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Kinetics and regioselectivity in the Diels–Alder reaction of fulleroids *vs.* methanofullerene and C_{60}†

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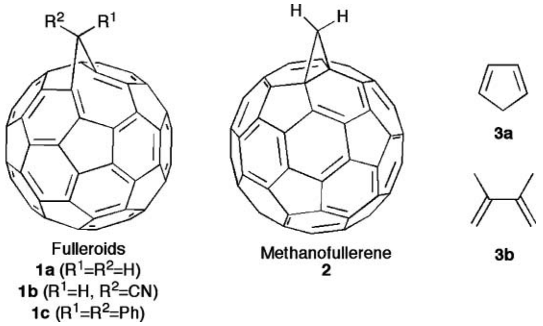
Fulleroids, obtained from the 1,3-dipolar cycloaddition of fullerene with a diazoalkane, have a [5,6]-open methylene bridge and two highly twisted bridgehead double bonds. The [H,H]- and [H,CN]-substituted fulleroids were found to display significantly enhanced and regioselective Diels–Alder addition as compared with the [6,6] closed methanofullerene and C_{60} with 2,3-dimethyl-1,3-butadiene, but reduced and nonregioselective addition with cyclopentadiene. NMR analysis of the 1 : 1 adduct and quantum calculations indicated that the high reactivity and the regioselective addition are due to π-orbital misalignment at the bridgehead double bond.

Introduction

Since the pioneering work by Wudl, Prato, and Bingel, cycloadditions and nucleophilic additions of fullerenes have attracted particular attention in view of the syntheses of many varieties of chemically modified derivatives.[1] In most of these reactions, a second addition at the reactive [6,6] bond leads to the formation of several regioisomers of bisadducts.[2] The number of possible regioisomers dramatically increases with an increasing number of introduced addends. Accordingly, the investigation of such global regiochemistry is one of the most important topics in recent fullerene chemistry.[3] Furthermore, the understanding of the factors which control the regioselectivity provides a useful insight into the further development of fullerene chemistry.

Among the established Huisgen reaction of C_{60}, diazoalkanes are known to provide the [5,6] open fulleroid **1** (60π system) and the [6,6] closed methanofullerene **2** (58π system) *via* a nitrogen release from the primary adduct pyrazolines.[4] Knowledge of the reactivity and the addition patterns (regiochemistry) of **1** and **2** will aid understanding of the physicochemical properties of these differently inflated fullerenes. In our literature search for the 58π conjugated system, the regioselectivity and the product distributions have been investigated for several typical addition reactions.[1e,2a,c] However, very little is known for the corresponding reaction of the 60π fulleroid system.[5,6]

Herein, we have investigated the kinetics and regiochemistry of Diels–Alder (DA) reactions of fulleroids **1a–c** with typical cyclic and acyclic 1,3-dienes **3a**,**b** (Scheme 1). In comparison with the reactions of methanofullerene **2** as well as the pristine C_{60},[2b,7] we have found that **1a**,**b** show a significant high reactivity at the bridgehead double bond due to the π-orbital misalignment like the anti-Bredt olefin.

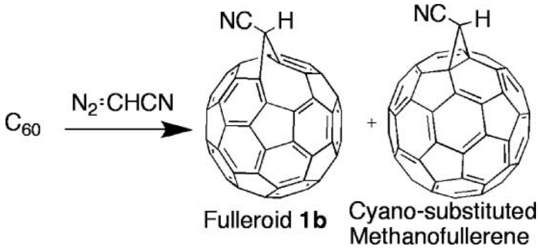


Scheme 1

Results and discussion

Synthesis and identification of fulleroids

The compounds **1a–c** and **2** were synthesized according to the literature methods[4d,8] (Scheme 2) and separated by preparative HPLC. The ^{1}H-NMR analysis of new compound **1b** indicated that the diagnostic methine H (3.8 ppm) lies above the hexagon ring (Fig. S1, See ESI†).[4d,9]



Scheme 2 Synthesis of fulleroid **1b**.

