



A STUDY ON THE SYNTHESIS AND STABILITY OF THE C₆₀ FULLERENE/TETRACENE ADDUCT

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A C₆₀ fullerene/tetracene adduct was synthesized and studied by electronic absorption spectroscopy and FT-IR spectroscopy. Essentially the mono-adduct was obtained as suggested by the spectroscopic analysis and by the thermogravimetric analysis (TGA). The stability and the retro Diels-Alder reaction of the C₆₀/tetracene adduct was studied by TGA, differential thermogravimetric analysis (DTG) and by differential scanning calorimetry (DSC). It was found that the adduct is stable above 300°C and decomposes at 323-390 °C according to the DSC analysis. The decomposition involves the release of tetracene and the restoration of C₆₀ in high yields. However, part of the C₆₀ is lost as amorphous carbon in the retro Diels-Alder reaction.

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Experimental

Materials and equipment

C₆₀ fullerene was 99+% pure grade and was obtained from MTR Ltd. (Cleveland, OH, USA). Tetracene and all solvents used were from Sigma-Aldrich (St. Louis, MO, USA).

The FT-IR spectra were recorded on the FT-IR spectrometer Nicolet 6700 from Thermo-Fischer in transmittance mode with samples embedded in KBr pellets. The electronic absorption spectra were recorded on a Shimadzu UV2450 spectrophotometer.

The thermogravimetric analysis (TGA) was performed on a Linseis apparatus model L81+DTA under nitrogen flow of 18 L h⁻¹ under a heating rate of 10 °C min⁻¹. The differential scanning calorimetric analysis (DSC) was made on a Mettler DSC 1 Star System apparatus using conventional Al crucible with punched caps at a heating rate of 10°C/min under N₂ flow.

Synthesis of C₆₀-tetracene adduct 1:1 molar ratio

Tetracene (15 mg, 6.98x10⁻⁵ mol) was dissolved in 50 ml of a stock solution of C₆₀ in toluene (C₆₀ conc. in stock solution 1 mg mL⁻¹; thus, 55 mg C₆₀ are 7.64x10⁻⁵ mol). The mixture was refluxed for 1h and then toluene was distilled under reduced pressure leaving a homogeneous and brown solid in quantitative yields.

When part of the reaction product (25 mg) is treated with 8 ml of n-hexane it shows a minimal solubility. The electronic absorption spectrum of the extract does not show any trace of unreacted tetracene but only a series of absorption bands at 209, 228, 255 and 326 nm which can be assigned to C₆₀ or directly to the mono-adduct.

The reaction between tetracene and C₆₀ was also followed spectrophotometrically using a C₆₀ and tetracene concentration in toluene of 1.46x10⁻⁴ M each.

Introduction

Fullerenes are able to form a series of interesting Diels-Alder adducts with polycyclic aromatic hydrocarbons (PAHs) and other dienes.¹⁻⁷ More in detail, C₆₀ fullerene forms a [4+2] addition products with acenes.¹⁻⁸ One of the most studied reaction in this field regards the adduct formation between C₆₀ and anthracene where the former acts as a dienophile while the PAH is the diene.⁸ The property of fullerenes to form adducts has been exploited in the synthesis of quite complex supramolecular structures.^{9,10} The Diels-Alder reaction applied on carbon materials is so versatile that it has been proposed as a tool for the synthesis of new carbon materials and surface functionalization.¹¹ The general interest on the fullerene/acene and then fullerene/PAHs adducts regards new molecules which may combine certain features of fullerenes with those of PAHs which show promising in molecular electronics or other materials science applications,¹² including also organic photovoltaics.¹³

Our interest on adducts between fullerenes and PAHs is linked to the search of such molecules in certain interstellar and circumstellar environments. Indeed, fullerenes were found mixed with PAHs in the circumstellar envelopes around low-mass evolved stars (the so-called planetary nebulae).¹⁴ The current debate involves not only how and where fullerenes were formed but also their possible interaction with PAHs, forming adducts.¹⁵⁻¹⁷ Thus, the present synthesis of the fullerene-tetracene adduct is a follow-up of our earlier study on the C₆₀-anthracene adduct.¹⁶ We are using the infrared spectra of these adducts as references of searching evidence for the presence of such quite complex molecules in space.¹⁶

Synthesis of C₆₀-tetracene adduct 1:2 molar ratio

Tetracene (22 mg, 9.6x10⁻⁵ mol) was dissolved in 35 ml of a stock solution of C₆₀ in toluene (C₆₀ conc. in stock solution 1 mg mL⁻¹; thus, 35 mg C₆₀ are 4.86x10⁻⁵ mol). The mixture was refluxed for 1h and then toluene was distilled under reduced pressure leaving a homogeneous and dark-brown solid in quantitative yields.

