High–yield reactive extraction of giant fullerenes from soot

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By the common Soxhlet extraction with 1,2,4-trichlorobenzene a mere 8 mass % of virgin fullerene soot can be dissolved. The extracted soot was subjected to a reactive extraction with 5-hexadecanamido-1,3-dihydro-2-benzothiophene 2,2-dioxide **(4)**, an *ortho*-quinodimethane precursor. Through an irreversible Diels–Alder cycloaddition an additional 12 mass % was solubilized. Mass spectrometry, vapour pressure osmometry and elemental analysis indicate that the soluble material consists of multiple adducts of fullerenes C_{60}–C_{418}.

Since the discovery of the fullerenes by Kroto *et al.*[1] and the preparation of macroscopic quantities of C_{60} by Krätschmer *et al.*,[2,3] the scientific community has been interested in fullerene soot. This material is a new kind of amorphous carbon consisting of globular and irregularly shaped carbon structures as well as stacks of bent and planar carbon sheets with different sizes and curvatures.[4] Considerable amounts of C_{60} and larger carbon clusters are embedded in this insoluble black fullerene matrix. Consequently, many reports have dealt with the extraction of fullerene soot using high-boiling solvents.[5–12] With 1,2,4-trichlorobenzene as solvent Diederich *et al.* isolated fullerenes up to C_{216}.[5] Ruoff and co-workers reported that up to 37% of virgin fullerene soot could be extracted using 1,2,4-trichlorobenzene.[6] However, the latter results are not backed up by elemental analyses so it is unclear whether the extracted material consists only of all-carbon molecules. Nevertheless, these studies[5,6,7,12] agree on the distribution of the fullerenes in the extracts, and carbon clusters up to a molecular mass of 2500 have been detected by time of flight mass spectrometry.

Several questions remain to be answered: (*i*) How much of the fullerene soot is actually soluble? (*ii*) What is the fullerene content of the virgin fullerene soot? (*iii*) Which fullerenes are most abundant in the soot? (*iv*) Can the catalytic activity of extracted fullerene soot (*e.g.* towards the conversion of methane into higher hydrocarbons) be traced back to residual (not extracted) fullerenes or is it actually a property of the pure soot?[13]

Answering these questions requires a method for the complete extraction of the soot. Reactive extraction seems to be especially well suited to this purpose. In this method, the extractable compounds are solubilized *via* reaction with a suitable partner in the liquid phase and are thus easily transferred into the liquid phase.[14]

Herein, we describe the reactive extraction of fullerene soot with *ortho*-quinodimethanes as modifying agents. The influence of the structure of the modifying reagent on the extraction yield and on the composition of the extracted material will be addressed and the results will be compared with common extraction methods.

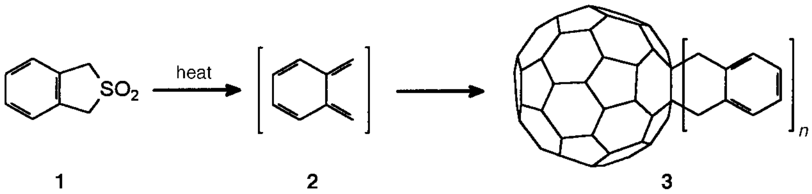
Results and Discussion

All experiments described in the following were performed with fullerene soot produced by the Krätschmer–Huffman process.[2,3] Prior to the experiments the soot was exhaustively Soxhlet extracted with either toluene (8.1 mass % soluble material) or successively with toluene and 1,2,4-trichlorobenzene (8.4 mass % soluble material).

Our first experiments were aimed at the reactive extraction of soot with modifying agents which form thermally unstable adducts with fullerenes. This approach would allow us to cleave the modifying agent after the extraction and thus to obtain unsubstituted fullerenes. Unfortunately, both the extraction with anthracene-9-methanol and with 2-trimethylsilyloxybutadiene which are both known to form reversible Diels–Alder adducts[15] with fullerenes in boiling toluene yielded only negligible amounts of soluble material.

Realizing that the thermal stability of the adducts is obviously a crucial condition for successful reactive extractions we turned towards *ortho*-quinodimethanes **2** as modifying agents. *ortho*-Quinodimethanes can be generated by thermal extrusion of sulfur dioxide from 1,3-dihydro-2-benzothiophene 2,2-dioxide **(1)** and its derivatives above 200 °C (Scheme 1). They are very reactive enophiles, which eagerly form [4+2] cycloaddition products **3** with fullerenes giving high yields as well.[16,17] These adducts are both thermally stable and highly soluble in common solvents due to their conformational mobility (cyclohexene ring inversion).

