Synthesis, separation and characterisation of the first pure multiple adducts of C_{2v}- and D_3-C_{78}

PERKIN 2

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Multiple cyclopropanation of an isomeric mixture of C_{2v}- and D_3-C_{78} (*ca.* 3:1) with diethyl 2-bromomalonate yielded two C_1-symmetrical bis-adducts, one of which was isolated without HPLC, and at least eight isomeric tris-adducts. Most of the adducts were isolated in pure state by HPLC and characterised by UV–VIS, ^{1}H and ^{13}C NMR spectroscopy, as well as by mass spectrometry. In the case of the tris-adducts, three isomers displayed a higher symmetry than C_1 and could therefore be unambiguously assigned to the C_{78} isomer from which they arise. Three possible structures were finally proposed for a C_2-symmetrical tris-adduct of C_{2v}-C_{78}, and two structures for a C_3-symmetrical tris-adduct of D_3-C_{78}. Based on the comparison of the spectra obtained for the C_2-symmetrical tris-adduct with those of the bis-adducts, three possible structures were proposed for one of the C_1-symmetrical bis-adducts, being the direct precursor of the corresponding tris-adduct. The compounds described in this work represent the first adducts of C_{2v}- and D_3-C_{78} isolated and characterised in a pure state.

C_{78} is the smallest fullerene for which several isomers have been isolated that satisfy the isolated pentagon rule (IPR).[1–5] The number of isomers obtained depends on the method used for the fullerene soot generation. By the resistive heating method used for the preparation of the samples described in this work, one C_{2v}-symmetrical and one D_3-symmetrical isomer of C_{78} are formed (Fig. 1[6]). Due to the low abundance of C_{78} in fullerene soot and the tedious, time-consuming procedures for its isolation and isomer separation, the chemistry of this fullerene is practically unexplored. Besides the kinetic resolution of chiral D_3-C_{78},[7] several groups reported reactions such as ozonation,[8] hydrogenation,[9] fluorination[10] or formation of methylene derivatives[11] which were performed on mixtures of higher fullerenes containing small amounts of C_{78}. No pure C_{78} adducts, however, have been isolated and characterised in any of these studies. The results obtained for the cyclopropanation of C_{70}[12,13] and C_{76},[14] by reacting the carbon spheres with 2-bromomalonate derivatives in the presence of base (Bingel-reaction), showed that addition preferentially takes place at the most curved 6–6 (at the junction between two six-membered rings) bonds located at the centre of pyracylene-type substructures. It can, therefore, be expected that these types of bonds (bonds of type α, β and γ,[15] in Fig. 2) are also the most reactive ones in C_{78}. Here, we describe a first investigation of the regioselectivity in the functionalisation of a mixture of C_{2v}- and D_3-C_{78} (*ca.* 3:1) using the Bingel reaction.[12]

Results and discussion

Preparation and isolation of pure C_{78} adducts

A total of 61.2 mg of C_{78}, which was obtained from three preparative HPLC separation steps[15] on a Buckyclutcher I[16] stationary phase in a purity of 97.8% as a *ca.* 3:1 mixture of C_{2v}- and D_3-symmetrical isomers, was reacted with diethyl 2-bromomalonate (1.8 equiv.) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Column chromatography gave five fractions (I–V). Besides small amounts of unreacted C_{78} (Fraction I), 3.3 mg of mono-adducts (Fraction II), 18.9 mg of bis-adducts (Fractions III and IV) and 34.4 mg of tris-adducts (Fraction V) were obtained after purification. The mono-adduct fraction consisted of at least four isomers, which, due to their small quantities, were not further analysed.

