The minor isomers and IR spectrum of [84]fullerene

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One hundred and fifty four lines have been detected in 120 000 and 50 000 scan ^{13}C NMR spectra of main and tail HPLC fractions, respectively, of [84]fullerene. Five minor isomers are deduced to be present (in *ca.* 25% and 40% overall yields in the main and tail cuts, respectively), as well as the two main isomers [D_2(IV) and D_{2d}(II), which are present in a ratio of *ca.* 2.25 : 1]. A second D_2 isomer, which calculations predict to be D_2(III), is firmly established as one of the components, and the other isomers are indicated to be: D_{3d}, D_{6h}, C_s(IV), and either C_s(V) or C_2(IV). The relative proportions of the isomers differ according to the HPLC fraction, and a partial elution order (Cosmosil Buckyprep/toluene) is $D_{3d}/C_s(\text{IV}) < D_2(\text{III})/D_{6h}$. The IR spectrum of [84]fullerene does not correlate well with theoretical predictions.

Theoretical methods have proved to be very successful in predicting not only which closed cage carbon molecules (fullerenes) should be readily isolable, but also which isomers of a given fullerene should be the stable ones.[1] A notable example is [84]fullerene, calculations of which predict that the D_{2d}(II) and D_2(IV) isomers[2] (referred previously to as nos. 22 and 23) should be the most stable isomers.[3–6] These two isomers are indeed the ones that constitute the bulk of [84]fullerene, and a consequence of their isoenergetic nature is that virtually identical isomer ratios [$D_2(\text{IV})/D_{2d}(\text{II}) = 2:1$] were reported from three different studies in which the arc-discharge reactor conditions differed (as shown by the different isomer ratios for [78]fullerene).[7–10] The calculations also predict correctly that the D_2(IV) isomer should be the main one.

Previously one of us drew attention to the probable existence of additional isomers as evidenced by the presence of 77 lines of greater than baseline intensity in the ^{13}C NMR spectrum of an HPLC purified sample.[9] Moreover, a few lines were of significant intensity, indicating that an isomer of high symmetry was present. More recently, Saunders and co-workers measured the ^{3}He NMR spectrum of [84]fullerene which indicated the presence of a number of minor but unidentified isomers.[11] Unfortunately the sample after helium incorporation was not examined by ^{13}C NMR spectroscopy and so the possibility that the isomer composition was substantially altered by the aggressive incorporation procedure (which leads to loss of almost 50% of material) remained a significant possibility.[11]

We now report the ^{13}C NMR spectrum of [84]fullerene. An initial spectrum of this material showed the majority of the low intensity lines that we tentatively identified in an earlier spectrum.[9] Data were therefore accumulated for 120 000 scans, giving much greater accuracy, thereby permitting assessment of the isomers probably present. A second strategy was involved, whereby a spectrum was also run on the tail fraction of [84]fullerene; it was hoped that this would contain less of the two main isomers, thereby enabling a higher concentration of the minor isomers in CS_2 to be obtained, and a more detailed spectrum to be obtained. This strategy proved to be correct and provided an unexpected benefit in that the relative peak intensities were substantially different in the two samples, thus permitting a more reliable analysis than would otherwise have been possible.

Theoretical predictions of the IR spectrum of [60]fullerene were crucial in the development of fullerene science. It was the recognition, by Huffman and Krätschmer, that their arc-produced soot gave the predicted number of IR bands,[12] that provided the foundation for the explosive growth in fullerene research. Even so, whilst the prediction[13] of the band positions is moderately successful, prediction of the band intensities is less good.[14] For [70]fullerene, prediction of both band positions and intensities is noticeably poorer,[14] which highlights the difficulties attendant upon such correlations.

Although the theoretical IR spectra for the two main components of [84]fullerene [the D_{2d}(II) and D_2(IV) isomers] have been published,[5] we are unaware of any report of an experimental spectrum. In this paper we remedy this deficiency, and compare the two results.

