Unprecedented thermal rearrangement of push-pull-chromophore-[60]fullerene conjugates: formation of chiral 1,2,9,12-tetrakis-adducts[†]

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Push-pull-chromophore-[60]fullerene conjugates featuring N,N-dimethylanilino-substituted 1,1,4,4-buta-1,3-dienes directly attached to the carbon sphere are transformed into chiral 1,2,9,12-tetrakis-adducts by a novel thermal rearrangement pathway.

Chemical functionalisation of fullerenes remains of great interest not only for deciphering fundamental aspects concerning the reactivity of curved π -electron systems but also for the production of covalent derivatives for use as organic materials in photovoltaic devices and solar cells.¹ We recently reported the synthesis of push-pull-chromophore-fullerene conjugates by [2+2] cycloaddition of electron-deficient olefins, such as TCNE (tetracyanoethene), to the electron-rich CC triple bond of 4-(N,N-dimethylamino)phenylethynyl[60]fullerene, followed by cycloreversion.² In the presence of a vicinal methyl group on the surface of the carbon sphere, the barrier for rotation around the central CC single bond of the fullerene-appended, N,N-dimethylanilino (DMA)-substituted 1,1,4,4-tetracyanobuta-1,3-diene moiety becomes slow and the axially chiral conjugate can be optically resolved at ambient temperature and the chiroptical properties of the enantiomers characterised. This finding motivated us to introduce bulkier vicinal addends to further raise the barrier for rotation and increase the optical stability of the conjugates. During this work, we encountered an unprecedented thermal rearrangement yielding the formation of C_1 -symmetric 1,2,9,12-tetrakisadducts of [60]fullerene,³ which is reported below.

The synthesis of the new conjugates is depicted in Scheme 1. The precursors **1a**,**b** with vicinal ethyl (Et) or isopropyl (^{*i*}Pr) addends next to the ethynyl residue, were prepared in 22% and 24% yield, respectively, by addition of lithiated DMA-acetylene to C₆₀, followed by ethylation (EtI) or isopropylation (^{*i*}PrI).⁴ Stirring a chlorobenzene solution of **1a**,**b** in the presence of TCNE at 20 °C led to a color change of the solutions from brown to red and afforded the formation of the charge-transfer (CT) chromophore–fullerene conjugates (±)-**2a**,**b** featuring nonplanar push–pull-substituted buta-1,3-dienes directly attached to the carbon sphere. The decreased yield of (±)-**2b** (21%) compared to (±)-**2a** (55%), is due to the larger steric hindrance of the bulkier vicinal ^{*i*}Pr group on the fullerene surface. The molecular structures of (\pm) -**2a,b** were characterised by ¹H and ¹³C NMR spectroscopy. Atropisomerism about the CC single bond connecting the buta-1,3-diene moiety to the fullerene core is observed by ¹H NMR analysis of (\pm) -**2a**. The two atropisomers of C_1 -symmetric (\pm) -**2a** appear in a 1.0:0.19 ratio at 296.6 K. Increased broadening of the peaks is observed upon heating the sample to 366.0 K (see Fig. 4 (ESI†)). In contrast, the ¹H NMR spectrum of (\pm) -**2b** only shows one C_1 -symmetric atropisomer: the equilibrium is apparently shifted because of the steric repulsion between the ^{*i*}Pr group on C₆₀ and the push–pull-chromophore moiety.

In sharp contrast, heating a solution of 1a,b in chlorobenzene to reflux (132 °C) in the presence of TCNE led to a drastic color change from brown to green and afforded the formation of the 1,2,9,12-tetrakis-adducts (±)-3a,b in 58% and 38% yield, respectively. Mass spectrometry clearly indicated that the products are isomers of (\pm) -2a,b because the spectra showed the same molecular masses for the parent ions. It is noteworthy that the green products (\pm) -3a,b can also be obtained by heating a chlorobenzene solution of (\pm) -2a,b, suggesting that (\pm) -2a,b are kinetic products whereas (\pm) -3a,b are thermodynamic products. The thermal conversion from (\pm) -2a,b to (\pm) -3a,b was almost quantitative and no degradation of the starting materials was observed (TLC). The thermodynamic products (\pm) -**3a,b** were also characterised by ¹H and ¹³C NMR spectroscopy, however, any further structural information was not gained because they are C_1 -symmetric. The new fullerene derivatives (\pm) -**3a,b** exhibited chargetransfer (CT) bands in their UV/Vis spectra at 601 and 604 nm, respectively. Clear hypochromic shifts were observed after addition of CF₃COOH, and the original CT bands were fully recovered upon addition of Et₃N (see Fig. 14 (ESI[†]) and



Scheme 1 Synthetic overview. a: R = Et, b: $R = {}^{i}Pr$.