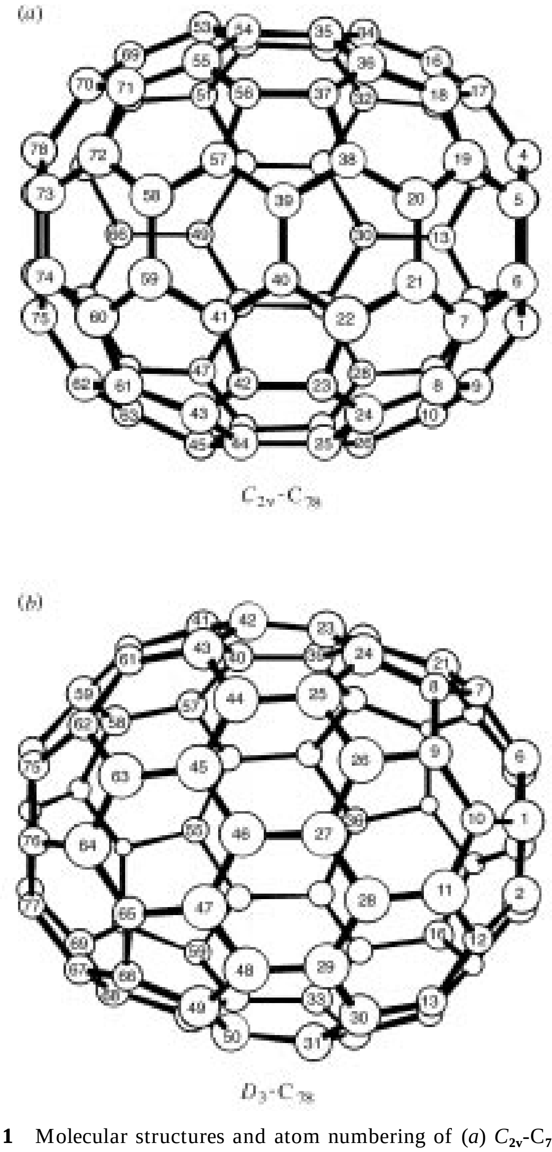
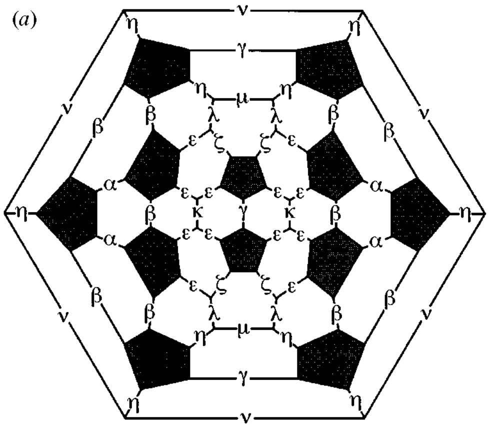


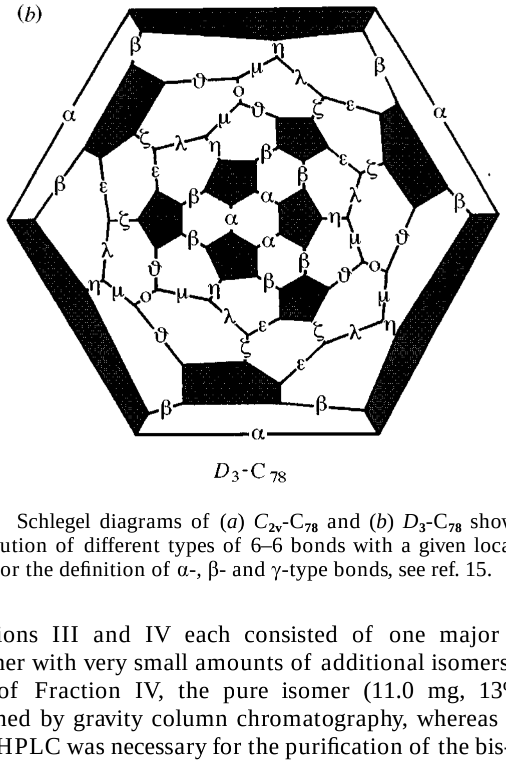
Fig. 1 Molecular structures and atom numbering of (*a*) C_{2v}-C_{78} and (*b*) D_3-C_{78} (only one enantiomer is shown)

(*a*)



C_{2v}-C_{78}

(*b*)



D_3-C_{78}

Fig. 2 Schlegel diagrams of (*a*) C_{2v}-C_{78} and (*b*) D_3-C_{78} showing the distribution of different types of 6–6 bonds with a given local curvature. For the definition of α-, β- and γ-type bonds, see ref. 15.

Fractions III and IV each consisted of one major isomer together with very small amounts of additional isomers. In the case of Fraction IV, the pure isomer (11.0 mg, 13%) was obtained by gravity column chromatography, whereas preparative HPLC was necessary for the purification of the bis-adduct obtained from Fraction III (7.9 mg, 10%). Fraction V contained at least eight isomeric tris-adducts, which were separated into seven fractions (Va–g) by preparative HPLC on a silica gel column.

Spectroscopic analysis

Mono-cyclopropanation at α- or β-type bonds of both C_{78} isomers (Fig. 2) leads to C_1-symmetrical products, which are indistinguishable by ^1H or ^{13}C NMR spectroscopy. The only exception is the addition to the β-type C(5)–C(6) bond, which gives a C_s-symmetrical adduct. In the case of bis-adducts, however, several isomers with either C_{2v}-, C_2- or C_s-symmetry can be formed in reactions at α-, β- or γ-type bonds of C_{2v}-C_{78}, whereas all bis-adducts of D_3-C_{78} at these bonds display C_1-symmetry.

The ^1H NMR spectra of both pure bis-adducts each displayed two multiplets between 4.6 and 4.3 ppm, integrating for two and six protons, respectively, and four triplets between 1.5 and 1.3 ppm, each arising from three protons, thus indicating C_1-symmetry for both compounds. This symmetry was further supported by their ^{13}C NMR spectra. Based on the spectroscopic data obtained, a structural assignment for the isolated bis-adducts was not possible.