Results and discussion

[84]Fullerene was prepared by the arc-discharge procedure, and purified at TechnoCarbo by HPLC using a Cosmosil Buckyprep column (toluene eluent). The elute was divided into two fractions, a centre (main) cut and a tail fraction. Both samples were shown by mass spectrometry to be entirely free of any higher fullerene, and neither of the ^{13}C NMR spectra obtained for each sample contained any of the peaks due to C_{82}.[7]

^{13}C NMR spectra

A CS_2 solution was used with $CDCl_3$ as lock signal, and $Cr(acac)_3$ as relaxant. Before discussing the ^{13}C NMR spectra it is appropriate to consider the theoretical predictions for the stabilities of [84]fullerene isomers. Calculations[4–6] agree well in predicting that the most stable isomers after D_2(IV) and D_{2d}(II) should be C_2(IV), C_1, C_s(IV), C_s(V), D_2(III), D_{3d} and D_{6h} (known previously as nos. 11, 12, 15, 16, 21, 19 and 24, respectively; the structures[1] are shown in Fig. 1). (For the IUPAC notation used in this paper, see ref. 2.) As a group they should have closely similar stabilities and be substantially more stable than the remaining 15 (isolated-pentagon) isomers; each method predicts the C_2(IV) isomer to be the most stable one. The number of lines that these isomers should produce in the ^{13}C NMR spectrum are as follows: C_2(IV), 42 × 2 C; C_1, 84 × 1 C; C_s(IV), (40 × 2 C) + (4 × 1 C); C_s(V), (41 × 2 C) + (2 × 1 C); D_2(III), (21 × 4 C); D_{3d}, (6 × 12 C) + (2 × 6 C); D_{6h}, (3 × 24 C) + (1 × 12 C). Thus, only two isomers are of high symmetry, and should be readily detectable if the yields are sufficiently high.

Approximately 150 lines can be distinguished in the spectra for the main and tail fractions [Figs. 1(*a*), (*b*), respectively, and