Kinetic measurements

The kinetic measurements were performed in duplicate by monitoring the decrease of **1a–c**, **2**, and C_{60} by HPLC under the pseudo-first-order conditions as described.[8] The plots of ln([**1a**]$_0$/[**1a**]) *vs.* time (Fig. 1) showed the first-order linearity ($R^2 > 0.98$), suggesting that the possible retro Diels–Alder reaction[7c] should be

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† Electronic supplementary information (ESI) available: Experimental procedure, NMR spectrum of **1b** and 1 : 1 adduct of **1b** and **3b**, and MO mappings of **1b**. See DOI: 10.1039/b918005b

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Table 1 Second-order rate constants ($10^5\ k/\mathrm{M^{-1}\ s^{-1}}$) and the relative rate ratios k/k_0 (*vs.* C_{60} reaction, in parentheses) for the DA reactions of fullerenes with dienes **3a**,**b** at 30 °C in toluene[a]

	C_{60}	**1a**	**1b**	**1c**	**2**
3a	19800 (1.00)	8220 (0.42)	21700 (1.10)	8560 (0.43)	7150 (0.36)
3b	7.70 (1.00)	195 (25.3)	297 (38.6)	4.95 (0.64)	2.93 (0.38)

[a] The k values are the average of two measurements. Error limit of k is ±2%

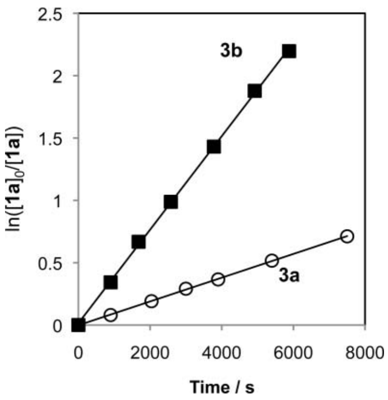
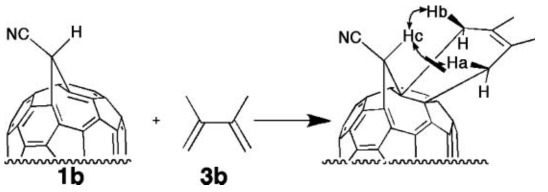


Fig. 1 The first-order plots of ln($[\mathbf{1a}]_0/[\mathbf{1a}]$) with excess dienes **3a-3b**.

negligible under these low temperature reaction conditions. The calculated second-order rate constants ($k/\mathrm{M^{-1}\ s^{-1}}$) are collected along with the relative rate ratios k/k_0 (*vs.* C_{60} reaction, in parentheses) in Table 1. A survey of the table indicated several points: (1) cyclopentadiene **3a** is more reactive than 2,3-dimethyl-1,3-butadiene **3b** for all dienophiles used; (2) interestingly, the fulleroids **1a**,**b** provided about 25- and 39-fold larger k/k_0 for the less reactive **3b**, but rather reduced or almost the same k/k_0 for the highly reactive **3a**; (3) the slightly higher reactivity of **1b** than **1a** may be ascribed to the electron withdrawing CN substituent; (4) In contrast, lower reactivity of **1c** than **1a** are presumably ascribed to the steric hindrance of the bulky phenyl substituents; (5) the methanofullerene **2** displayed *ca.* 3-fold reduced k/k_0 for both the **3a** and **3b**.

Isolation and NMR analysis of the 1 : 1 adduct

Why do the [5,6] open **1a**,**b** enjoy enhanced reactivity with only **3b**? This intriguing finding can be explained by assuming that **3b** exclusively reacts at the bridgehead double bond of fulleroids as represented for **1b** (Scheme 3). To confirm this, we followed the reaction by HPLC and attempted to isolate the 1 : 1 adducts of **1a**,**b** with **3a**,**b** under the appropriate low conversion of fullerenes.



Scheme 3

On HPLC analysis, the reaction of **1a** and **1b** showed only one adduct with **3b**, but a regioisomeric mixture of several inseparable 1 : 1 adducts with **3a** (Fig. 2). However, a similar reaction of **1c** and **2** with **3a**,**b** yielded a mixture of inseparable regioisomers of possible 1 : 1 adducts as previously reported for the bisaddition reactions of fullerene.[2] The 1 : 1 adduct of **1b** with **3b** was easily isolated by preparative HPLC and the C_1 symmetry structure was deduced from the ^{1}H- and ^{13}C-NMR spectroscopy (Fig. S2†).[10] The addition at the bridgehead double bond was ascertained by the appearance of NOE peaks (Fig. S6†). Consistently, the DFT calculation (B3LYP/6-31G*)[11] revealed the relevant two hydrogen atoms (H_a and H_b) of the adduct of **1b** with **3b** have enough proximity to the methano-bridged H_c (2.44 and 3.35 Å) as denoted in Fig. 3.

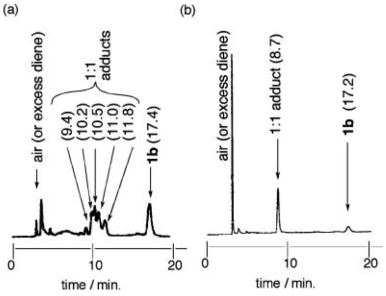


Fig. 2 HPLC trace (Buckyprep, eluent: toluene) of the samples of **1b** with (a) **3a** (reaction time; 25 min) and (b) **3b** (49 min), The numbers in parentheses are the retention times.