At low degrees of functionalisation, the probability for obtaining mainly C_1-symmetrical isomers increases with an increasing number of addends. The assumption, that the Bingel reaction preferentially occurs at the most curved 6–6 bonds lying at the centre of pyracylene subunits (α-, β- and γ-type bonds), reduces the number of possible isomers. Tris-adducts of C_{2v}-C_{78} can only be C_1-, C_2-, C_s- or C_{2v}-symmetrical, whereas in the case of D_3-C_{78}, only isomers with either C_1- or C_3-symmetry are possible; the formation of C_2- or D_3-symmetrical tris-adducts of D_3-C_{78} can be excluded under the above assumptions. For both C_{2v}- and D_3-C_{78}, there exists in theory 28 different constitutionally isomeric tris-adducts having a symmetry higher than C_1, and they can unambiguously be assigned to C_{2v}- or D_3-C_{78} as the parent fullerene. Three out of the 28 isomers display C_2-symmetry and three others C_3-symmetry, two have C_{2v}-symmetry and the remaining 20 isomers are C_s-symmetrical.

Product from fraction Vc

Product from fraction Vg

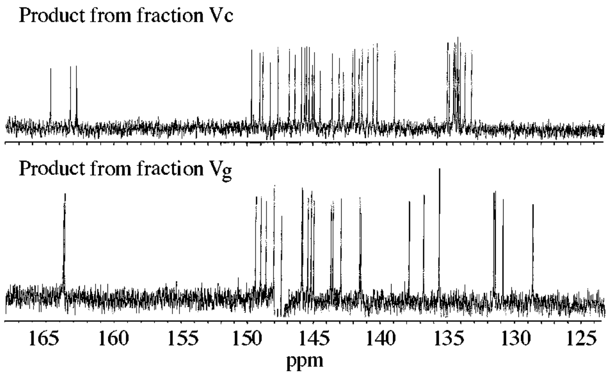


Fig. 3 Expansions of the sp^2-C atom region of the ^{13}C NMR spectra (125.8 MHz, $CDCl_3$) of the C_{78} tris-adducts obtained from Fractions Vc (top) and Vg (bottom). The spectrum of the product from Fraction Vg was recorded in the presence of $Cr(acac)_3$ (*ca.* 40 mM) as a paramagnetic relaxant.[17]

A first indication for the symmetry of the different tris-adduct isomers isolated from Fraction V was obtained by the analysis of their ^1H NMR spectra. All spectra displayed several multiplets between 4.0 and 5.0 ppm for the CH_2 groups and a distinct number of triplets in the region between 1.2 and 1.6 ppm for the CH_3 groups of the ethyl ester chains. The structures of the products contained in Fractions Va, Vb, Vd and Ve were assigned C_1-symmetry, whereas the products isolated from Fractions Vc and Vf are either C_2- or C_s-symmetrical. Finally, the tris-adduct obtained from Fraction Vg displays C_3-symmetry (Table 1).

Further support for the structural assignment was obtained from the ^{13}C NMR spectra of the different compounds. The amounts of compound in Fractions Va and Vf, however, were too small to record their ^{13}C NMR spectra. Also, Fraction Ve was not further investigated since it contained a mixture of two C_1-symmetrical isomers.

The ^{13}C NMR spectrum of the product obtained from Fraction Vc [(±)-**1**] displayed 36 resonances with equal intensity in the fullerene sp^2-region (Fig. 3). This is in agreement only with a C_2- or a C_s-symmetrical structure, and the compound is therefore an adduct of C_{2v}-C_{78}. Only six out of the 23 theoretically possible isomers display 36 signals of equal intensity for the fullerene sp^2-C atoms and, for symmetry reasons, one of the three addends must be located at the C(39)–C(40) bond (type γ) (Fig. 4).† The C_s-symmetrical isomers give rise to four additional signals for the fullerene sp^3-C atoms (two of them with half

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† This is generally the case for all C_2-symmetrical derivatives of C_{2v}-C_{78} bearing an odd number of addends since the C_2-axis passes through this bond. Furthermore, in all C_s-symmetrical adducts for which no fullerene sp^2-C resonances of half intensity are observed in the ^{13}C NMR spectrum, one addend must also be located at this same bond, since it is lying in one of the two mirror planes of the parent fullerene.