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Fig. 15 (ESI[†])). Similarity between (\pm) -**3a** and (\pm) -**3b** was also found in their IR spectra (see Fig. 20 (ESI) and Fig. 21 (ESI)).

Finally, the molecular structures of (\pm) -**2a**, (\pm) -**3a** and (\pm) -**3b** were elucidated by X-ray crystallography as depicted in Fig. 1.‡ As for (\pm) -**2a** (**R** = Et) the two addends are attached to the [6,6] junction (addition to the double bond shared by two six-membered rings). The two dicyanovinyl groups are highly distorted with the torsion angle θ (C71–C63–C64–C76) = 75.56°. The DMA ring and the neighbouring dicyanovinyl group are less distorted with a torsion angle θ (C70–C65–C64–C76) = 44.63°.

The X-ray crystallographic analysis disclosed that (\pm) -**3a,b** are 1,2,9,12-tetrakis-adducts of C₆₀, with a cyclopentene ring fused to a [5,6] junction. In the structure of (\pm) -**3a** (the structure of (\pm) -**3b** is very similar), one dicyanovinyl and a third cyano group are found almost in the plane with the cyclopentene ring, whereas the fourth cyano group is attached to the neighbouring carbon atom on the fullerene surface. The DMA ring is almost perpendicular to the cyclopentene ring with a torsion angle θ (C68–C67–C71–C72) = 84.56°. The functionalised carbon atoms (C1, C2, C19 and C22) on



Fig. 1 ORTEP plots of (\pm) -**2a** (a), (\pm) -**3a** (b), and (\pm) -**3b** (c) with thermal ellipsoids at 123 K shown at the 50% probability level. Solvate molecules are omitted for clarity.



Scheme 2 Proposed mechanism for the thermal rearrangement of push-pull-chromophore-fullerene conjugate (\pm)-2 to 1,2,9,12-tetrakis-adduct (\pm)-3. R = Me, Et, ^{*i*}Pr.

the fullerene surface strongly protrude from the spherical surface because of their sp³-character. Indeed, the bonds C19–C1 (1.612 Å), C1–C2 (1.644 Å) and C2–C22 (1.602 Å) are single bonds, whereas the C20–C21 bond (1.356 Å) possesses double bond character.

The proposed mechanism for the rearrangement of (\pm) -**2a,b** to (\pm) -**3a,b** is shown in Scheme 2. The dicyanovinyl group adjacent to the DMA ring in (\pm) -**2** is located very closely to the fullerene surface (distance between C76 and C13 = 3.308 Å (see Fig. 1)) and attacks the fullerene. This ring-closing step generates a fullerenyl anion, which subsequently attacks a cyano group to afford, by an addition–elimination-type mechanism, the tetrakis-adduct (\pm) -**3**. This thermal rearrangement was also observed for the methylated analogue (R = Me) of (\pm) -**2a,b** while it does not proceed when R = H.

Computational studies⁵ were applied to gain deeper insights into the mechanism of the rearrangement. We applied the ONIOM⁶ approach, using DFT B3LYP/6-31G(d) for the high-level layer and SVWN/STO-3G or AM1 for the low-level layer (see Fig. 2 and ESI[†] for the precise partitioning of the ONIOM layers). These ONIOM approaches were previously applied to reactivity studies of fullerenes and nanotubes.⁷ Both approaches resulted in essentially identical activation and reaction energies. Fig. 2 summarises the results. Our findings support the mechanism proposed in Scheme 2. The attack of the N,N-dimethylanilino-substituted buta-1,3diene onto the fullerene sphere in (\pm) -2a has an activation barrier of $\Delta G^{\ddagger} = 117.6 \text{ kJ mol}^{-1}$ and is accompanied with a charge transfer⁸ of -0.17e from the dimethylanilinosubstituted butadiene to the fullerene moiety. A partial negative charge results on the carbon atom C22 (-0.22e) adjacent to the cyclopentyl addend in Int-2a.⁹ An orbital analysis of the intermediate (Int-2a) shows a significant lobe of the HOMO also on the latter carbon atom (see ESI⁺ for further information). Thus, cyanide transfer subsequently takes place with a relatively low activation barrier ($\Delta G^{\ddagger} = 38.5 \text{ kJ mol}^{-1}$). Overall, the rearrangement is exergonic by $\Delta G_{rxn} = -31.4 \text{ kJ mol}^{-1}$. The rearrangement of the analogue of 2 with R = H is similarly exergonic ($\Delta G_{rxn} = -24.3 \text{ kJ mol}^{-1}$), but proceeds with a roughly 18 kJ mol⁻¹ higher 'rate-controlling' activation barrier ($\Delta G_{2}^{\ddagger} \rightarrow _{TS2} = 159.1 \text{ kJ mol}^{-1}$ for R = H and 141.5 kJ mol⁻¹ for R = Et). Thus, the rearrangement is disfavoured under the experimental conditions applied. The increase in barrier (if R = H) is primarily due to the greater stabilisation of the reactant as a result of decreased steric interaction.