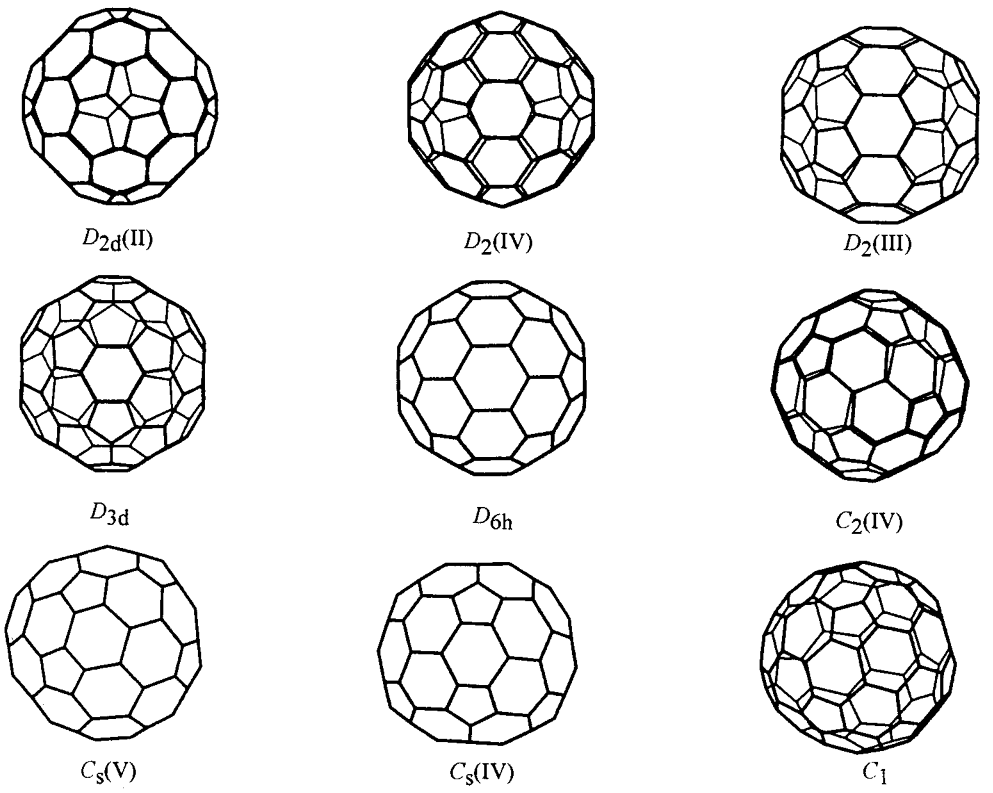

Fig. 1 Structures of the nine [84]fullerene isomers described in this paper

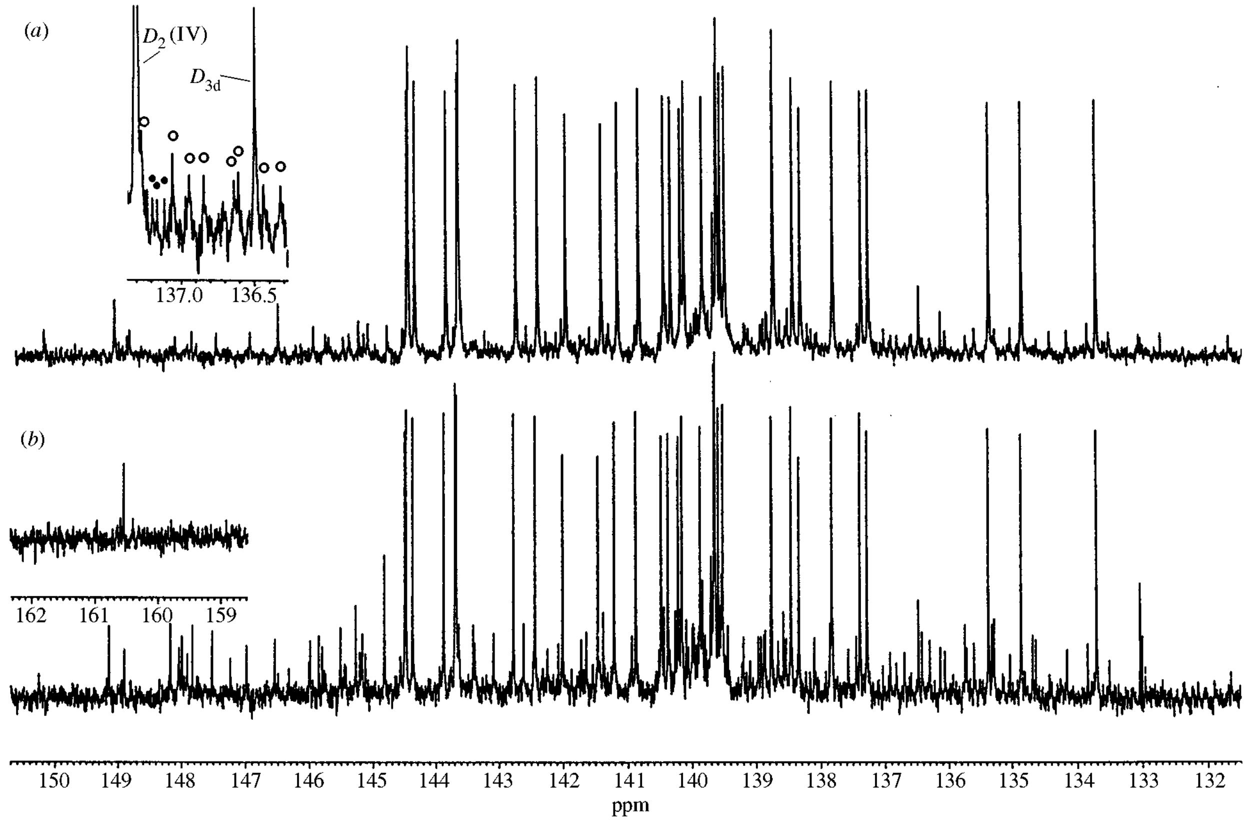

Fig. 2 (*a*), (*b*) ^{13}C NMR spectrum of [84]fullerene: (main fraction, 120 000 scans, upper spectrum), (tail fraction, 50 000 scans, lower spectrum). The inset (expanded) shows examples of three sets of minor lines in the upper spectrum [○ = C_2(IV)/C_s(IV or V)]; the lines indicated by ● are not evident in the lower spectrum and may be due to the C_1 isomer (which elutes 'early'). Lower inset shows the single downfield peak.

Tables 1–3]; the inset to Fig. 2(*a*) shows an expanded section of the spectrum for the main cut, with some minor lines indicated. There are additional lines evident in the background to the spectrum in Fig. 2(*a*) (approximately 75 were detected) but these were not reproduced in the second spectrum [Fig. 2(*b*)]. We therefore discount these in our analysis since they could in principle arise from noise, but note that they could also be due to the C_1 isomer if this tends to elute with the main isomers rather than the tail fraction.

