, for example, has been shown to reach an equilibrium involving appreciable quantities of the reactants at 0°C,^[4] and other examples are provided in the equilibria involving certain furans and 1,1,1-trichloro-3-nitro-2-propene.^[5] There is much room for further work to elucidate the factors controlling the reversibility of DA reactions. Progress has certainly been made through computational studies largely focused on estimation of activation energies and thus upon calculation of both ground- and transition-state structures and energies.^[6-9] Recent work using the highly accurate compound method CBS-QB3 on DA reactions of maleimide^[7] has shown that the reaction thermodynamics are functionally tunable and can cover a wide range of reaction free energies based on a relatively simple chemical substitution strategy. For DA adducts formed from substituted cyclopentadienes and benzoquinone in particular,^[6c] it has also been shown that electron-density transfer from the substituents on the bridge of the adduct to the σ^* molecular orbital of the adduct bonds is an important factor in increasing the bond length, an aspect of the adduct ground-state, which can

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be considered to decrease the activation energy for the rDA step.

So as to rationally expand the range of rDA reactions, a deeper understanding of the electronic factors that influence the overall free energy change is needed. This change reflects the difference between ground-state energies of the adduct, the diene and the dienophile. In simple thermodynamic terms, given that the forward reaction takes place with a decrease in entropy, the lower the reaction enthalpy, the more favourable should be the retroreaction. Given the common observation of marked bond-length distortions within DA adducts, it is assumed that the ground-state enthalpy of the adduct is the most significant variable determining the overall enthalpy change, and hence considerable effort has been devoted both to characterisation of bond deformations in the adduct by crystallographic studies and to computation of the groundstate properties.^[6-9] These calculations necessitate the use of detailed electronic-structure theory, which we have applied in the present work to the analysis of equilibrium-constant measurements as well as to the interpretation of bond distortions apparent in several structure determinations.

Our motivation for investigating the factors controlling reversibility in the DA reaction stems from its great potential for applications in dynamic combinatorial chemistry (DCC)^[10] or controlled release.^[11] The DA reaction is synthetically versatile, thus providing access to structural and functional diversity, and, as noted elsewhere,^[12] it is a self-contained process. In seeking to broaden the scope of reactions that can be exploited in DCC, we have previously described systems based on the DA reaction of anthracenes or fulvenes with certain cyano-ole-

Abstract in French: La détermination des structures cristallographiques par diffraction des rayons X de quatre adduits de Diels-Alder issus des réactions d'alcènes substitués par des groupements nitriles et esters avec l'anthracène et le 9,10-diméthylanthracène montre que les liaisons formant les adduits sont particulièrement longues. Leurs longueurs vont de 1.58 à 1.62 Å, les classant parmi les plus longues connues pour des adduits de Diels-Alder. La formation des quatre adduits est réversible à température ambiante et est associée à des énergies libres de réaction comprises entre -2.5 et -40.6 kJmol⁻¹. Les équilibres en solution sont caractérisés expérimentalement par spectroscopie de RMN. Des calculs de la fonctionnelle de densité au niveau mPWPW91/6-31 + g(d,p) utilisant le modèle de solvatation PCM sont en accord avec les valeurs expérimentales avec des erreurs moyennes de 6 kJ mol⁻¹ en énergie libre de réaction et de 0.013 Å pour les longueurs des liaisons. Pour comprendre plus en profondeur l'origine de la réversibilité et sa relation avec la longueur importante des liaisons de l'adduit, l'analyse des orbitales naturelles de liaison (de type NBO) est utilisée pour quantifier les interactions de type donneur-accepteur au sein des molécules. Les densités électroniques augmentées dans l'orbitale anti-liante σ^* et réduites dans l'orbitale liante σ de la liaison de l'adduit ont été identifiées responsables de cet allongement des liaisons.

fins that reach an equilibrium under ambient conditions.^[12,13] To shed light on the factors operating at the molecular level, we report here X-ray structure determinations of four of these adducts, which we use in association with computational studies to analyse the thermodynamic parameters obtained from variable-temperature studies (using NMR spectroscopy) of the solution equilibria. The lengths of the bonds formed in the adduction reactions are among the longest that have been reported for DA systems. We provide compelling theoretical evidence that the bond elongation observed results from both the presence of electron-withdrawing substituents in the dienophile and the electron-donating effect of the diene substituents at the bridgehead of the aromatic group.