Table 1 Structural assignment of the bis- and tris-adducts of C_{78}

Adducts	Product fraction	Symmetry deduced from	Symmetry	Derivative of
Bis-adducts	Fraction III	^{1}H and ^{13}C NMR	C_1	C_{2v}- or D_3-C_{78}
	Fraction IV	^{1}H and ^{13}C NMR	C_1	C_{2v}-C_{78}
Tris-adducts	Fraction Va	^{1}H NMR	C_1	C_{2v}- or D_3-C_{78}
	Fraction Vb	^{1}H and ^{13}C NMR	C_1	C_{2v}- or D_3-C_{78}
	Fraction Vc	^{1}H and ^{13}C NMR	C_2	C_{2v}-C_{78}
	Fraction Vd	^{1}H and ^{13}C NMR	C_1	C_{2v}- or D_3-C_{78}
	Fraction Ve	^{1}H NMR	C_1 (2×)	C_{2v}- or D_3-C_{78}
	Fraction Vf	^{1}H NMR	C_2 or C_s	C_{2v}-C_{78}
	Fraction Vg	^{1}H and ^{13}C NMR	C_3	D_3-C_{78}

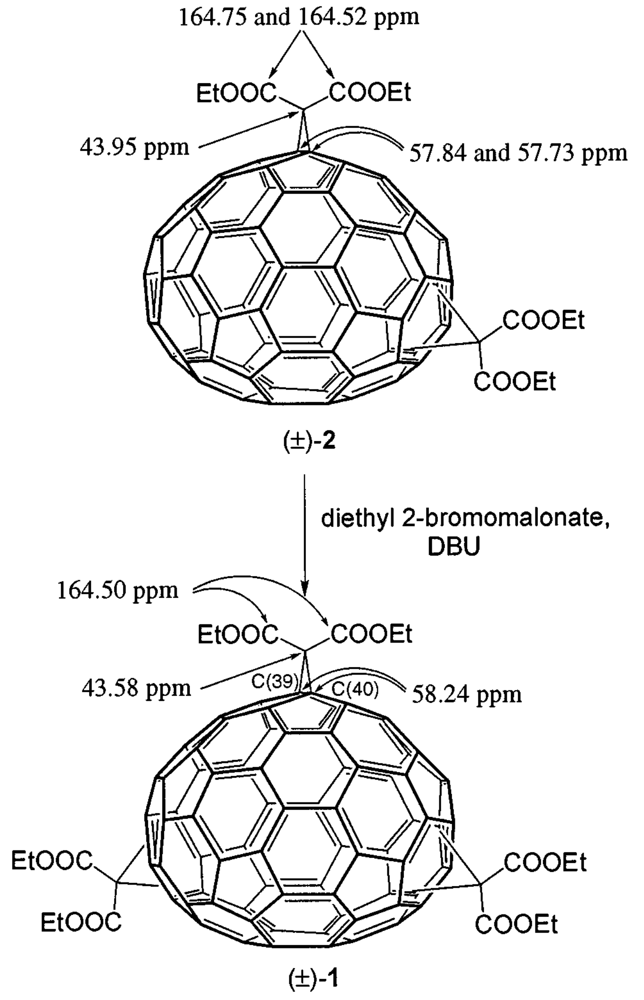

Fig. 4 Three possible structures of the pure C_1-symmetrical bis-adduct of Fraction IV [(±)-**2**] and the pure C_2-symmetrical tris-adduct of Fraction Vc [(±)-**1**] derived from it. In both (±)-**1** and (±)-**2**, the first addend is located at the C(39)–C(40) bond and the second addend at one of three 6–6 bonds in one of the hexagons close to one pole; the third addend in (±)-**1** occupies a symmetry-equivalent position to the second one in the corresponding hexagon close to the other pole. The ^{13}C NMR resonances of the addends located at C(39)–C(40) are assigned.

intensity), whereas the C_2-symmetrical compounds display three peaks of equal intensity for these atoms. The detection of three signals at 78.52, 76.92 and 58.24 ppm for the fullerene sp^3-C atoms therefore suggests C_2-symmetry for the isomer isolated from Fraction Vc.‡ As shown in Fig. 4, three structures of (±)-**1** are possible, with the first addend located at the C(39)–C(40) bond, the second addend at one of the three 6–6 bonds (one α-type, two β-type) in one of the hexagons close to one pole and the third one in the symmetry-equivalent position in the corresponding hexagon close to the other pole. Based on the experimental data, we cannot at present distinguish which one of the three structurally closely related isomers has been isolated in pure form. According to π-bond order considerations,[6] taking into account steric hindrance between addends, the most probable structure of (±)-**1** would be the C_2-symmetrical tris-adduct formed by addition to the C(39)–C(40), C(9)–C(10) and C(69)–C(70) bonds.§ However, note that in the case of nucleophilic additions to C_{70}, predictions for the regioselectivity based on π-bond orders (bonds with higher π-bond order are more reactive) are not in full agreement with the obtained experimental results.[12,13]