The resonances listed in Tables 1–3 are referenced to [60]fuller-

Table 1 ^{13}C NMR chemical shifts (δ) for [84-D_2(IV) + 84-D_{2d}(II)]-fullerene[a]

144.51	142.80	140.51	139.68	138.49	*134.88*
144.49	142.46	140.40	139.66	*138.37*	133.72
144.39	*142.03*	*140.24*	139.61	137.85	
143.89	*141.49*	140.18	139.54	137.41	
143.71	*141.24*	139.90	*138.80*	137.30	
143.69	140.90	*139.73*[b]	138.79	*135.39*	

[a] *Italicised* peaks are attributed provisionally to the D_{2d}(II) isomer. [b] Half-intensity peak.

Table 2 ^{13}C NMR chemical shifts (δ)

a For the major lines of [84-D_{3d}]fullerene

149.16	146.56(5)	143.65	140.47	139.86	136.50

b For the major lines of [84-D_{6h}]fullerene

144.84	139.70	139.56

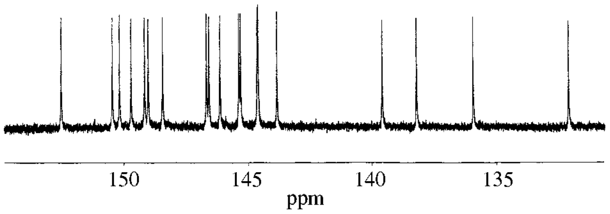

Fig. 3 Reference ^{13}C NMR spectrum of [76-D_2]fullerene

Table 3 ^{13}C NMR chemical shifts (δ) for the isomers believed to be a mixture of [84-D_2(III)]fullerene (*italicised* values), [84-C_s(IV)]fullerene and [84-C_2(IV) or -C_s(V)]fullerenes[a]

160.58	145.53	142.10	139.92	138.26	135.61
150.28	145.44	*141.89*	139.91	138.20	135.33
148.96*	145.43	141.81*	139.82	138.13	135.32
148.92	145.29	*141.74*	139.80	138.10	135.30
148.19	145.21	141.66	*139.58*	*137.59*	135.05
148.06	145.14	141.40	139.50	137.47	134.66
148.01	144.59	141.37	139.46	137.27	134.45
147.93	144.57	140.96	139.25	137.06	134.18
147.85	143.95	140.58	139.22	136.95	133.86
147.54	143.78	140.54	139.18	136.85	133.53
147.25	143.70	*140.29*	139.12	*136.72*	133.06
147.00	*143.42*	140.22	138.99	136.64	133.03
146.34	*143.40*	140.20	138.98*	136.61	*132.98*
146.04	143.28*	*140.11*	138.95	136.44	132.72
146.00	*143.10*	140.07	138.90	136.32	131.68
145.87	142.64	140.02	138.89	136.15	
145.81	142.34	*140.00*	138.69	136.08	
145.79	*142.26*	139.99	138.61	135.76	
145.76	142.18	139.96	138.57	135.73	

[a] Starred (*) values are attributed to the minor resonances of the C_s(IV) isomer, not seen in the tail-cut spectrum. The *italicised* resonances are not seen in the main cut spectrum.

ene at 143.15 ppm rather than 142.68 ppm used previously,[9] and therefore are all 0.47 ppm downfield. Five main sets of lines can be distinguished.