Results and Discussion

Synthesis of the dienes, dienophiles and their DA adducts

We based the present study on DA reactions of the commercially available dienes 9,10-dimethylanthracene (1) and anthracene (2) with three cyano-olefins 3-5 acting as dienophiles (Scheme 1). The synthesis of dienophile 3 has been reported in the literature.^[13] Dienophiles 4 and 5 were obtained in one step from commercially available starting materials (Scheme S1 in the Supporting Information). Formation of the four DA adducts [1,3], [1,4], [2,4] and [2,5] was monitored by recording the ¹H NMR spectra of equimolar amounts of the reactants in CDCl₃ solution (100 mM) at room temperature.

The reversibility of the initial DA reaction was confirmed by adding 10 equivalents of the competing dienophile tetracyanoethylene (**6**) to each reaction mixture (Scheme 2).^[14] This led to the appearance of new DA adducts [**1**,**6**] or [**2**,**6**] with a concomitant increase in the intensity of the peaks of the dieno-



Scheme 1. Diels–Alder equilibria between 3 and 1, 4 and 1 or 2 as well as 5 and 2 and their corresponding DA adducts [1,3], [1,4], [2,4] and [2,5]. a) CDCl₃, 25 $^{\circ}$ C.

Chem. Eur. J. 2014, 20, 1073 – 1080

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Scheme 2. Dynamic equilibria between adducts [1,3], [1,4], [2,4] and [2,5] with tetracyanoethylene (TCNE, 6). a) addition of 10 equiv 6 in CDCl₃ at 25 $^{\circ}$ C.

philes **3**, **4** and **5**, respectively. The extent to which the diene was abstracted by the competing dienophile **6** provided another index of the position of the dynamic equilibrium in each system studied (Table S1 in the Supporting Information).

Equilibrium thermodynamics of the DA reactions

In the systems presently described, the rDA reaction was readily detectable at room temperature, meaning that both the starting materials and the DA adducts were present and their concentrations readily measured by ¹H NMR spectroscopy. Using such data to determine the equilibrium constants over a range of temperature (Figure S1 in the Supporting Information, the thermodynamic parameters ΔG_r^0 , ΔH_r^0 and ΔS_r^0 for CDCl₃ solution were extracted (Figure S2 in the Supporting Information) for each adduct system and are given in Table 1.

electron-accepting power of the dienophile, with the exception of the about 10 kJ mol⁻¹ shift towards the DA adduct comparing the dicyano fumarates [2,4] to [1,4]. In this case, this difference is related to the increased donating power of the diene caused by the donating methyl groups or possibly by steric interactions. Stronger donor–acceptor character would likely favour more loosely associated adducts that can benefit from strong charge-transfer stabilisation while avoiding the increased steric strain that comes with tighter associations. This basic concept is well demonstrated in the analysis of the single crystal X-ray data below.

X-ray crystallography

Our studies of reversible DA reactions have dealt with a variety of DA adducts.^[12,13] The dynamic nature of the adducts, leading to the presence of the starting materials in the media in which the crystallisations take place, complicates the preparation of crystals suitable for X-ray diffraction. Thus, only the four adducts described in this study ([1,3], [1,4], [2,4] and [2,5]) afforded crystals of sufficient quality for structural analysis by X-ray diffraction (Figure 1 and Figures S3–S14 in the Supporting Information). Use of CrystalExplorer^[15] to analyse interactions within the lattices shows that, unsurprisingly, supramolecular contacts involve largely just the polar substituents (cyano, ester and nitro groups), with π - π stacking seemingly playing a minor role, if any, with the shortest centroid…centroid separation of parallel rings being more than 3.8 Å in the most likely

instance. Significantly, there are no indications of contacts to the atoms linked by the adduct bonds, implying that there are no direct solid-state influences upon the length of these bonds.