Refluxing 1,2,4-trichlorobenzene-extracted fullerene soot (500 mg) together with 175 mg (1.04 mmol) 1,3-dihydro-2-benzothiophene 2,2-dioxide **(1)** (Scheme 1) in 1,2,4-trichlorobenzene for 24 h (Table 1, Entry 1) followed by filtration from insoluble material afforded a black solution. This solution was again filtered through a glass frit (pore size 10–16 µm) to avoid contamination with small, insoluble particles of soot. Afterwards the solution was evaporated and the residue suspended in ethanol and sonicated for 5 min. Unreacted **1**, byproducts and residual solvent were dissolved in ethanol and could be easily separated by filtration. The black powdery



1 **2** **3**

Scheme 1 Generation of *ortho*-quinodimethane **2** from 1,3-dihydro-2-benzothiophene 2,2-dioxide **(1)** and its cycloaddition reaction with C_{60}

Table 1 Entries; compounds **1**, **4** used for reactive extraction or solvent used for extraction; amount of extracted soot; extraction yields; elemental analyses of extracted material; fullerene distributions determined by LD–TOF MS; M_n (g mol^{-1}) determined by vapour pressure osmometry

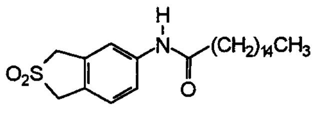
entry	extraction/ reactive extraction with	carbon soot	yield of extracted fullerene adducts or fullerenes /mg	elemental analysis			H/N	C_{Full} (%)	yield C_{Full} /mg	yield fullerenes (%)[c]	LD–TOF[d] MS	vapour pressure tosmometry M_n [g mol^{-1}][e]
				C (%)	H (%)	N (%)						
1[a]	**1** (175 mg)	500 mg	45	92.36	2.74	<0.2	>13	59.7	27	5.4	C_{60}–C_{344}	2590
2[a]	**1** (88 mg)	from 1	9	90.34	2.63	<0.3	>8	59.0	5	1.0	C_{60}–C_{396}	—
3[a]	**4** (440 mg)	500 mg	164	83.40	7.59	2.70	2.82	27.8	46	9.2	C_{60}–C_{400}	6610
4[a]	**4** (220 mg)	from 3	46	82.84	6.91	2.70	2.56	27.2	13	2.6	C_{60}–C_{418}	6480
5[a]	**4** (330 mg)	52 mg	24	83.33	6.85	2.84	2.41	24.9	6	11.5	C_{60}–C_{418}	—
6[a]	**4** (100 mg)	500 mg	51	85.72	6.40	2.50	2.56	27.7	14	2.8	C_{60}–C_{348}	3770
7[a]	**4** (100 mg)	1000 mg	56	85.46	7.04	2.50	2.82	34.0	19	1.9	C_{60}–C_{308}	4010
8[a]	**4** (440 mg)	10 g	113	90.79	4.08	1.45	2.81	61.0	69	0.7	C_{60}–C_{350}	1930
9	toluene soxhlet	10 g	810	99.10	0.27	0.22	1.23	99.1	810	8.1	C_{60}–C_{180}	—
10[b]	1,2,4-trichlorobenzene soxhlet	30 g	81	93.68	0.71	<0.1	>7.1	93.7	76	0.25	C_{60}–C_{192}	—
11[b]	1,2,4-trichlorobenzene reflux	10 g	26	96.46	0.40	<0.1	>4	96.5	25	0.25	C_{60}–C_{196}	—
12[b]	quinoline soxhlet	25 g	389	87.63	2.09	2.28	0.92	70.0	272	1.1	C_{60}–C_{260}	—

[a]1,2.4-Trichlorobenzene-extracted soot. [b]Toluene-extracted soot. [c]Calculated with respect to soot. [d]Positive ion LD–TOF MS. [e]Vapour pressure osmometry in tetrahydrofuran (measured at 30 °C).

filtration residue was washed several times with ethanol and dried under vacuum. Finally, a yield of 45 mg of material was obtained, which readily dissolved in $CHCl_3$ or tetrahydrofuran (THF). According to its H : C ratio, which was determined by elemental analysis, this corresponds to a yield of fullerenes of 5.4 mass % (calculated with respect to soot). The sum of the proportions of elements C, H, N and S determined by elemental analysis is only 95%. We assume that the residual amount consists of oxygen which has reacted with the fullerenes. It is well known that epoxidation of fullerenes in solution is induced by UV irradation[18] or heating[19] in the presence of oxygen.