1. [84-D_2(IV) and -D_{2d}(II)]fullerenes. The 32 major lines (Table 1) are due to the mixture of D_2(IV) and D_{2d}(II) isomers.[7–10] There is a significant difference in peak intensities which permits identification of the peaks due to each isomer. It is first necessary to correct for the intensity enhancement of buttressed peaks. Fig. 3 is a reference spectrum of [76-D_2]fullerene[15] (the first published for this fullerene since the original spectrum reported by Diederich *et al.*);[16] the δ_C values are 149.96, 147.88, 147.58, 147.13, 146.58, 146.53, 145.85, 144.08, 143.98, 143.54, 142.80, 142.73, 142.07, 142.03, 141.28, 136.99, 135.60, 133.33 and 129.50. Seventeen of the nineteen lines in the spectrum have an almost constant integrated intensity, whereas the integrated intensities of the buttressed lines are 10% too high as a result of this buttressing. For [84]fullerene there are four sets of similarly buttressed lines, including the half-height peak for the D_{2d} isomer. By correcting the integrated intensities of these peaks by a similar 10%, the ten peaks of lowest intensity have an average integrated intensity of 31.1 units (with the half-height peak being 16.2 units) whereas the remaining 21 peaks have an average intensity of 34.3 units. The peaks thereby provisionally assigned to the D_{2d} isomer are italicised in Table 1, and from the intensities we calculate that the D_2(IV)/D_{2d}(II) isomer ratio is *ca.* 2.25. Likewise, from the intensities in the main-cut spectrum (and discounting any possible contribution from a C_1 isomer), these isomers are calculated to constitute 75% of the [84]fullerene total in the main fraction, so that the respective yields are 51% and 23%. The proportion of these isomers is reduced to 60% in the tail cut.

2. [84-D_{3d}]fullerene. In the spectrum of the main HPLC fraction, amongst the minor isomers, there are six lines of significantly greater intensities than the remainder (Table 2a). These can be due only to the D_{3d} isomer, as no other isolated pentagon isomer can give six lines of equal intensity;[1] the remaining half-intensity lines for this isomer will be indistinguishable from the large set of other lines arising from the other isomers. From the integrated line intensities, and including half-integration values for the two indistinguishable half-intensity lines, the yield of this isomer in this fraction is calculated to be *ca.* 3.5%. Although these peaks also appear in the tail-fraction spectrum, they are now no longer prominent compared to the rest. This isomer must therefore elute 'early' amongst the minor components.

3. [84-D_{6h}]fullerene. Three peaks that are indistinguishable from the rest in the main fraction spectrum, are enhanced in the tail-fraction spectrum (Table 2b). Only the D_{6h} and T_d isomers can give three lines of equal intensity (together with one of half intensity which cannot be distinguished from the remainder of similar intensities arising from the other isomers), but the latter isomer is predicted to be extremely unstable. We therefore conclude that the D_{6h} isomer is present, and its enhancement in the second spectrum indicated that it tends to elute 'late' amongst the minor components.

4. [84-D_2(III)]fullerene. There is clear evidence for this isomer as follows. Comparison of the peaks recorded for both samples reveals the appearance of 22 lines in the tail fraction (italicised in Table 3) that are absent in the main fraction (one of the two weak lines at δ 145.79 and 132.98 can probably be disregarded). These can only be due to a D_2 isomer, which calculations indicate must be isomer (III) since isomers (I) and (II) are predicted to be very unstable. This isomer evidently elutes 'late' relative to some of the others.

5. [84-C_s(IV) and either -C_2(IV) or -C_s(V)]fullerenes. Our analysis has thus accounted for 32 peaks [D_{2d}(II) + D_2(IV)], eight peaks (D_{3d}), four peaks (D_{6h}), and 21 peaks [D_2(III)], leaving 86 to be assigned. Now the C_1 isomer requires 84 lines but this can be ruled out as being responsible because (*a*) there is a fourfold variation in intensities within a given spectrum, and (*b*) there is a wide variation in relative intensities for a given line between the two spectra. This shows that more than one isomer is present. A clue to the nature of one of these isomers is given by the fact that four lines appear in the first spectrum (at δ 148.96, 143.28, 141.81 and 138.98) but are not distinguishable in the second. This may be attributed to [84-C_s(IV)]fullerene which alone requires four lines of half intensity. If the concentration of this is greater in the early fraction (*i.e.* this isomer elutes 'early') then the 'loss' of the four lines (see Table 1) in the tail fraction spectrum is accounted for.

The C_s(IV) isomer requires 40 other lines which leaves 42 lines to be explained. There are nine isomers that would produce 40–42 main lines, but six are predicted to be too unstable. Of the remaining three [C_2(IV), C_s(V) and C_s(IV)] the last has already been assigned, leaving either of the others (which require 42 and 43 lines, respectively) as the remaining candidate.