For the four present structures, the lengths of the two bonds formed between the diene and dienophile are given in Table 1 as B1 and B2 and defined in the caption of Figure 1. Where the molecules contain a C_2 symmetry element the two bonds are unequal due to asym-

Table 1. E [2,5]. ^[a]	xperimental	thermodynamic	parameters of	of DA reactions	affording D	OA adducts	[1,3], [1,4],	[2 , 4] and
Compound	d ΔH_r	ΔS_r	ΔG	, K	a	Adduc	t bond leng	gths [Å]

Compound	ΔH_r	ΔS_r	ΔG_r	K _{eq}	Adduct bond lengths [A]		engths [A]	
	[kJ mol ⁻¹]	$[J mol^{-1} K^{-1}]$	[kJ mol ⁻¹]		B1	B2	average	
[1,3]	-66.3 ± 7.3	-214.2±2.6	-2.50 ± 0.3	$(2.4\pm0.2)\times10^{0}$	1.622	1.614	1.618	
[1,4]	-164.4 ± 18.1	-449.3 ± 49.4	-30.5 ± 3.4	$(2.9\pm0.9)\times10^4$	1.591	1.588	1.590	
[2,4]	-197.9 ± 21.8	-527.5 ± 58.0	-40.7 ± 4.5	(3.3±1.7)×10 ⁶	1.579	1.584	1.583	
[2,5]	-49.8 ± 5.5	-101.5 ± 11.2	-19.6 ± 2.2	$(3.7\pm0.7)\times10^3$	1.575	1.590	1.582	
[3] The enthalpies (AH) and free energies (AG) of reaction are given at 208 K. Adducting bond lengths for R1								

[a] The enthalpies (ΔH_r) and free energies (ΔG_r) of reaction are given at 298 K. Adducting bond lengths for B1 and B2 (defined in Figure 1) determined from single crystal X-ray crystallography and their averaged values [Å] are also presented.

Relative to the measurements obtained using fulvenes as dienes, the equilibria here are shifted more towards the DA adducts.^[11] This may be due to the energetic stabilisation arising from the formation of two aromatic systems in the DA adducts derived from anthracene or derivatives thereof. The equilibration kinetics varied greatly, although the dimethylanthracene **1** gave in all cases the more rapid reaction, those with tricyanoacrylates and dicyanofumarates requiring 1 and 3 h, respectively, to reach effective equilibrium. Reactions of diene **2**, however, took several days to reach equilibrium although they were more complete. The formation of DA adduct **[1,3]** is an extreme case and was by far the least complete reaction, as indicated by its small equilibrium constant. The series follows a pattern of decreasing reaction free energy with increasing

metries induced by crystallisation, but the differences in their lengths are very small. There is an apparent correlation between the mean bond lengths and the equilibrium constants and free energies, where, in general, the shorter the adduct bonds, the greater is the equilibrium constant and more negative the free energy.

The formally single bonds between saturated carbon atoms show relatively large values, which would be slightly larger after librational corrections, and a search of the Cambridge Structural Database (CSD), using the software ConQuest,^[16] for bond lengths in similar DA adducts (Figure S15 in the Supporting Information) shows that they are amongst the highest values known. The longest bond found in this compilation was one of 1.62 Å for a fullerene adduct with 9,10-dimethylanthra-



Figure 1. X-ray crystal structures of DA adducts [1,3] (B1: C7–C20, B2: C15–C17), [1,4] (B1: C15–C17, B2: C7–C22), [2,4] (B1: C14–C15, B2: C7–C20) and [2,5] (B1: C14–C16, B2: C7–C15).

cene, in which special consequences may arise from the fullerene structure.^[17] The extreme effects in the present cases thus make these adducts especially useful for investigation of the origins of the bond extensions. The small increase in mean bond length for [1,4] compared to [2,4] (0.007 Å) has no apparent effect on the conformational situation of the fumarate substituents in the crystal structure other than distal changes to the orientation of bromine that presumably arise from crystalpacking effects. Thus, 9,10-dimethyl substitution of anthracene likely acts to increase the bond length by through-bond hyperconjugative donation. Adduct [2,5] contains the shortest adducting bond presented here for B1 (see caption of Figure 1) at 1.575 Å, which is nearly the same as B1 for [2,4]. At the same time, the adducting bond formed with the dicyanomethylene group in [2,5] (B2) is 1.590 Å, one of the longer adducting bonds, but considerably shorter than the analogous bond (B2) in [1,3] (1.614 Å) where, again, 9,10-dimethyl substitution may play a role in this extra elongation. The other adducting bond here (B1) is the longest bond presented in this study (1.622 Å) with the nitrophenyl substituents directly atminology of Hammond. Without further kinetic studies little more can be said at this time.