Laser desorption time-of-flight (LD–TOF) mass spectra of this sample showed a distribution of *unmodified* fullerenes from C_{60} to C_{344}, due to retro-Diels–Alder reaction of the formed adducts during the ionization process. Vapour pressure osmometry which gave a number-average molecular mass of $M_n = 2590$ g mol^{-1} also indicated that the soluble material consisted of Diels–Alder adducts of high molecular mass fullerenes (giant fullerenes). Additional soluble fullerene material was obtained when the once-extracted soot was subjected to a second reactive extraction. This yielded another 1 mass % of soluble material. The LD–TOF mass spectra of this sample showed slightly higher fullerenes up to C_{396}.

This experiment clearly showed that *ortho*-quinodimethanes are very well suited for reactive extraction. Obviously, the solubility of the adducts is the crucial point for the additional yield and the distribution of extractable material. We therefore synthesized the *ortho*-quinodimethane precursor 5-hexadecanamido-1,3-dihydro-2-benzothiophene 2,2-dioxide (**4**) carrying a long flexible alkyl chain.



4

The fixed H : N mass ratio of 2.8 in **4** allows a more precise calculation of the product composition and can serve as an indicator for the purity of the extracted products. The H : N mass ratio can be determined by elemental analysis and must have a value of 2.8 for the formed adducts assuming that pure addition products of **4** and carbon clusters are formed. Again the sums of proportions of elements C, H, N and S determined by elemental analyses are only 96–98%. As mentioned above we assign the missing amount of 2–4% to oxygen resulting from epoxidation products of fullerenes.

Treatment of 1,2,4-trichlorobenzene-extracted fullerene soot (500 mg) with **4** (440 mg, 1.04 mmol) according to the above procedure led to the isolation of 164 mg of soluble material (Table 1, Entry 3). The elemental analysis of this material showed a H : N ratio of 2.8 which proved that the sample consisted entirely of modified carbon clusters. The total amount of carbon clusters extracted from the soot was calculated to be 9.2 mass %. This is considerably higher than the 5.4 mass % which was achieved with the less flexible **1**. From this it follows that the higher the solubility of the adducts the higher the extraction yields.

As described before for **1**, a second extraction of the soot with **4** yielded another 2.6 mass % of soluble material (Table 1, Entry 4). It follows that approximately 12 mass % of the soot can be extracted by this approach. In comparison, the total extraction of a small amount of soot (52 mg) within one step with an extremely large excess of **4** (330 mg, 0.69 mmol) yielded 11.5% soluble material (Table 1, Entry 5).

The soluble material which was received from the first reactive extraction (Table 1, Entry 3) was fully characterized by means of mass spectrometry, vapour pressure osmometry and thermogravimetric analysis. Positive as well as negative ion LD–TOF mass spectra again show, due to retro-Diels–Alder reactions of the adducts during the ionization process, a distribution of even numbered *unmodified* carbon clusters (Fig. 1). The positive ion mass spectrum shows fullerenes up to mass *ca.* 4800 corresponding to C_{400} (Fig. 1, top panel). 170 peaks can be assigned to fullerenes with good signal to noise ratio. The molecular mass of fullerenes in the negative ion mass spectrum is somewhat lower compared to that in the positive ion mass spectrum. Strong signals of C_{60}, C_{70} and C_{84} can be observed (Fig. 1, bottom panel). 125 peaks can be counted for fullerenes with good signal to noise ratio. Ruoff