Part of the reaction product (20 mg) was treated with 5 ml of n-hexane. The soluble fraction was analyzed by electronic absorption spectroscopy and show a series of new absorption bands which can be attributed to the mono- and bis-adduct. The absorption bands were found at 209, 228, 255, 261, 272, 291, 310 and 325 nm. The insoluble residue after n-hexane extraction displays the same infrared spectrum of the starting product. Therefore, the nature of the soluble fraction is identical to the insoluble fraction and it can be assigned to the mono-adduct and, possibly, with a contribution also from the bis-adduct.

Results and Discussion

Spectrophotometric analysis of the reaction between C₆₀ and tetracene

The kinetics of the reaction between anthracene and C₆₀ and tetracene and C₆₀ has been studied spectrophotometrically.¹⁸ It was found that tetracene reacts much more readily with C₆₀ than does anthracene. In fact at 40°C the kinetic rate constant *k* for the formation of the anthracene/C₆₀ adduct was found at 7.8x10⁻⁴ M⁻¹s⁻¹ while at the same temperature *k* = 0.16 M⁻¹s⁻¹ was measured for the tetracene/C₆₀ adduct. This behavior was theoretically predicted since the different reactivity's of anthracene and tetracene towards C₆₀ correlate with the respective aromaticity loss upon cycloaddition.¹⁹⁻²¹ The two mono-adducts display different behavior as regards the retro Diels-Alder reaction (dissociation back to the reagents), being negligible in the case of the tetracene adduct and important in the case of the anthracene mono-adduct.

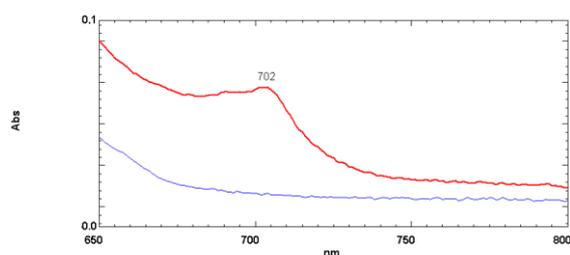


Figure 1. Electronic absorption spectra showing the adduct formation between C₆₀ and tetracene (red line).

The Diels-Alder addition of acenes to C₆₀ is an equilibrium reaction and in the case of anthracene addition it was necessary to use a stoichiometric excess to achieve the formation of the mono-adduct.¹⁸ On the other hand, in the case of tetracene addition to C₆₀ the mono-adduct was obtained even by working in a 1:1 molar ratio between the dienophile and the diene.¹⁸

The formation of the C₆₀/acene mono-adduct can be followed by the growth of the characteristic absorption band at 706 nm accompanied by a shoulder at 640 nm and the evidence of the mono-adduct formation is suggested by a series of isobestic points in the electronic absorption spectrum which in the case of C₆₀/tetracene adduct are located at 409, 436, 586 and 612 nm. The eventual absence of isobestic points can be considered as an evidence of the formation of multiple adducts.¹⁸ Fig. 1 shows the detail of the weak absorption band of the C₆₀/tetracene adduct synthesized by us. The absorption band occurs at 702 nm and is characterized by a relatively small molar extinction coefficient of only 350 L mol⁻¹ cm⁻¹.

FT-IR spectroscopy on the C₆₀/tetracene adduct

The FT-IR spectrum of the C₆₀/tetracene adduct is fundamental for the search and potential identification of this adduct in space. In Figs. 2 and 3 are shown the FT-IR spectra of the C₆₀/tetracene adduct prepared in 1:2 and 1:1 molar ratio. In both spectra there are no significant differences, so that it can be assumed that prevalently a mono-adduct was obtained in both cases. It was also crucial the experiment of n-hexane extraction of the C₆₀/tetracene adduct resulting from the 1:2 molar ratio. The FT-IR spectrum of the insoluble part resulted identical to that of the whole sample before the n-hexane treatment. Furthermore, the solubilised fraction displayed an electronic absorption spectrum which appeared different from that of pure C₆₀ and pure tetracene. Consequently, the spectrum could be attributed to the mono- and bis-adduct.