A comparison of the ^{13}C NMR spectra of the products isolated from the bis-adduct Fraction IV and the tris-adduct Fraction Vc showed some interesting similarities, although they were recorded in different solvents. The signals for the fullerene sp^3-C atoms appear at 77.67, 76.42, 57.84 and 57.73 in the case of the product isolated from Fraction IV (in $CDCl_3$) and at 78.52, 76.92 and 58.24 ppm for the compound from Fraction Vc (in CD_2Cl_2). The resonances of the methano bridges from product Fraction IV were recorded at 50.58 and 43.95, those of Fraction Vc at 50.21 and 43.58 ppm. These similarities suggest that the bis-adduct of Fraction IV [(±)-**2**] is the direct precursor of the tris-adduct isolated from Fraction Vc [(±)-**1**] (Fig. 4). If one of the addends of the C_2-symmetrical tris-adduct from Fraction Vc is located at the C(39)–C(40) bond (type γ), as unambiguously shown above, this addend must already be present in the bis-adduct of Fraction IV. A C_2-symmetrical tris-adduct of C_{2v}-C_{78} can only be obtained from a C_1-symmetrical bis-adduct if one of the addends in the bis-adduct is located at the bond crossing the symmetry axis of the tris-adduct to be formed [γ-type bond at C(39)–C(40)]. This assumption is further supported by the fact that the two methano bridge C atoms in (±)-**2** are of comparable intensity, whereas the signal at 50.21 ppm in the spectrum of (±)-**1** is about twice as intense as the resonance at 43.58 ppm. This shows that the methano bridge introduced with the third addend must be equivalent to one already present in the bis-adduct. Since the γ-type bond is unique, it must be already functionalised in the bis-adduct and the resonance at 43.95 ppm is assigned to the methano bridge connected to that bond [C(39)–C(40)]. The fact that two signals around 58 ppm are present in (±)-**2** and only one in (±)-**1** allows the assignment of these resonances to the fullerene sp^3-C atoms C(39) and C(40) and, following the same reasoning, the carbonyl resonances resulting from this addend are those appearing at *ca.* 164.5 ppm. The similarity of the two structures is also nicely reflected in their UV–VIS spectra shown in Fig. 5, which have almost identical shapes.

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‡ Similar spectra have been obtained from ^{13}C NMR measurements in $CDCl_3$ and CD_2Cl_2. In $CDCl_3$, however, the peak corresponding to that at 76.92 ppm in CD_2Cl_2 was hidden under the solvent signal.

§ We are grateful to one of the reviewers of the manuscript for pointing out to us the structural assignment based on π-bond order considerations.

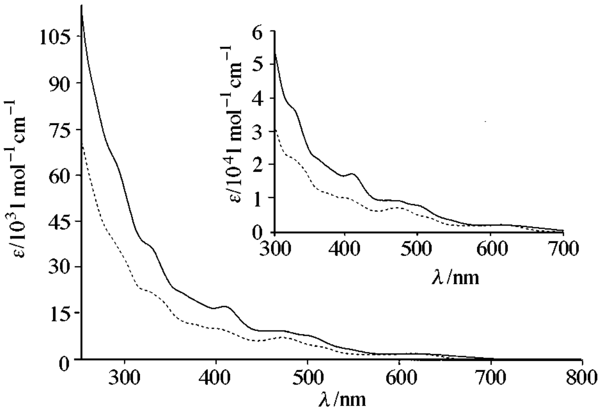


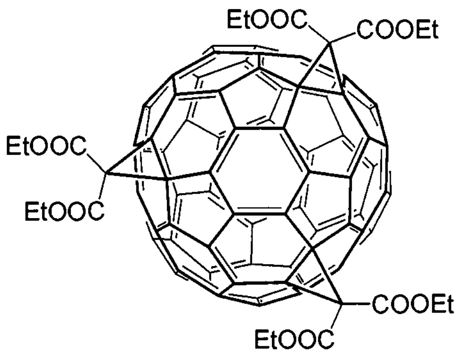
Fig. 5 UV–VIS spectra (CH_2Cl_2) of the bis-adduct of Fraction IV (——) [(±)-**2**] and the tris-adduct of Fraction Vc (– – –) [(±)-**1**]

In the ^{13}C NMR spectrum ($CDCl_3$) of the product from Fraction Vg, only 23 resonances were observed between 125 and 150 ppm (Fig. 3). Two signals were recorded for each of the C=O and the CH_2 groups as well as for the fullerene sp^3-C atoms, and one resonance at 48.30 ppm was assigned to the methano bridge. This spectrum is only in agreement with a C_3-symmetrical structure. The isolated isomer must therefore be a tris-adduct of D_3-C_{78} and is the first pure adduct reported for this fullerene. Based on the symmetry, all three addends must have reacted within the same hemisphere of the carbon allotrope. Theoretically, there are three possible isomers giving rise to C_3-symmetry, resulting from reaction at three α-type (one possible isomer) or three β-type bonds (two possible isomers), respectively. Reaction at three bonds of type α, which are those in the polar six-membered ring, is unlikely, since it would result in substantial steric hindrance. More likely is the reaction at three bonds of type β, which are located at a greater distance from the poles. Since two different sets of β-type bonds can be distinguished [C(9)–C(10), C(14)–C(15), C(19)–C(20) and C(7)–C(8), C(12)–C(13), C(17)–C(18), see Figs. 1 and 2], regioisomers (±)-**3** and (±)-**4** shown in Fig. 6 are both in agreement with the recorded spectra. According to π-bond order considerations, structure (±)-**4** is formed preferentially.[6]