Fig. 2 Reaction path for the rearrangement of (\pm) -**2a** to (\pm) -**3a**. Free energies in kJ mol⁻¹ are given, calculated at the ONIOM(B3LYP/ 6–31G(d):AM1) level. The ONIOM partitioning is illustrated with (\pm) -**2a** —the atoms highlighted in green correspond to the high-level layer.⁹

In summary, we have described a novel thermal rearrangement of push-pull-chromophore-fullerene conjugates to yield new CT chromophore-fullerene conjugates possessing a 1,2,9,12-tetrakis-addition pattern, which was unambiguously elucidated by X-ray crystallography. This reaction will now be further exploited and its broad scope explored by introducing different R-residues on the surface, substituting different donors (such as ferrocene, tetrathiafulvalene) for the DMA moiety and by investigating the rearrangements of fullerene conjugates with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and tetrafluoro-TCNQ-based push-pull chromophores.

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Notes and references

‡ Crystal data of (±)-**2a** at 123 K (CCDC-770343): C₇₈H₁₅N₅ · 3 CS₂, $M_r = 1250.430$, triclinic, space group PI (no. 2), $\rho_c = 1.596$ Mg cm⁻³, Z = 2, a = 13.0651(3), b = 13.5710(3), c = 15.9971(5) Å, $\alpha = 74.0161(11)$, $\beta = 77.3303(12)$, $\gamma = 75.1841(12)^\circ$, V = 2602.02(12) Å³, $\mu = 0.325$ cm⁻¹. Numbers of measured and unique reflections were 19258 and 11674, respectively ($R_{int} = 0.061$). Final R(F) = 0.0748, $wR(F^2) = 0.2109$ for 893 parameters and 8566 reflections with $I > 2\sigma(I)$ and $3.27 < \theta < 27.46^\circ$ (corresponding R-values based on all 11674 reflections are 0.1008 and 0.2294, respectively). Crystal data of (±)-**3a** at 123 K (CCDC-770342): C₇₈H₁₅N₅ · 1.5 C₆H₅Cl, $M_r = 1190.851$, monoclinic, space group $P2_1/c$ (no. 14), $\rho_c = 1.578$ Mg cm⁻³, Z = 4, a = 15.9413(3), b = 18.6916(3), c = 17.0131(3) Å, $\beta = 98.6182(6)^\circ$, V = 5012.1(2) Å³, $\mu = 0.170$ cm⁻¹. Numbers of measured and unique reflections were 19793 and 10912, respectively ($R_{int} = 0.057$). The structure contains 1.5 chlorobenzene molecules. Final R(F) = 0.0664, $wR(F^2) = 0.1874$ for 902 parameters and 8574 reflections with $I > 2\sigma(I)$ and 5.91 < $\theta < 27.48^\circ$ (corresponding *R*-values based on all 10912 reflections are 0.0864 and 0.2032, respectively). Crystal data of (±)-**3b** at 123 K (CCDC-770541): $C_{79}H_{17}N_5 \cdot 3 C_6H_5Cl$, $M_r = 1373.717$, Triclinic, space group PI (no. 2), $\rho_c = 1.552$ Mg cm⁻³, Z = 2, a = 9.9620(7), b = 17.8492(9), c = 18.4538(12) Å, $\alpha = 64.282(3)$, $\beta = 84.813(2)$, $\gamma = 85.112(2)^\circ$, V = 2940.3(3) Å³, $\mu = 0.222$ cm⁻¹. Numbers of measured and unique reflections were 9701 and 5697, respectively ($R_{int} = 0.145$). Final R(F) = 0.1200, $wR(F^2) = 0.2542$ for 882 parameters and 3469 reflections with $I > 2\sigma(I)$ and $4.92 < 0 < 20.68^\circ$ (corresponding *R*-values based on all 5697 reflections are 0.1841 and 0.2873, respectively).

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