Computational study

In order to identify the origin of the especially long adduct bonds in molecules [1,3], [1,4], [2,4] and [2,5], we have optimised the molecular structures and analysed the reaction thermochemical parameters using density functional theory (DFT). Computed gas-phase structures are at the MPW1K/6-31 + G(d,p) density functional level of theory with solution-phase thermochemical analysis performed at this same level, but with optimisation using the PCM solvent model in CHCl₃. Further details can be found in the Experimental Section and optimised coordinates are provided in the Supporting Information (Table S2). MPW1K has been shown to give accurate structures and energies for DA-type reactions involving cyano-olefins^[18] and is the best performer out of a number of DFT methods in predicting heats of formation from atomisation energies of cyano-rich organic molecules.^[19] DA adducts of anthracene

tached. Thus, bond elongation would seem to follow the same pattern as the free energies, for which increasing electron-accepting power of the directly attached groups increases the adducting bond length.

We have also looked in detail at the pyramidalisation of the carbon atoms involved in adduct bond formation measured as the improper dihedral angle, for example C14-C17-C16-C15 and C8-C6-C14-C7 in [2,5]. The increase of this geometric feature is associated with increased p-atomic orbital character of the formed bonds, and thus, bond elongation. However, all adducting carbon atoms express improper dihedral angles of between 27° and 36° without any obvious correlation to bond length. This compares to the fully tetrahedral improper dihedral angle in methane, for example, of roughly 35°. It can be said that the adducts are "fully" formed through unsaturated C--C bonds. Additionally, the long bond lengths should be associated with relatively "late" transition-state structures in the adducting reaction and "early" transition states for the rDA reaction leading to putative low transition-state energies for the latter using the ter**Table 2.** Theoretical thermodynamic parameters of DA reactions affording DA adducts [1,3], [1,4], [2,4], [2,5], [2,6], [2,7] and [2,8] at the MPW1K/6-31 + G(d,p) level of theory with PCM solvation in CHCl₃.^[a]

Compound	$\Delta H_{\rm r}$ [kJ mol ⁻¹]	ΔS_r [J mol ⁻¹ K ⁻¹]	ΔG_r [kJ mol ⁻¹]	Adduc B1	t bond le B2	engths [Å] average	
[1,3]	-68.0	-267.4	11.6	1.604	1.596	1.600	
[1,4]	-109.1	-285.3	-24.0	1.589	1.589	1.589	
[2,4]	-105.8	-231.3	-36.8	1.567	1.567	1.567	
[2,5]	-85.6	-223.0	-19.1	1.565	1.584	1.575	
[2,6]	-87.7	-218.8	-22.5	1.581	1.581	1.581	
[2,7]	-122.0	-202.6	-61.6	1.549	1.549	1.549	
[2,8]	-102.9	-209.1	-40.6	1.559	1.559	1.559	
[a] The calculated enthalpies (ΔH_i) and free energies (ΔG_i) of reaction are given at 298 K. Adducting bond lengths for B1 and B2 (Figure 1) and their averaged value [Å] are also presented.							

with tetracyanoethylene (6), ethene (7) and 1,2-dicyanoethene (8) ([2,6], [2,7] and [2,8], respectively) were also analysed and used as base models to make comparisons (Table 2). Except for [2,4], all molecules adopt their ground-state conformation in the crystal lattices based on comparison to the minimumenergy structures computed in the gas-phase. For [2,4], the bromo-alkyl groups rotate away from the position above the adduct bonds in the compact structure they present in the solid-state to a more open structure with these chains more proximal to the anthracene ring systems having a slightly reduced molecular energy according to the gas-phase computational results. Apart from this and other small deviations in bond torsions, the gas-phase computed and X-ray structures of [1,3], [1,4], [2,4] and [2,5] are in excellent agreement (Table S3 in the Supporting Information). In particular, the adduct bonds have a mean absolute deviation (M.A.D.) of 0.013 Å (standard deviation, S.D. = 0.004 Å), confirming that the long bonds are dictated by molecular forces and are not an artefact of crystal packing. The DFT calculations give slightly shorter bond lengths in general. It should be noted that this is a comparison between gaseous molecules (C2 symmetric in some cases) to those in the solid-state with unit cell symmetry distortions. The errors are most likely beyond improving and are within reason for the present analysis. The theoretical solution-phase adduct bond lengths for compounds [1,3], [1,4], [2,4] and [2,5] as well as [2,6], [2,7] and [2,8] are listed in Table 2 along with their average bond lengths. The bond lengths with and without PCM solvation in CHCl₃ are nearly identical in all cases, also indicating that the use of single crystal X-ray data in interpreting solution-phase reaction thermodynamics is reasonable.