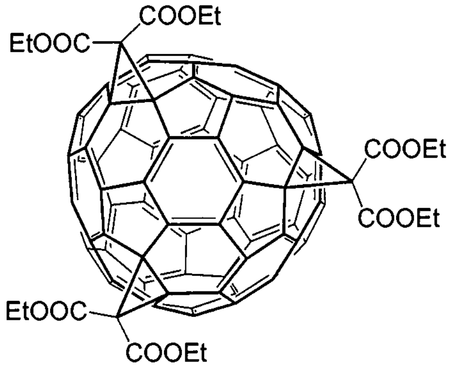
It should be noted that the relative arrangement of all three addends in both structures proposed in Fig. 6 is similar to the addition pattern observed for the multiple cyclopropanation of C_{70} within the same hemisphere.[13] This similarity further supports the assignment of either one of the proposed structures to the C_3-symmetrical isomer isolated from Fraction Vg. It seems to be a general trend that nucleophilic additions to fullerenes, *e.g.* the multiple cyclopropanations described in this paper, preferentially occur at bonds of high curvature and, presumably for electronic reasons, in a relative arrangement known as 'equatorial' in the functionalisation of C_{60}.[18]

Conclusions

HPLC on a silica gel stationary phase afforded a remarkable separation of the covalent adducts formed in the Bingel reaction with a *ca.* 3:1 mixture of C_{2v}- and D_3-C_{78}. Whereas individual C_1-symmetrical mono(diethyl malonate) adducts were not separated or structurally characterised, two C_1-symmetrical bis-adducts and eight tris-adducts, five with C_1-symmetry and three with higher symmetry were isolated as the first pure derivatives of the two isomeric higher fullerenes. Based on extensive ^1H and ^{13}C NMR spectroscopic analysis, bond reactivity and symmetry considerations, structural assignments could be proposed for two of the higher symmetrical tris-adducts. Three possible structures are in agreement with the spectral data for the isolated C_2-symmetrical tris-adduct of C_{2v}-C_{78}, whereas two structures are supported by the spectroscopic data collected for the pure C_3-symmetrical tris-adduct of D_3-C_{78}. NMR spectral correlations also permitted to propose three structures for one of the C_1-symmetrical bis-adducts of C_{2v}-C_{78}. Predictions of reactivity based on π-bond orders permit the tentative assignment of one single structure to each of the two pure tris-adducts. A general trend in the preferred multiple functionalisation pattern, that had previously been observed in the nucleophilic functionalisation of C_{60} and C_{70}, was also found in the cyclopropanation of D_3-C_{78}. Second and higher addends are preferentially introduced in a relative relationship known as 'equatorial' addition in the chemistry of C_{60}. With the development of highly efficient chromatographic separation protocols, the regiochemistry in the covalent functionalisation of the higher fullerenes will increasingly become the subject of further investigations, which, ultimately, should yield a general, comprehensive view of the reactivity principles across the entire family of soluble molecular carbon allotropes.



(±)-**3**



(±)-**4**

Fig. 6 Possible C_3-symmetrical tris-adducts (±)-**3** and (±)-**4** resulting from cyclopropanation of two different sets of β-type bonds of (±)-D_3-C_{78}. The two structures of the same enantiomer of D_3-C_{78} are shown in a polar view along the C_3-axis.

Experimental

Purification of C_{78} by HPLC

A total of 700–800 µl of a solution (conc. *ca.* 8 mg ml^{-1}) of soot extract enriched in higher fullerenes from Hoechst AG, Germany (C_{60}: ≈9%, C_{70}: ≈22%, C_{76}: ≈21%, C_{78}: ≈12%, C_{84}: ≈36%) in *o*-dichlorobenzene were injected onto a preparative Buckyclutcher I column. The flow rate of the eluent *n*-hexane–toluene 3:2 was 14 ml min^{-1}. In a first run, fractions of C_{60}, C_{70}, enriched C_{76} containing C_{78}, a mixture of C_{76} and C_{78}, enriched C_{78} containing C_{76} and C_{84} were collected. The enriched C_{78} fraction required two further purification steps under the same conditions (with a flow rate of 8 ml min^{-1}) to give a *ca.* 3 : 1 mixture of the C_{2v} and D_3 isomers, respectively, in a purity of 97.8%, which was used for the derivatisations.