The main infrared feature of the C₆₀/tetracene adduct in the C-H stretching region (Fig. 2) is the presence of a series of absorption bands which are completely absent in pure C₆₀ and which are found at 3042 cm⁻¹ in the case of pure tetracene. The FT-IR spectrum of the C₆₀/tetracene adduct is characterized by two aromatic C-H stretching bands respectively at 3045 and 3021 cm⁻¹ followed by a group of infrared bands at 2950, 2910 and 2848 cm⁻¹ which are due to cycloaliphatic C-H stretching and are due just to the tetracene C-H groups attached to the fullerene cage.²² A similar (but not identical) spectrum was observed in the case of the C₆₀/anthracene adduct.^{8, 16}

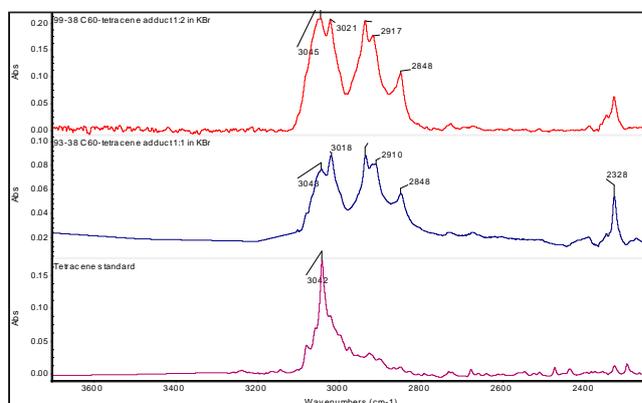


Figure 2. FT-IR spectrum in KBr in the C-H stretching region of C₆₀/tetracene adduct prepared from a 1:2 (top) and 1:1 (middle) molar ratio. The spectra at the bottom of the figure are due to pure tetracene standard.

Fig. 3 shows the spectra of the C₆₀/tetracene adduct in the mid-infrared spectral region in comparison to the spectra of pure C₆₀ and pure tetracene. The new infrared bands attributable to the adduct are certainly those at 1673, 1490, 1480, and 1460 cm⁻¹ and the other series at 804, 727, 699, 671, and 640 cm⁻¹ which could be attributed to the C-H bending modes of the tetracene CH groups after the addition to C₆₀.²² The C₆₀ cage is still intact and displays the typical bands at 1426 and 526 cm⁻¹. The other two C₆₀ infrared bands at 1180 and 574 cm⁻¹ appear weaker or even absent in the spectrum of the C₆₀/tetracene adduct. Similarly, also some strong absorption bands of reference tetracene, for example those at 902 and 471 cm⁻¹ appear very weak in the infrared spectrum of the adduct. Thus, the infrared spectrum of the adduct looks consistent with the known Diels-Alder structure.

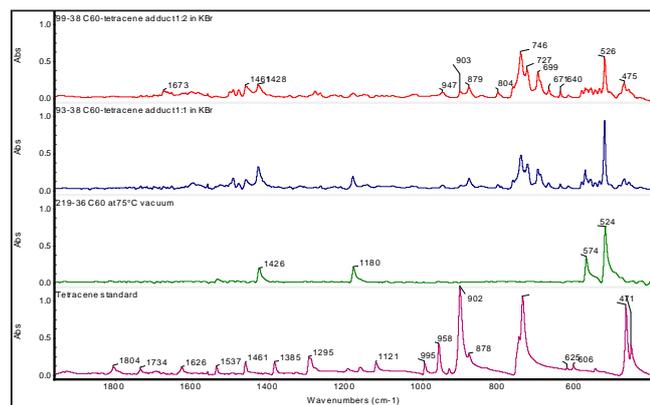


Figure 3. FT-IR spectrum in KBr in the mid infrared region of C₆₀/tetracene adduct prepared from a 1:2 (top) and 1:1 (second from top) molar ratio. The two spectra at the bottom of the figure are due to pure C₆₀ and to tetracene standard, respectively.