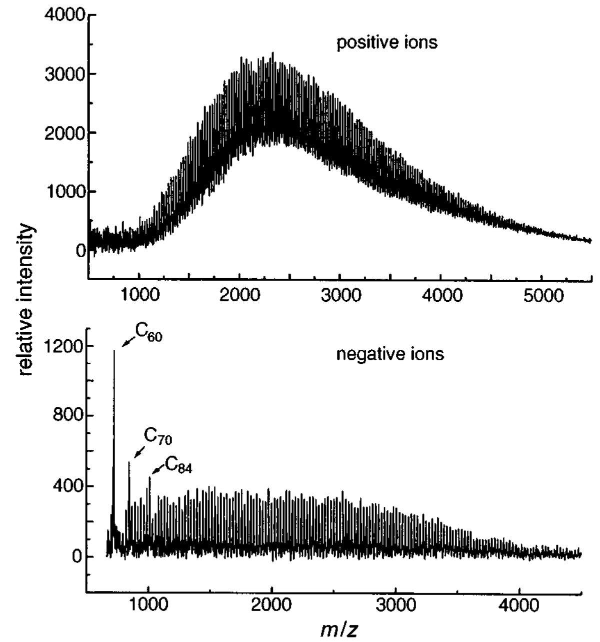


Fig. 1 (*a*) Positive and (*b*) negative ion LD–TOF MS of fullerene sample from reactive extraction with 5-hexadecanamido-1,3-dihydro-2-benzothiophene 2,2-dioxide **4**

et al. discuss some reasons for differences in negative and positive ion mass spectra.[5] They suggest that different ionization probabilities for positively and negatively charged carbon clusters in LD–TOF MS experiments lead to significant differences in the distributions of fullerenes. Field-desorption (FD) MS is a well-known technique for detecting fullerenes and fullerene adducts without fragmentation during the ionization process. FD MS of this sample showed, apart from multi-adducts of C_{60} and C_{70}, mono- and bis-adducts of the recently isolated and characterized C_{80} (see Experimental).[20]

There are also significant differences in the fullerene distributions of samples received from conventional and reactive extractions. Fig. 2 shows the positive ion LD–TOF mass spectrum of pure fullerenes from 1,2,4-trichlorobenzene extract (Table 1, Entry 10). Fullerenes up to mass 2100 (C_{192}) can be detected. The FD mass spectrum of this sample indicates the existence of fullerenes with more than 100 carbon atoms too (see Experimental).

It follows that reactive extraction enables the extraction of fullerenes with approximately double the molecular mass compared to conventional extraction.

The number-average molecular mass M_n of the sample from entry 3 was determined by vapour pressure osmometry as 6610 g mol^{-1}. Thermogravimetric analysis showed that these fullerene adducts are thermally stable up to at least 310 °C which is in accordance with results obtained for *ortho*-quinodimethane adducts of C_{60}.[21] From the analytical results it is evident that the soluble material consists of fullerenes C_{60}–C_{400} which are multiply functionalized with *ortho*-quinodimethanes. However, isolation of single adducts from the adduct mixture with HPLC was not achieved due to the unavoidable formation of multiple adducts and the corresponding regioisomers; the soluble material consists of more than 1000 compounds.

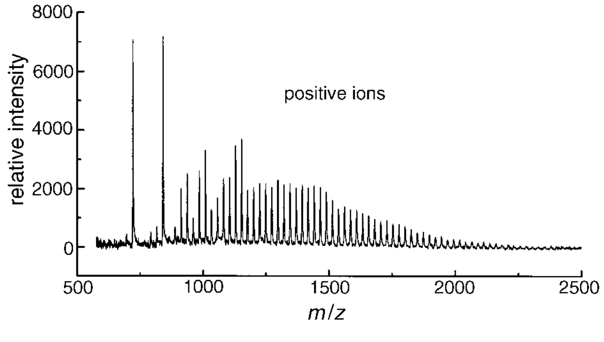


Fig. 2 Positive ion LD–TOF MS of 1,2,4-trichlorobenzene-extracted fullerenes

Further experiments with different stoichiometries show that both the yields of fullerenes and the composition of the extracted material can be influenced. Reaction of 500 mg of soot with 100 mg (0.23 mmol) of **4** (Table 1, Entry 6) yielded 51 mg of fullerene adducts (fullerene content: 27.7%) which corresponds to 2.8 mass % pure fullerenes (calculated with respect to soot). In comparison, reaction of 1000 mg of soot with 100 mg (0.23 mmol) of **4** (Table 1, Entry 7) yielded 56 mg of fullerene adducts (fullerene content: 34%) which is equivalent to 1.9 mass % pure fullerenes. These results show that increasing soot to reagent ratios lead both to diminished yields of fullerenes and increasing fullerene content of the extracted material. With that, the number of attached *ortho*-quinodimethanes is also decreasing. The latter result is supported by the reaction of 440 mg (1.04 mmol) of **4** with a very large excess of soot (10 g) (Table 1, Entry 8) since this extraction yields a highly fullerene-enriched sample with a fullerene content of 61 mass %.