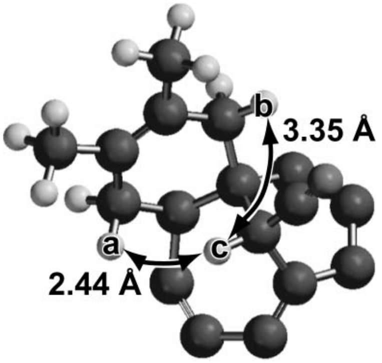


Fig. 3 Estimated structures by B3LYP/6-31G* calculation around bridgehead of Diels–Alder reaction products of **1b** with 2,3-dimethylbutadiene **3b**. The arrows indicate NOE active H–H adjacency.

Rationale for the high regioselectivity of fulleroids 1a and 1b

It is reported that the secondary cycloaddition of the C_{60} monoadducts proceeds to provide the complex regioisomeric mixtures *via* the nonregioselective addition at the remaining [6,6] conjunct double bonds as found in Bingel reactions,[2a,c] DA reactions,[2b] and Huisgen cycloadditions.[2c,d] Therefore, the high regioselectivity of the DA reaction of fulleroids **1a**,**b** with **3b** is unprecedented and the reason why this phenomenon occurs only for diene **3b** deserves to be elucidated.

Since the DA reaction of fullerenes involves the electrophilic orbital interactions with dienes in the concerted $[4\pi_s + 2\pi_s]$ cycloaddition, we have resorted to the DFT calculation[11] to get information on the reactivity. Although the LU and LU+1 have no appreciable MO coefficients at the bridgehead double

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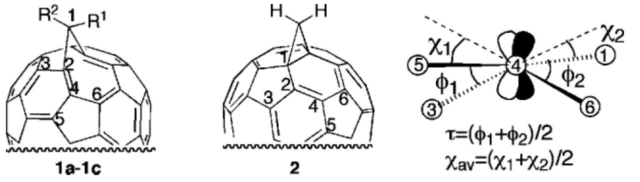
Table 2 Calculated orbital energies (eV, by B3LYP/6-31G*), twisting angles (τ) and averaged pyramidality angles (χ_{av}) at the bridgehead double bonds of **1a–c** and the comparable bond of **2**

	E_{LU}	E_{LU+1}	E_{LU+2}	τ (°)	χ_{av} (°)
1a	−3.14	−3.11	−3.08	32.28	30.25
1b	−3.36	−3.36	−3.34	32.23	31.13
1c	−3.10	−3.07	−3.04	33.06	28.72
2	−3.13	−3.08	−2.85	5.17	39.30



bond (Fig. S7†), the LU+2 of **1a**,**b** seems to contribute the DA reaction irrespective of the 0.02–0.06 eV higher energy (Table 2). Incidentally, the LU with the appreciable MO coefficients in the equatorial region is still silent in the reaction with **3b**.

The DFT calculation also showed the bridgehead double bond is highly twisted like anti-Bredt olefins.[12] Such double bonds have higher reactivity than planar ones on epoxidation[13] and 1,3-dipolar cycloaddition with azides.[14] Similarly, the DA-addition of the fulleroids should be favored at the bridgehead by the release of the distortional energy.

The high reactively of the anti-Bredt olefins is argued to come from two strain effects; (i) π-orbital misalignment[15] and (ii) pyramidalization of sp^2-carbon.[16] Pyramidality was observed not only in anti-Bredt olefins but ball-shaped π-conjugated compounds such as fullerenes. Indeed, a computer simulation showed the pyramidality plays a key role in the reactivity of DA reaction of pristine C_{60}.[17] However, Meier *et al.* reported that π-orbital misalignment is responsible for the regioselective hydrogenation at the bridgehead double bond of **1a**.[5] In our case, the calculation indicated the twisting angles (τ) of the bridgehead C2=C4 bond of **1a–c** are considerably larger than that of the corresponding double bond C2=C4 of **2**. By contrast, the averaged pyramidality angles (χ_{av}) of **1a–c** are rather smaller than that of **2** as depicted in the Newman projection (Table 2).[18,19] Accordingly, we consider that the π-orbital misalignment plays a crucial role in the enhanced reactivity of the fulleroids.