Thermogravimetric analysis (TGA) of the C₆₀/tetracene adduct

The TGA of the C₆₀/tetracene adduct is useful not only to establish the stability of the adduct but especially also for the interpretation of the stoichiometry of the adduct. In Fig. 4 it is reported the TGA made on the C₆₀/tetracene adduct prepared from a molar ratio 1:1. It is evident that the adduct decomposition occurs above 300 °C (see next section for a deeper discussion) and then a large plateau is reached up to 650 °C. The decomposition of the adduct implies the vaporization of the tetracene leaving C₆₀, which is much less volatile as residue. Surprisingly, the weight loss observed at the plateau above 300 °C is only -15.4 % which once corrected for the weight loss at 300°C (-4.0 %) becomes -11.4 %. This value is much less than the weight loss theoretically expected for the retro Diels-Alder reaction of C₆₀/tetracene 1:1 adduct. In fact, the theoretical weight loss due to tetracene vaporization should be 24.05 %. Since we have evidence that the reaction between C₆₀ and tetracene was practically complete, as suggested by the n-hexane extraction experiment, it is reasonable to think that the thermal decomposition of the C₆₀/tetracene adduct does not yields quantitatively the reactants, at least above 300 °C but in part produces a crosslinked carbon soot. This is clearly confirmed by the TGA of Fig. 4 where it is possible to observe that above 900°C under N₂, about 50 % of the starting adduct was not vaporized as C₆₀ but remained as non-volatile carbon black. Instead, we know that pure C₆₀ is completely volatile above 750 °C.²³

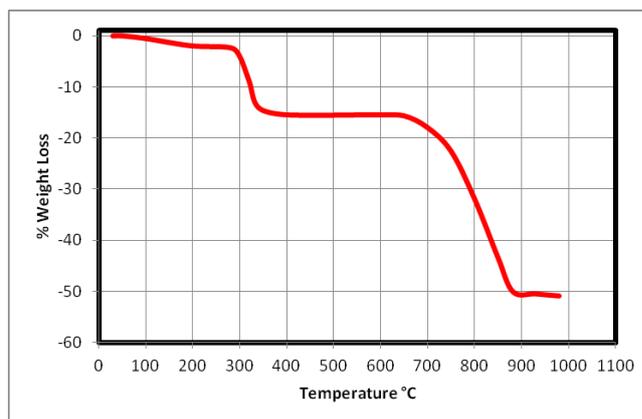


Figure 4. Thermogravimetric analysis of the C₆₀/tetracene adduct prepared from a 1:1 molar ratio

The TGA of the C₆₀/tetracene adduct prepared from a 1:2 molar ratio is shown in Fig. 5. The adduct decomposition occurs again above 300 °C but this time the plateau weight loss is -31.0 % which corrected by the weight loss measured at 300 °C (-7.6 %) it gives -23.4 % in good agreement with the theoretical value of -24.0 % for the mono-adduct. However, as said in the previous case, the decomposition of the C₆₀/tetracene adduct is not a smooth reaction in the TGA. In fact, also Fig. 5 shows that a carbonaceous residue remained in the crucible above 900 °C under N₂. The residual amount is about 34 % by weight of the starting sample.

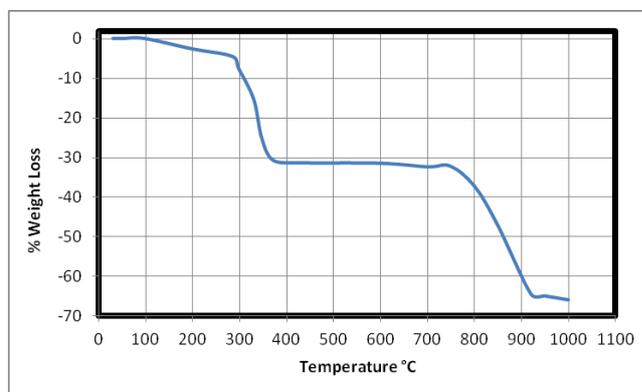


Figure 5. Thermogravimetric analysis of the C₆₀/tetracene adduct prepared from a 1:2 molar ratio

Study of the decomposition reaction of the C₆₀/tetracene adduct

The C₆₀/tetracene adduct prepared from a 1:2 molar ratio was heated in a DSC crucible at a heating rate of 10°C/min under N₂ flow. One sample was heated to 350°C and then cooled under N₂ and then analyzed by FT-IR, while another sample was heated to 630°C and then cooled to room temperature under N₂ and analyzed by FT-IR as well. The FT-IR spectra are shown in Fig. 6.