HPLC columns: Regis Buckyclutcher I Trident-Tri-DNP (10 µm), 500 × 21.1 mm id and Macherey-Nagel Nucleosil 100-7 silica gel (7 µm), 250 × 21 mm id. HPLC instrumentation: Knauer HPLC Pump 64 with preparative pump heads and vacuum online degasser, electrical injection valve AA A0619 and Variable Wavelength Monitor UV–VIS detector from Knauer. All chromatograms were recorded at ambient temperature with the detector wavelength fixed at 310 nm. UV–VIS spectra: Varian-CARY-5 spectrometer. ^{1}H and ^{13}C NMR spectra: Bruker-AMX-500 spectrometer with solvent peak as reference. MALDI-TOF mass spectra with reflectron detection were measured in the negative ion mode on a Bruker REFLEX spectrometer.

Derivatisation of C_{78} with diethyl 2-bromomalonate

C_{78} (0.061 g, 0.065 mmol) was dissolved in dry toluene (150 ml). The solution was sonicated and purged with argon, after which diethyl 2-bromomalonate (0.028 g, 0.118 mmol) and DBU (0.018 g, 0.118 mmol), each dissolved in toluene, were added. The solution was stirred overnight at room temperature. The solvent was evaporated to dryness and the mixture, dissolved in CH_2Cl_2–*n*-hexane, was chromatographed (SiO_2, CH_2Cl_2–*n*-hexane 1 : 1→2 : 1) to give five fractions (I–V). Besides small amounts of unreacted C_{78} (Fraction I), 3.3 mg of mono-adduct (Fraction II), 18.9 mg of bis-adducts (Fractions III and IV) and 34.4 mg of tris-adducts (Fraction V) were obtained as black solids after purification. For further purification, bis-adduct Fraction III was dissolved in CH_2Cl_2 (2 ml) and 150 µl were injected per run onto the preparative Buckyclutcher I HPLC column. Elution with *n*-hexane–CH_2Cl_2 3 : 2 at a flow rate of 15 ml min^{-1} gave 7.9 mg (10%) of the pure bis-adduct. Column chromatography of Fraction IV (SiO_2 H, *n*-hexane–CH_2Cl_2 2 : 1→1 : 1) afforded 11 mg (13%) of the pure bis-adduct. Fraction V was separated by preparative HPLC on a SiO_2 column. The mixture was dissolved in CH_2Cl_2 (≈1.4 ml), and an average of 200 µl was injected per run and eluted with CH_2Cl_2–*n*-hexane 3 : 2 at a flow rate of 30 ml min^{-1}. Seven fractions (Va–Vg) were collected. Fraction Va, 2.1 mg (2%); Fraction Vb, 5.6 mg (6%); Fraction Vc, 6.7 mg (7%); Fraction Vd, 5.7 mg (6%); Fraction Ve, two isomers, 5.6 mg (6%); Fraction Vf, 3.5 mg (4%) and Fraction Vg, 5.2 mg (6%). Drying of the samples at *ca.* 10^{-7} Torr (room temp.) did not remove small amounts of hexane, which could be identified by NMR spectroscopy even after prolonged drying.

Tetraethyl 1,2 : 39,40- or 9,10 : 39,40- or 11,12 : 39,40-dimethano[78]fullerene-79,79,80,80-tetracarboxylate [(±)-2]

Product of Fraction IV: $\lambda(CH_2Cl_2)$/nm 625 (ε/dm^3 mol^{-1} cm^{-1} 2000), 549 (sh, 3300), 509 (sh, 7100), 464 (9300), 409 (17 200), 357 (sh, 22 300), 331 (sh, 35 500) and 297 (sh 57 200); δ_H(500 MHz, $CDCl_3$) 4.60–4.41 (6 H, m), 4.39–4.33 (2 H, m), 1.45 (3 H, t, *J* 7.1), 1.44 (3 H, t, *J* 7.1), 1.38 (3 H, t, *J* 7.1) and 1.35 (3 H, t, *J* 7.1); δ_C(125.8 MHz, $CDCl_3$) 164.75, 164.52, 163.04, 162.58, 150.43, 149.71, 148.54, 148.02, 147.86 (2 C), 147.80, 147.34, 147.15, 147.10, 147.06, 146.86, 146.78, 146.56, 146.45, 146.41, 146.40, 146.30 (2 C), 145.96, 145.91, 145.84, 145.44, 145.15, 145.03, 144.50, 144.32, 144.30, 144.22, 143.95, 143.73, 143.69, 143.59, 143.54, 143.53, 143.44, 143.39, 143.25, 143.17, 142.85, 142.31, 142.08, 141.89, 141.72, 141.62, 141.18, 140.48, 140.44, 140.33, 140.14, 139.96, 139.62, 139.31, 137.93, 135.47, 135.26, 135.01, 134.81, 134.52, 134.50, 134.45, 134.41, 134.39, 134.12, 134.01, 133.98, 133.84, 133.66, 133.65, 133.53, 133.31 (2 C), 133.06, 132.67, 77.67, 76.42, 63.52, 63.46, 63.39, 63.33, 57.84, 57.73, 50.58, 43.95, 14.23 (2 C), 14.18 and 14.11; *m*/*z* [MALDI-TOF MS, 2,5-dihydroxybenzoic acid (DHB)] 1252.1 (100, M$^-$, $^{12}C_{91}{}^{13}CH_{20}O_8$ requires 1253.1), 1094.2 {38, [M − $C(CO)_2(C_2H_5)_2]^-$}, 948.0 (14) and 935.8 (19, $C_{78}{}^-$).