It can be concluded that the reactive extraction proceeds in three separate steps: (*i*) fullerenes which are firmly embedded in the soot matrix and are not extractable by conventional Soxhlet extraction react with *ortho*–quinodimethanes, (*ii*) the modified and therefore soluble fullerenes dissolve in 1,2,4-trichlorobenzene, and (*iii*) by further reaction of excess *ortho*-quinodimethanes with dissolved fullerene adducts multiple adducts are formed.

The advantage of the described reactive extraction becomes evident by comparing it with conventional Soxhlet extraction. The yield of fullerenes from conventional Soxhlet extraction of virgin soot with toluene is found to be 8.1% (Table 1, Entry 9). A subsequent extraction with 1,2,4-trichlorobenzene yields only additional 0.25% fullerenes (Table 1, Entry 10) and with quinoline 1.1% (Table 1, Entry 12). Furthermore, elemental analysis of the quinoline extract indicates that the sample contains large, not removable amounts of impurities due to decomposition of the solvent. Hence, the yields of reactive extraction are superior to those of conventional extraction.

Conclusions

Giant fullerenes which are barely soluble in common solvents and are firmly embedded in the solid fullerene soot matrix can be efficiently functionalized by means of reactive extraction with *ortho*-quinodimethanes. The fullerenes are thus made soluble in 1,2,4-trichlorobenzene and are extractable in very high, so far unprecedented, yields.

Commercially available fullerene soot which yields 8.4 mass % of soluble fullerenes by entire extraction with common solvents affords additional 11.8 mass % of soluble material (functionalized fullerenes C_{60}–C_{418}) by reactive extraction with an *ortho*-quinodimethane precursor (**4**). The above experiments indicate that the conformational flexibility of the *ortho*-quinodimethanes is the key factor for the amount of extracted material. Therefore, further experiments will make use of *ortho*-quinodimethanes substituted with highly branched (extremely flexible) groups. Our studies show that the amount and the composition of the extracted material can be significantly influenced by differing the ratio of fullerene soot to modifying agent.

The entirely extracted soot will be utilized to study if the catalytic activity of fullerene soot is due to the soot itself or comes from included redox active fullerenes.

Experimental

Carbon soot: for all experiments, samples of the same soot were used. The soot was prepared by arc synthesis according to the Krätschmer–Huffman[2,3] process and was provided by

Hoechst AG. The soot was previously extracted with toluene to remove C_{60} and C_{70} (approximately 8.1 mass %).

LD–TOF MS was performed using a Bruker Reflux mass spectrometer with a 337 nm N_2 laser. Laser power was adjusted to be the lowest level at which an ion signal was observed.

A VG Instruments ZAB 2–SE–FPD mass spectrometer was used for recording FD mass spectra.

1,3-Dihydro-2-benzothiophene 2,2-dioxide (1)

The reagent was synthesized as described by Cava and Deana.[22] δ_H (300 MHz, [$^2H_6$]acetone, 21 °C) 4.35 (s, 4H, CH_2), 7.29–7.40 (m, 4H, CH). δ_C (75 MHz, $CDCl_3$, 28 °C) 47.3 (CH_2), arom. C atoms: 126, 129 and 131.5. Positive ion FD MS: 168 ([M^+], 100%). Mp 150–152 °C.

5-Hexadecanamido-1,3-dihydro-2-benzothiophene 2,2-dioxide (4)