The infrared spectra of Fig. 6 show that when heated at 350°C the C₆₀/tetracene adduct is just at an incipient decomposition stage as suggested by the presence of the C-

H stretching bands at 3045 and 3021 cm⁻¹ followed by a group of infrared bands at 2950, 2910, and 2848 cm⁻¹ which are typical of the adduct.

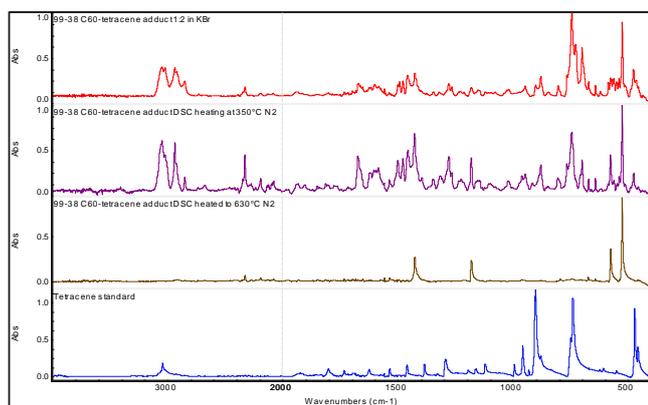


Figure 6. FT-IR spectrum in KBr of C₆₀/tetracene adduct prepared from a 1:2 (top); after heating at 350°C under N₂ (second from top); after heating at 630°C under N₂ (third from top); The spectrum at the bottom of the figure is due to pure tetracene standard.

Fig. 6 shows also that at 630 °C the adduct is completely decomposed and the tetracene was completely vaporized leaving a residue of C₆₀. Based on these spectral data it can be affirmed that the decomposition of the C₆₀/tetracene adduct is complete with the restoration of the reagents. Tetracene is vaporized while C₆₀ remains in the crucible since its vaporization occurs above 750 °C as it can be observed also in the TGA of Fig. 4 and 5.²³

The TGA of Fig. 5 shows that at above 900 °C the total weight loss after C₆₀ vaporization corresponds to -66 %. The amount of C₆₀ formed by the retro Diels-Alder and vaporized corresponds to 31-66 = 35 % of the starting adduct. This implies that about 35/75.95 = 46 % of the C₆₀ formed from the retro Diels-Alder was vaporized while the remaining 54% was transformed into a non-volatile carbon black. This behaviour is typical for all fullerene adducts including also the C₆₀/anthracene adduct which however is not able to give back so large amounts of C₆₀ as in the case of the tetracene adduct discussed here.⁸

For a further insight into the decomposition reaction of the C₆₀/tetracene adduct in Fig. 7 is reported the DSC trace of the sample heated up to 630 °C under N₂. Two endothermic transitions are observed. The first one is observed at 323 °C with an onset at 315°C and an enthalpy of 10.2 J g⁻¹ (9.7 kJ mol⁻¹) while the second transition is more energetic with an enthalpy of 37.7 J g⁻¹ (35.7 kJ mol⁻¹) with peak at 390°C and onset at 378 °C. The tetracene melting point occurs at 375°C, thus in the middle of the two DSC transitions. The sublimation enthalpy of tetracene is reported at 126 kJ mol⁻¹.²⁴

The exact assignments of these two endothermic transitions remain uncertain although it is possible to assume that the first transition is associated to the initial breakdown of the adduct while the second with the vaporization of tetracene resulting from the retro Diels-Alder.