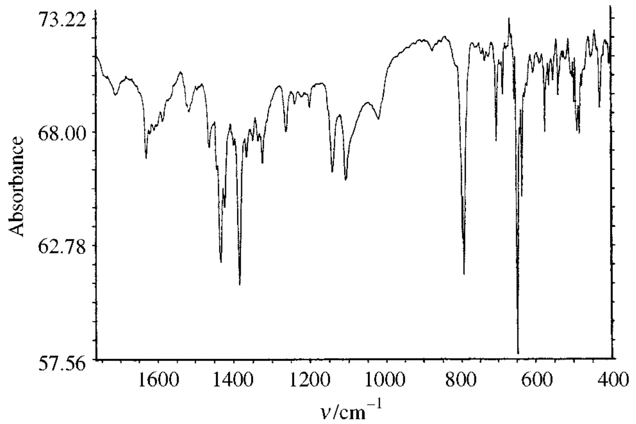

Fig. 4 IR spectrum (KBr disc) of [84]fullerene (main fraction)

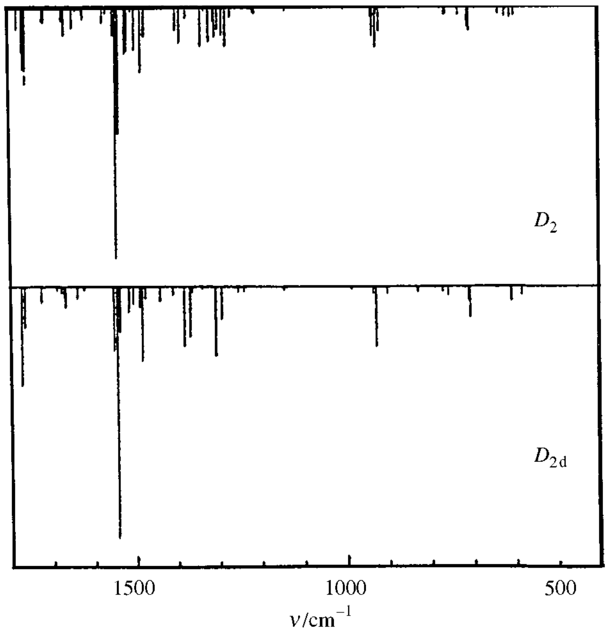

Fig. 5 Calculated IR spectra for [84-D_2(IV) and -D_{2d}(II)]fullerenes[5]

If the individual isomers eventually become isolated, a few of the assignments may need adjustment, because of the possibility of peak coincidences which cannot at present be evaluated. The number of isomers identified is compatible with the results of Saunders *et al.*,[11] and we believe the analysis contributes towards understanding of the preferred fullerene structures and, ultimately, the mechanism of fullerene formation.

IR spectrum

The IR spectrum of the main fraction (KBr disc) is shown in Fig. 4, with the main bands appearing at 1432, 1384, 1142, 1107, 798, 793, 704, 648, 635, 575, 490, 484 and 430 cm^{-1} and minor ones at 1712, 1630, 1587, 1517, 1462, 1421, 1365, 1325, 1262, 1200, 688, 657, 565, 554, 540, 498, 479 and 405 cm^{-1} This spectrum may be compared with those calculated (MNDO) for the D_2(IV) and D_{2d}(II) isomers, reproduced in Fig. 5. In discussing these spectra, the predicted wavenumbers are scaled by 0.9 to allow for the usual overestimation inherent in the MNDO method.[13,14] Main features are:

1. Dominant bands are predicted to occur around 1600 cm^{-1}, a group (including the main band) between 1390 and 1125 cm^{-1}, and bands around 840 and 630 cm^{-1}. Experimentally, there is a modest band at 1630 cm^{-1}, a group between 1432 and 1108 cm^{-1} and two bands at 798/793 and 648/635 cm^{-1}; notably there is no major peak in the region predicted.

2. A group of minor bands are predicted to occur between 585 and 520 cm^{-1}; a group is found between 635 and 404 cm^{-1}.

3. A cluster of minor bands are predicted to occur at higher wavenumbers than the main band. Only trivial bands are evident in this region.

Overall, the general pattern of the spectrum is predicted with modest success only, and it is clear that one of the objectives of the theoretical work, namely the distinguishing between the D_2(IV) and D_{2d}(II) isomers through the use of the predicted IR spectra, cannot be accomplished. The presence of the minor isomers will obviously have some effect on the observed spectrum, but probably insufficient to detract from the main conclusion.

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