The calculated reaction enthalpies and free energies at 298 K are given in Table 2. All four reactions were found to be exothermic, with reaction enthalpies ranging over some $50 \text{ kJ} \text{ mol}^{-1}$ (298 K) and decreasing in the order [**2**,**4**] to [**1**,**4**] to [**2**,**5**] and [**1**,**3**]. The exothermicity of these reactions is offset by unfavourable entropic factors as expected for a bimolecular reaction, giving a range of reaction free energies of -36.8 to $11.6 \text{ kJ} \text{ mol}^{-1}$ with only [**1**,**3**] on the endergonic side. The trend in these values follows that of the experimental measurements,

although the formation of [1,3] is experimentally found to be weakly exergonic. The agreement between experimental and theoretical free energies is very good (M.A.D. = 5.9 kJ mol^{-1} , S.D. = 4.8 kJ mol⁻¹). However, the enthalpies perform less well $(M.A.D. = 56.3 \text{ kJ mol}^{-1}, S.D. = 28.0 \text{ kJ mol}^{-1})$, but the experimental data for the enthalpy and entropy expresses uncertainties in the same range. The free energies ($R^2 = 0.87$) correlate well to the average adduct bond lengths over all adducts considered. Considering only anthracene-based adducts of 2 this correlation is improved (R²=0.91). When only [2,6], [2,7] and [2,8] are considered the increasing cyano substitution and consequent increasing electron-accepting power of the central double bond of the dienophile is clearly directly related to the decrease in reaction endergonicity and an increase in adducting bond length ($R^2 = 0.94$). It should be noted, however, that [2,6] displays rather short bond lengths (1.581 Å) despite the expectation that TCNE is the most electron-accepting dienophile present in this study. The reaction free energy affording [2,6] is intermediate in value at -22.5 kJ mol⁻¹. The sterically less demanding nitrile groups clearly allow for shorter bond lengths while maintaining favourable charge-transfer interactions (vide infra).

It is expected that the electron distribution within the adduct bonds and hence their length should be sensitive to substituents such as aromatic rings and cyano groups. Patil et al.^[6c] investigated the rDA reaction of cycloadducts formed from cyclopentadiene and *p*-benzoquinone. Using the naturalbond-orbital (NBO) approach,[20] they found that the groundstate adduct-bond elongation was predominantly caused by the increase in electron population of the σ^* -anti-bonding orbital of the adduct bond. Herein, the NBO second-order perturbation analysis of the interaction energy of the two-central bonds using the gas-phase MPW1K wavefunctions show clear correlations between bond lengths. The extent of interaction between the adducting bonds with its neighbours can be seen in Figure 2 and Figure 3. In Figure 2, the stabilisation energies of all donating interactions from neighbouring groups, for example, $\sigma(CH_2-H)$, $\pi(C\equiv N)$ and $\pi(C=C)$ to each of the adducting



Figure 2. The correlation between the bond length [Å] of the adduct bonds of DA adducts [1,3], [1,4], [2,4] and [2,5] and [2,7], [2,8] and [2,6] plotted against their total σ -bonding donor (**•**) and σ^* -anti-bonding acceptor (**▲**) interaction energies.

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Chem.	Eur. J.	2014.	20.	10/3-	1080

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 $\sigma^*(C-C)$ bonds have been summed and plotted against the associated bond length. The donating interaction from a given σ (C–C) to the relevant neighbours, for example, σ *(C–N), $\pi^*(C \equiv N)$, $\sigma^*(C - C)$ and $\pi^*(C = C)$ are also summed and plotted against the bond length. We assume that donation into the $\sigma^*(C-C)$ adducting bond will increase the anti-bonding character between these atomic centres leading to an elongation in bond length. In addition, donation from the occupied adducting bonds $\sigma(C-C)$ to its neighbours will lower their electron occupancy also leading to adducting-bond elongation. Together, these effects should contribute to a weaker interaction between the two entities, as the interaction energy (bond enthalpy) should decrease with increasing bond length according to the Morse potential relationship. When the adducting σ -bond interacts more strongly with its neighbours, the bond length increases as in Figure 2 concomitant with the greater interaction energies for the accepting σ^* -orbital. When the two factors are working roughly together the result is the longest bond lengths of the series presented herein, around 1.6 Å. A correlation is also observed when plotting the NBO electronoccupancy values against the adduct bond length (Figure 3). It is found that a lower electron occupancy in the donating $\sigma(C-$ C) orbital leads to a longer bond length. In contrast, a higher electron occupancy of the accepting $\sigma^*(C-C)$ orbital of the adduct bond results in shortened bond lengths.