Hexaethyl 1,2 : 39,40 : 77,78- or 9,10 : 39,40 : 69,70- or 11,12 : 39,40 : 67,68-trimethano[78]fullerene-79,79,80,80,81,81-hexacarboxylate [(±)-1]

Product of Fraction Vc: $\lambda(CH_2Cl_2)$/nm 615 (ε/dm^3 mol^{-1} cm^{-1} 2100), 514 (sh, 4200), 472 (7100), 407 (sh, 9600), 379 (sh, 11 100), 326 (sh, 22 000) and 285 (sh, 39 500); δ_H(500 MHz, $CDCl_3$) 4.58–4.45 (4 H, m), 4.49 (4 H, q, *J* 7.1), 4.40 (4 H, q, *J* 7.1), 1.45 (6 H, t, *J* 7.1), 1.39 (6 H, t, *J* 7.1) and 1.38 (6 H, t, *J* 7.1); δ_C[125.8 MHz, CD_2Cl_2, *ca.* 40 mM $Cr(acac)_3$] 164.50, 163.00, 162.55, 149.52, 148.88, 148.71, 148.11, 147.53, 146.74, 146.42, 145.77, 145.57, 145.41, 145.24, 145.18, 144.83, 144.34, 143.62, 142.90, 142.85, 141.95, 141.78, 141.64, 141.23, 140.86, 140.50, 140.08, 138.89, 134.91, 134.78, 134.38, 134.36, 134.30, 134.19, 134.15, 134.02, 133.92, 133.55, 133.13, 78.52, 76.92, 63.62, 63.57, 63.50, 58.24, 50.21, 43.58, 14.09, 14.05 and 14.00; *m*/*z* (MALDI-TOF MS, DHB) 1410.6 (100, M$^-$, $^{12}C_{98}{}^{13}CH_{30}O_{12}$ requires 1411.2), 1387.3 (12) and 1253.2 {17, [M − $C(CO)_2(C_2H_5)_2]^-$}.

Hexaethyl 9,10:14,15:19,20-trimethano[78]fullerene-79,79,80,80,81,81-hexacarboxylate [(±)-3] or hexaethyl 7,8:12,13:17,18-trimethano[78]fullerene-79,79,80,80,81,81-hexacarboxylate [(±)-4]

Product of Fraction Vg: $\lambda(CH_2Cl_2)$/nm 672 (sh, ε/dm^3 mol^{-1} cm^{-1} 400), 587 (1200), 549 (sh, 1200), 495 (sh, 2100), 424 (5700), 390 (sh, 5100), 316 (15 100), 293 (sh, 20 000) and 258 (sh, 35 600); δ_H(500 MHz, $CDCl_3$) 4.52–4.27 (12 H, m), 1.42 (9 H, t, *J* 7.1) and 1.29 (9 H, t, *J* 7.1); δ_C[125.8 MHz, $CDCl_3$, *ca.* 40 mM $Cr(acac)_3$] 163.72, 163.64, 149.31, 148.91, 148.52, 147.94, 147.37, 145.85, 145.79, 145.38, 145.13, 144.93, 143.62, 143.48, 142.88, 141.50, 141.41, 137.82, 136.74, 135.60, 135.58, 131.49, 131.38, 130.78, 128.54, 64.46, 62.94, 62.72, 60.41, 48.30, 13.82 and 13.80; *m*/*z* (MALDI-TOF MS, DHB): 1410.6 (100, M$^-$, $^{12}C_{98}{}^{13}CH_{30}O_{12}$ requires 1411.2), 1252.9 {19, [M − $C(CO)_2(C_2H_5)_2]^-$}, 1095.1 {9, [M − 2 $C(CO)_2(C_2H_5)_2]^-$} and 935.7 (7, $C_{78}{}^-$).

Acknowledgements

This work was financially supported by the Swiss National Science Foundation. We are grateful to Hoechst AG, Germany (Dr Hans-Ulrich ter Meer, Dr Wolfgang H. Müller and Dr Wolfgang Appel) for providing us with fullerene soot extract enriched in higher fullerenes. We thank Dr Carlo Thilgen for constructive comments on the manuscript, Dr Monika Šebova for the high-field NMR measurements and Mr Hans-Ulrich Hediger for recording the MALDI-TOF MS spectra.

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Paper 7/01549F
Received 4*th March* 1997
Accepted 9*th April* 1997