Transition state calculation of fulleroids and dienes

Transition state geometry for the bridgehead addition was also evaluated to disclose the marked difference in regioselectivity between dienes **3a** and **3b**. The rigid **3a** was found to display the unfavorable orbital interaction with the responsible bridgehead LU+2 double bond of **1** (Fig. 4a), instead being forced to react at the other probable [6,6] conjunct bonds. The reactivity of the latter bonds seems to depend on the levels of the unoccupied orbitals delocalized on them, as well as the total number of reaction sites (30 sites to 28 sites); the higher LUMO levels of **1a** (−3.14 eV) and **1c** (−3.10 eV) than that of C_{60} (−3.23 eV calculated by B3LYP/6-31G*) lead to lower reactivity (k_{rel} = 0.42 and 0.43, respectively), whereas lower the LUMO level of **1b** (−3.36 eV) leads to higher reactivity (k_{rel} = 1.1). On the other hand, the acyclic **3b** can allow a favorable orbital overlapping due to the torsional freedom of the diene linkage C_a–C_b–C_c–C_d (Fig. 4b,c). For fulleroid **1c**, the bulky diphenyl methylene bridge should prevent any dienes from attacking the bridgehead double bonds, reducing the reactivity with **3a** and **3b**.

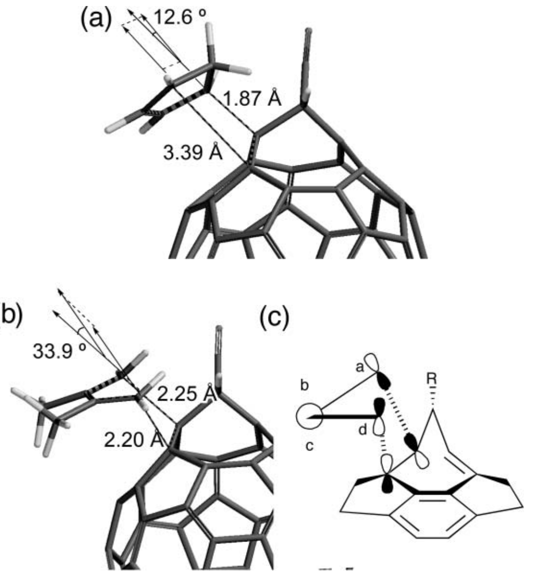


Fig. 4 (a) Less favorable transition state geometry for **1b** and the rigid cyclopentadiene **3a** (imaginary frequency: −516 cm^{-1}); (b) favourably distorted transition state geometry for **1b** and the flexible 2,4-dimethyl-1,3-butadiene **3b** (−691 cm^{-1}); (c) distorted orbital interaction for DA reaction of fulleroids **1** (in part) at the bridgehead double bond. Based on the semiempirical PM3 calculation.

Conclusions

The less sterically-hindered fulleroids are more reactive than methanofullerene and display a characteristic regioselective addition at the bridgehead double bond for the dienes allowing the topologically favorable MO interaction. In addition, this finding will provide useful information for the application of [5,6]-open fulleroids as starting materials for further ring-enlargement reactions as is known for azafulleroids.[6]

Experimental

Synthesis of fulleroid 1b

To a solution of C_{60} (100 mg, 0.139 mmol) in *o*-dichlorobenzene (10 mL) was added a concentrated solution of cyano diazomethane (1.2 equiv.).[20] The reaction solution was stirred for 30 min at 80 °C in the dark. The reaction was monitored by HPLC on a Buckyprep column with toluene as eluent. The fulleroid **1b** was separated from C_{60} and cyano-substituted methanofullerene as well as the multiadducts by HPLC on a Buckyprep column with toluene. The isolated yield was 6% based on used C_{60} and the spectral data as follows. ^{1}H-NMR (1 : 1 CS_2 : $CDCl_3$, 270 MHz): δ 3.82 (s, 1H); ^{13}C-NMR (1 : 1 CS_2 : $CDCl_3$, 67.5 MHz): δ 147.2 (2C), 144.8 (2C), 144.6 (2C), 144.2 (1C), 144.0 (2C), 143.8 (2C), 143.7 (2C), 143.7 (2C), 143.6 (2C), 143.5 (2C), 143.3 (2C), 143.3 (2C), 143.3 (2C), 143.3 (2C), 143.1 (2C), 143.1 (2C), 142.8 (2C), 141.9 (2C), 141.9 (2C), 141.8 (2C), 141.0 (1C), 140.4 (2C), 139.1 (2C), 138.8 (2C), 138.3 (2C), 138.3 (1C), 137.5 (2C), 133.8 (2C), 132.8 (2C), 128.2 (1C), 126.8 (2C), 118.0 (CN), 40.2 (CH). UV-Vis (Toluene) λ_{max}

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541, 597 nm. HR-MASS Calced for ($C_{60}NH$) 759.0109, Found 759.0125.