Figure 3. The correlation between the adduct bond lengths of DA adducts [1,3], [1,4], [2,4], [2,5], [2,6], [2,7] and [2,8] plotted against their NBO occupancy values in the σ - (**n**) and σ *-orbitals (**A**).

Looking at the specific interactions, Figure 4 shows a generic energy-level diagram for all adducts, highlighting the key interactions between orbitals with their relative magnitudes indicated by the arrow thickness. The relative arrow thicknesses are averaged from the results of all eight molecules from the NBO second-order perturbation analysis. Solid arrows indicate donation into the adduct σ^* -anti-bonding orbital from all others, $\sigma^*(C-C)$, and dashed arrows indicates donation from the adducting σ -bond, $\sigma(C-C)$, into all others.

Flanking interactions from the π system of anthracene (π (C= C)) are strongly donating to the σ^* (C-C) adducting bonds and should lead to an increase in their anti-bonding character and thus bond length. Their average value is at about 10 kJ mol⁻¹.



Figure 4. A generic molecular-energy-level diagram for DA adducts highlighting the magnitude of the donating interactions *to* (solid) and accepting interaction *from* (dashed) the adducting bonds to their neighbours.

More minor contributions from donating interactions from the nitrile triple bonds (π (C \equiv N)) and the σ -bond donation from the C–O σ -bond (σ (C–O)) of the ester functionalities in [1,4], [2,4] and [2,5] to σ *(C–C) are also present and could result in further elongation of the adducting bonds. The methyl C–H donation (σ (CH₂–H)– σ *(C–C)) of the dimethyl anthracene adducts are also particularly strong at about 20 kJ mol⁻¹ confirming the analysis above of the strong hyperconjugative effects for these groups. Also, the Ph(*p*-NO₂) group interaction (π (C=C)– σ *(C–C)), which donates electrons through its π -bonds towards the σ *-anti-bonding orbital are present but of less importance for [1,3].

Donation from the adducting C–C σ -bond (σ (C–C)) into the anti-bonding orbitals $\sigma^*(C-N)$ and $\pi^*(C\equiv N)$ of the nitrile group, as well as to $\sigma^*(C-C)$ and $\pi^*(C=C)$ of the anthracene aromatic rings will all serve to remove electron density from the adduct bond thereby also leading to elongation of the adduct bond length. The interaction energies with the $\sigma^*(C-N)$ and $\pi^*(C \equiv N)$ are the largest observed at 19 and 20 kJ mol⁻¹, respectively. Thus considering the major contributors to the interaction energies, the combined donation into the nitrile σ^* and π^* -orbitals is the largest thermal driving force with the greatest potential effect on bond-length elongation. This effect is augmented considerably by strong donation into the $\sigma^*(C-$ C) orbital of the adduct bond by flanking aromatic double bonds and in some cases hyperconjugative interactions from the 9,10-dimethyl groups of anthracene. Thus, when both the donating and accepting interactions are strong the bond length will increase and the reaction free energy will decrease. This can be considered as an increase in the ionic character of the interaction between the diene and dienophile moving away from formally covalent bonds (strong bonds) towards ionic or charge-transfer associations as in a molecular complex (weak bonding). Again, [2,6] would appear to be a special case having shorter adducting bond lengths and strong acceptor interactions due to the ability of the less voluminous nitrile to accommodate shorter bonds.



Conclusions

NBO calculations on compounds [1,3], [1,4], [2,4] and [2,5] as well as [2,7], [2,8] and [2,6] have provided calculated bond lengths to compare with experimental data for compounds [1,3], [1,4], [2,4] and [2,5], which are in excellent agreement. Relative reaction free energies have been calculated and agree with those collected from experimental work. The significant energy values for interactions that occur between the donating σ -bonding orbital of the adduct bond and other substituents as well as the interactions of these groups with the accepting σ^* -anti-bonding orbital of the adduct bond are shown. Strong correlation between the bond length of the adduct bond and the energy and electron-occupancy values calculated is also observed. Bond elongation results from the presence of both highly electron-withdrawing substituents in addition to the large electron-donating effect of the anthracene ring system and the attachment of electron-donating substituents. Finally, we have undertaken this study, in part, due to an increasing interest in the limits of our conventional knowledge of bonding.^[21] Recent studies have shown that extremely long C-C bonds can exist both in the presence^[22] and absence^[23] of supporting interactions. In this context, bond formation in the present DA adducts is supported by strong ionic interaction between the donor and acceptor reactants that allows for a stable bond at increased distance, thereby minimising repulsive terms.