1,3-Dihydro-5-amino-2-benzothiophene 2,2-dioxide[23] (2.87 g; 15.7 mmol) and triethylamine (2.1 g; 20 mmol) were dissolved in 1,4-dioxane (250 ml). Hexadecanoyl chloride (4.73 g; 17.3 mmol) was added dropwise at room temp. over 20 min. The solution was stirred under reflux for 20 min. The solution was cooled to room temp. and then added to H_2O (300 ml), giving a white precipitate. The precipitate was collected by filtration, washed with H_2O and Et_2O and dried *in vacuo*. Yield: 5.75 g (13.6 mmol; 87%). δ_H (500 MHz, $C_2D_2Cl_4$, 100 °C) 0.87 (t, 3H, CH_3), 1.26 (br, 24H, CH_2), 1.66 (m, 2H, CH_2), 2.34 (t, 2H, CH_2), 4.25 (s, 2H, CH_2), 4.27 (s, 2H, CH_2), 7.13 (s, 1H, CH), 7.18 (d, 1H, CH), 7.3 (d, 1H, CH), 7.65 (s, 1H, NH). δ_C (125 MHz, $C_2D_2Cl_4$, 100 °C) 14.2 (CH_3), aliph. CH_2: 22.80, 25.64, 29.63 (several signals overlapping), 32.08, 37.85, 57.08 (CH_2) and 57.63 (CH_2), arom. CH: 117.71, 120.64 and 126.76, quart. arom. C atoms: 126.78, 132.0 and 139.03, 171.0 (C=O). Positive ion FD MS: 421.2 ([M^+] 100%). Elemental analysis: $C_{24}H_{39}NO_3S$, calc. C 68.52%, H 9.29%, N 3.29%, S 7.47%. Found C 68.37%, H 9.32%, N 3.32%, S 7.6%. Mp 152–154 °C.

General procedure for reactive extractions with 1 and 4 (Table 1, Entry 1–8)

All reactions were carried out under a dry, oxygen-free argon atmosphere. Soot and **1** or **4** were added to 150 ml of 1,2,4-trichlorobenzene. Refluxing for 24 h followed by filtration from insoluble material afforded a black solution. The solution was evaporated and the residue suspended in 150 ml of ethanol and sonicated for 5 min. Unreacted **1** or **4** and residual solvent were dissolved in ethanol while a suspension of the reaction products was formed. Filtration, washing with ethanol and drying gave a black powder.

Positive ion FD MS of crude material obtained from entry 3

C_{60}-monoadduct 1078.4 ([M^+], 25%), C_{60}-bisadduct 1435.8 ([M^+], 35%), C_{60}-trisadduct 1791.9 ([M^+], 45%), C_{60}-tetraadduct 2151.4 ([M^+], 100%), C_{60}-pentaadduct 2508.6 ([M^+], 45%), C_{70}-monoadduct 1197.6 ([M^+], 35%), C_{70}-bisadduct 1555.5 ([M^+], 70%), C_{70}-trisadduct 1912.5 ([M^+], 55%), C_{70}-tetraadduct 2270.2 ([M^+], 45%), C_{70}-pentaadduct 2627.3 ([M^+], 10%), C_{80}-monoadduct 1317.1 ([M^+], 20%), C_{80}-bisadduct 1674.8 ([M^+], 15%).

Thermogravimetric analysis of the extract from entry 3

(Mass 7.5 mg, heating rate 10 K min^{-1}, N_2 atmosphere) 313–560 °C (−54.23%, maximum at 408.3 °C, residue 3.43 mg).

Soxhlet extractions of the soot (Table 1, Entries 9, 10, 12)

The soot was placed in the thimble of a Soxhlet extractor. The extractions were carried out for 24 h. After filtration, the solution was evaporated and the residue suspended in 150 ml ethanol and sonicated for 5 min. After filtration, washing with ethanol and drying a black powder was obtained.

Extraction of the soot under reflux (Table 1, Entry 11)

The soot was placed in a flask and 200 ml of the solvent was added. After refluxing for 24 h, the suspension was filtered. The solution was evaporated and the residue suspended in 150 ml ethanol and sonicated for 5 min. Filtration, washing with ethanol and drying gave a black powder.

Positive ion FD MS of crude material from entry 10

C_{60} 720.6 (95%), C_{70} 840.7 (100%), C_{76} 911.7 (15%), C_{78} 935.6 (31%), C_{82} 983.7 (13%), C_{84} 1009.9 (14%), C_{86} 1031.6 (21%), C_{88} 1056.5 (22%), C_{90} 1079.9 (21%), C_{92} 1104.5 (10%), C_{94} 1127.0 (8%), C_{96} 1152.9 (20%), C_{98} 1177.9 (5%), C_{100} 1201.7 (11%), C_{106} 1272.2 (11%), C_{110} 1321.7 (7%), C_{112} 1343.9 (8%), C_{114} 1367.7 (17%), C_{116} 1392.4 (16%), C_{118} 1418.9 (9%), C_{120} 1439.1 (22%), C_{124} 1489.1 (22%), C_{136} 1633.5 (12%).

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