Kinetic measurements for the Diels–Alder (DA) reactions of fulleroids with 1,3-dienes

For the sake of simplicity, the kinetic measurement was carried out under pseudo-first-order conditions, using a large excess of dienes (30–100000 equiv.) with respect to fulleroid ($0.723–4.43 \times 10^{-3}$ mM). Thus, a toluene solution (1 mL) of the excess diene was rapidly introduced into a screw-capped test tube containing a 1 mL toluene solution of fulleroid, which was preheated at 30 °C in a thermostated bath. The reaction solution was heated for the requisite time (~10 min.) at 30 ± 0.05 °C and a constant aliquot (10 μL) was removed by a microsyringe at regular time intervals for HPLC analysis as described below. The progress of reactions was followed by monitoring the decrease of the absorption peak intensity of fulleroid with an HPLC instrument equipped with a UV operating at 310 nm, a calculating integrator, and an analytical Buckey-prep column (4.6 mm × 250 mm). Toluene was used as a mobile phase. Monitoring the kinetic reaction by HPLC showed the gradual increase of 1 : 1 DA adduct (several 1 : 1 adducts were found for cyclopentadiene **3a** probably due to the regioisomeric mixture) accompanied by the first-order decay of fulleroid as represented for the reaction of **1b**. The natural logarithmic plot of the signal intensities of the remaining fulleroids relative to those of the first aliquots ($t = 0$) gave a linear correlation against time over 50% completion of the reaction. The obtained pseudo-first order rate constants k_{obs} from the slope were divided by the corrected concentration of the dienes to provide the second-order rate constant k.

1 : 1 Addition product of cyano-substituted fulleroid 1b and 2,3-dimethyl-1,3-butadiene 3b

^{1}H-NMR (1 : 1 CS_2 : $CDCl_3$, 270 MHz): δ 5.71 (s, 1H), 4.33 (d, J = 19.8 Hz, 1H), 4.23 (d, J = 19.8 Hz, 1H), 4.23 (d, J = 20.8 Hz, 1H), 3.76 (d, J = 20.8 Hz, 1H), 2.20 (s, 3H), 2.11 (s, 3H); ^{13}C-NMR (1 : 1 CS_2 : $CDCl_3$, 67.5 MHz): δ 155.8 (1C), 150.4 (1C), 149.1 (1C), 148.1 (1C), 147.8 (1C), 147.3 (1C), 147.1 (1C), 146.7 (1C), 146.6 (1C), 146.2 (1C), 146.0 (1C), 145.9 (1C), 145.7 (1C), 145.7 (1C), 145.6 (1C), 145.6 (1C), 145.5 (1C), 145.0 (1C), 144.8 (1C), 144.7 (1C), 144.4 (1C), 144.3 (1C), 144.2 (1C), 144.1 (1C), 143.2 (1C), 143.2 (1C), 143.0 (1C), 143.0 (1C), 142.9 (1C), 142.8 (1C), 142.5 (1C), 142.1 (1C), 142.0 (1C), 141.5 (1C), 141.3 (1C), 140.9 (1C), 140.8 (1C), 140.4 (1C), 139.5 (1C), 139.2 (1C), 138.3 (1C), 138.2 (1C), 138.1 (1C), 137.2 (1C), 135.8 (1C), 135.5 (1C), 135.2 (1C), 135.0 (1C), 131.5 (1C), 129.1 (1C), 128.8 (1C), 128.7 (1C), 128.1 (1C), 128.1 (1C), 124.8 (1C), 124.7 (1C), 117.8 (CN), 69.8 (1C), 48.0 (CH_2), 47.3 (CH_2), 46.5 (1C), 38.4 (CH), 19.3 (CH_3), 18.4 (CH_3). This compound cycloreverted to the component diene and C_{60} under the high temperature MASS conditions. The ^{1}H, ^{13}C NMR, COSY, HMBC, HMQC and NOESY charts are shown in the supporting information.

Acknowledgements

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19 Haddon suggested the pyramidalization angle ($\theta_p = \theta_{\sigma\pi} - 90°$) from the π-orbital axis vector (POAV) analysis where the vector makes equal angle to the three σ-bonds at the conjugated carbon atom. See ref. 16.

20 Cyanodiazomethane was prepared from aminoacetonitrile hydrochloride and $NaNO_2$. The crude product was used immediately without further purification for the sake of safety. The introduced amount was not so large with respect to fullerene, in order to suppress the formation of bisadducts.

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