Experimental Section

Computational details

Post Hartree-Fock calculations were implemented with the Gaussian 09 software package^[24] to optimise final molecular structures. Initial conformational analysis was performed in advance with Macromodel.^[25] The generalised gradient approximation (GGA) hybrid exchange-correlation density functional MPW1K (mPWPW91) with 42.8% Hartree–Fock exact-exchange (X=42.8) and with the 6-31+ G(d,p) basis set was used to optimise the structures of all molecules studied herein. For [1,3], [1,4], [2,4], [2,5], [2,6], [2,7] and [2,8], conformational searches, using as initial coordinates those from the crystal structures in the first four cases, were performed with MacroModel to identify any significant alternative conformers. Structures within approximately 10 kJ mol⁻¹ of the lowest structure identified using the MMFF molecular mechanics force field were further optimised at the MPW1K/6-31+G(d,p) level in the gasphase and also with PCM solvation in CHCl₃ and their harmonic frequencies determined at these same levels to establish that these structures were indeed ground-state minima and for use in obtaining thermochemical reaction parameters, which are reported without scaling. All thermochemical analysis is on solvated structures. The PCM model accounts for solvent effects using a polarisable continuum of overlapping spheres to treat electrostatic forces without explicit solvent molecules. Optimised structural coordinates can be found in the Supporting Information along with the computed energies and thermal corrections (Table S2 in the Supporting Information). NBO calculations were performed on the gasphase optimised structures using the population analysis as implemented in Gaussian 09.[24]

General experimental details

Reagents were used as received from commercial suppliers. All reactions were carried out under an atmosphere of dry N2. Yields refer to homogeneous, analytically pure (¹H NMR spectroscopy) compounds and have not been optimised. Melting points were measured on a Büchi B-540 melting-point apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance spectrometer at 400 or 100 MHz, respectively, and are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant J in Hz, number of protons). The residual deuterated solvent was used as the internal reference (CDCl₃: $\delta_{\rm H}$ = 7.26 ppm, $\delta_{\rm C}$ = 77.0 ppm). The resonance multiplicity is described as s = singlet, d = doublet, t = triplet, q =quartet, br = broad, m = multiplet. High-resolution mass spectra were recorded on a Bruker Micro TOF or a Bruker AutoFlex II mass spectrometer at the Service de Spectrométrie de Masse (Université de Strasbourg). X-ray crystallography was performed at the Service de Radiocristallographie (Université de Strasbourg).

Synthesis of the Diels-Alder adducts

General procedure A: Dienophile (0.3 mmol) was added to a solution of diene in CHCl₃ (100 mM, 3 mL). The reaction mixture was left to stir at 25 $^{\circ}$ C, overnight, the solvent then evaporated and the residue was purified by recrystallisation.

General procedure B: A solution of the diene in $CHCl_3$ (200 mM, 3 mL) was added to a solution of the dienophile in $CHCl_3$ (200 mM, 3 mL). The reaction mixture was left to stir at 25 °C, overnight, the solvent then evaporated and the residue was purified by recrystallisation.

Compounds and characterisation

15,16-Bis(2-bromoethyl) 15,16-dicyanotetracyclo[6.6.2.0.0]hexadeca-2,4,6,9,11,13-hexaene-15,16-dicarboxylate ([**2**,4]): Using GPA [**2**,4] was obtained as a crystalline solid from $CHCl_3/iPr_2O$ 1:1. M.p. 133–135 °C; ¹H NMR (400 MHz, [D]CHCl_3, 25 °C): $\delta = 7.55-7.57$ (m, 2H), 7.43–7.44 (m, 2H), 7.31–7.21 (m, 4H), 4.93 (s, 2H), 4.54 (t, J = 6.4, 4H), 3.65–3.43 ppm (m, 4H); ¹³C NMR (100 MHz, [D]CHCl_3, 25 °C): $\delta = 163.32$ (2C), 138.58 (2C), 137.10 (2C), 127.99 (4C), 127.96 (2C), 127.74 (2C), 125.38 (2C), 115.19 (2C), 67.16 (2C), 56.39 (2C), 50.63 (2C), 27.12 ppm (2C); HRMS (ESI): m/z calcd for $C_{24}H_{18}Br_2N_2NaO_4^+$: 580.951 ([M+Na]⁺); found: 580.948.