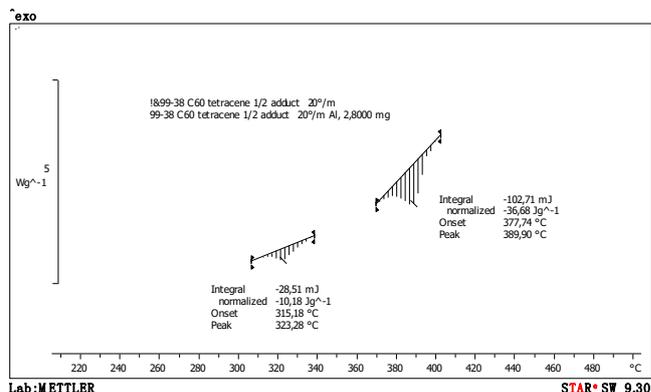


Figure 7. DSC trace of the C₆₀/tetracene adduct prepared from a 1:2 molar ratio. Two endothermic transitions can be distinguished at 323°C and 390°C.

It is interesting in any case to compare the DSC results with the DTG data obtained from the first derivative of the TGA curve of Fig. 4 and Fig. 5. Both the C₆₀/tetracene adducts prepared from 1:1 molar ratio and 1:2 molar ratio show in the DTG of Fig. 8 two transitions connected with the weight loss and hence to the decomposition episodes of the adduct. The first transition occurs at 336 °C followed by another transition at higher temperature: 369 °C. Thus, there is a parallelism in the double endothermic transitions observed both with DSC and with DTG irrespective of the C₆₀/tetracene molar ratio used confirming the idea that first it occurs the adduct breakdown and then the vaporization of the products.

The last annotation here regards the enthalpy of the Diels-Alder reactions. All the spontaneous Diels-Alder reactions are exothermic reactions in the formation of the adduct and endothermic reactions in the retro reactions.²⁵ For example, the acene dimerization involving anthracene dimerization is reported to be an exothermic reaction with release of -22.6 kJ mol⁻¹.²⁵ Of course, the retro reaction is instead endothermic and at least 22.6 kJ mol⁻¹ plus the activation energy should be administered to decompose the adduct. Consequently, since the decomposition of the C₆₀/tetracene adduct requires the administration of 45.4 kJ mol⁻¹ plus the activation energy, the reaction enthalpy for the formation of the adduct is exothermic and should be of the order of -45.4 kJ mol⁻¹.

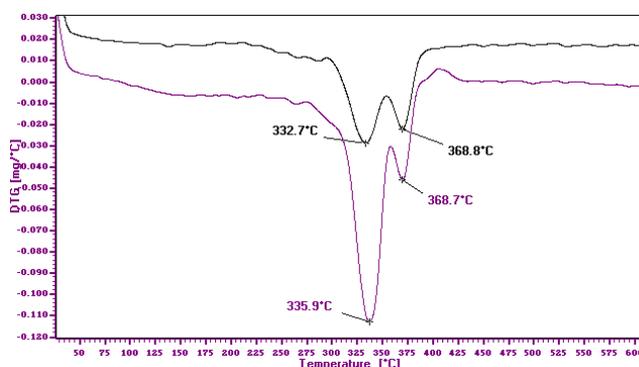


Figure 8. DTG of the C₆₀/tetracene adduct prepared from 1:1 molar ratio (upper trace) and 1:2 molar ratio (lower trace). Two transitions at about 335 °C and 369 °C were detected.

The interpretation of the DSC data is complicated by the fact that the decomposition of the adduct and the vaporization of tetracene may occur also at the same time and this hinders the separation of the reaction enthalpy from the vaporization enthalpy.

Conclusions

In toluene solution C₆₀ and tetracene react swiftly to produce mainly a mono-adduct, which is stable above 300 °C and decompose at 323- 390 °C according to the DSC analysis. The decomposition temperature of the C₆₀/tetracene adduct is considerably higher than that of the C₆₀/anthracene adduct studied previously and that decomposes between 225-260°C.⁸

The thermal decomposition of the C₆₀/tetracene adduct causes the release of tetracene and the recovery of the starting C₆₀ in relatively high yields. However, about 50 % of the C₆₀ employed as reactant is lost as amorphous carbon in the retro Diels Alder reaction.

The C₆₀/tetracene adduct can be easily recognized through the electronic absorption spectroscopy by the development of the absorption band at 702 nm, which, however, is characterized by a low molar extinction coefficient. More useful is the FT-IR spectroscopy which show clear evidence of the formation of the C₆₀/tetracene adduct, especially in the C-H stretching region due to aromatic and cycloaliphatic chemical structure, completely in line with the C₆₀/tetracene adduct structure.

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