15,16-Bis(2-bromoethyl) 15,16-dicyano-1,8-dimethyltetracyclo[6.6.2.0.0]hexadeca-2,4,6,9,11,13-hexaene-15,16-dicarboxylate ([1,4]): Using GPB [1,4] was obtained as a crystalline solid from CHCl₃/*n*-heptane 1:1. M.p. 155–157 °C; ¹H NMR (400 MHz, [D]CHCl₃, 25 °C): δ = 2.28 (s, 3 H), 3.45–3.36 (dt, *J* = 6.1, 12.2, 2H), 3.50 (dt, *J* = 12.2, 6.2, 2H), 4.42 (dt, *J* = 12.2, 6.2, 2H), 4.56 (dt, *J* = 12.2, 6.1, 2H), 7.40–7.29 (m, 4H), 7.50–7.40 (m, 2H), 7.53–7.55 ppm (m, 2H); ¹³C NMR (100 MHz, [D]CHCl₃, 25 °C): δ = 163.34 (2C), 141.25 (2C), 139.94 (2C), 127.58 (2C), 124.81 (2C), 122.97 (2C), 115.36 (2C), 67.17 (2C), 63.04 (2C), 48.59 (2C), 27.27 (2C), 15.05 ppm (2C); HRMS (ESI): *m/z* calcd for C₂₆H₂₂Br₂N₂NaO₄⁺: 608.982 ([*M*+Na]⁺); found: 608.980.

Prop-2-yn-1-yl 15,16,16-tricyanotetracyclo[6.6.2.0.0]hexadeca-2,4,6,9,11,13-hexaene-15-carboxylate ([**2,5**]): Using GPA [**2,5**] was obtained as a crystalline solid from CHCl₃/*n*-heptane 1:1. M.p. 148–149 °C; ¹H NMR (400 MHz, [D]CHCl₃, 25 °C): δ = 7.31–7.59 (m, 8H), 5.02 (s, 1H), 4.99 (s, 1H), 4.88 (dd, *J*=15.4, 2.4, 1H), 4.73 (dd, *J*= 15.4, 2.4, 1H), 2.60 ppm (t, *J*=2.4, 1H); ¹³C NMR (100 MHz, [D]CHCl₃, 25 °C): δ = 161.64, 137.72, 135.96, 135.64, 134.67, 129.34, 128.94 (2C), 128.53, 127.92, 126.65, 126.22, 125.94, 114.06, 112.26, 111.88, 77.60, 74.90, 57.50, 55.82, 53.68, 49.82, 45.05 ppm; HRMS





(ESI): m/z calcd for $C_{23}H_{13}N_3NaO_2^+$: 386.090 ([M+Na]⁺); found: 386.086.

15-[4-Nitrophenyl]-1,8-dimethyltetracyclo[6.6.2.0.0]hexadeca-

2,4,6,9,11,13-hexaene-15,16,16-tricarbonitrile] **([1,3])**: Using GPA **[1,3]** was obtained as a crystalline solid from CHCl₃/MeOH 1:1. M.p. 55–57 °C; ¹H NMR (400 MHz, [D]CHCl₃, 25 °C): δ = 7.36–7.67 (m, 12H), 2.48 (s, 3H), 1.90 ppm (s, 3H); ¹³C NMR (100 MHz, [D]CHCl₃, 25 °C): δ = 148.87, 142.68, 139.68, 139.52, 138.38, 137.94, 130.84, 130.11, 129.17, 129.07, 128.74, 128.58, 125.55, 125.23, 124.94, 124.69, 124.42, 123.67, 117.20, 112.77, 112.32, 63.50, 50.90, 50.60, 16.09, 15.44, 14.31 ppm; MS (ESI): *m/z* calcd for C₂₇H₁₈N₄NaO₂⁺: 453.4 ([*M*+Na]⁺); found: 453.2.

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Keywords: bond lengths · cycloaddition · density functional calculations · natural bond orbitals · X-ray diffraction

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