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Host-Guest complexation of 1,8,15,22-tetraphenyl[14] metacyclophan-4,11,18,25-tetramethyl-3,5,10,12,17,19,24,26-octol with C_{60}

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Abstract: Two new complexes **2** and **3** between fullerene C_{60} and metacyclophane **1** were prepared and characterized by spectroscopic methods. Metacyclophane **1** was studied in solution by NMR and in the solid state both by NMR and X-ray diffraction. Two different conformers of **1** were detected. The macrocycle **1** can guest **1** or **2** fullerene molecules in its structure. For the complexes **2** and **3**, π-π, σ-π and n-π interactions were observed by ^{13}C CP-MAS, FTIR analysis data.

Keywords: Metacyclophane ; fullerene; host-guest complexation

Introduction

The placement of a C_{60} guest into a suitably designed host molecule represents an initial step forward in efforts directed towards the synthesis of supramolecules involving fullerenes.[1] Indeed, supramolecular complexes have been obtained using cyclic host macromolecules like cyclodextrines,[2,3] calixarenes, [4-11] crown ethers [12] and cycloveratrilenes,[13] that possess cavities having suitable dimensions for the inclusion of a fullerene guest. The inclusion properties of these compounds have been shown to result from π ··π, O-H ··π and σ ··π interactions.[4,8,13] Understanding the interactions which exist between fullerenes and macromolecules is important. This is not only because it may be possible to prepare water soluble fullerene complexes with potential biomedical applications, [14] but complexes of this type also serve as a facile purification method for specific fullerenes present in the usual mixtures of carbon soot,[15,16] or may be used for the synthesis of new materials for electronic devices. [17]

Recently, we reported the pressure area isotherms for Langmuir films made of calix[8]arene, calix[8]arene/C_{60} complex and calix[8]arene/C_{70} complex.[11] This experimental information is consistent with the assumption that C_{60} is situated inside the cavity of calix[8]arene.

In the present work we report our findings on the interactions of fullerenes with metacyclophane **1**, forming two solid-state complexes. These are: C_{60} with **1**, in a 1:1 (**2**) and 2:1 (**3**) ratio, respectively.

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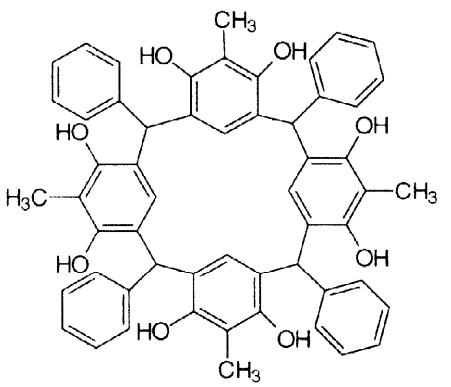
Results and Discussion

Metacyclophane **1** was prepared following a synthetic methodology previously described.[17] The product was crystallized from DMSO at -20°C and the X-ray crystallographic determination was performed at -50°C. For this compound the results show a "sofa" conformation, with the four phenyl groups in axial positions (**1a**). The crystal structure also shows 7 molecules of DMSO as crystallization solvent. However, the presence of an additional conformer **1b** was established by ^{13}C CP-MAS and low temperature NMR experiments which are described below. To prepare the adducts, a DMSO solution of **1** (117 mg, 0.138 mmol) was added to a benzene solution of C_{60} (100 mg, 0.138 mmol), and stirred vigorously at 80°C for 3.5 days. After this period, a brown precipitated was formed. The solid was filtered and washed with benzene affording 153 mg of compound **2**. Results of microanalytical determinations were consistent with a 1:1 stoichiometry. When the reaction time was extended to 7 days, a new complex **3** was formed. Elemental analysis of this complex suggested two molecules of C_{60} with one of macrocycle **1** (See Experimental Section).



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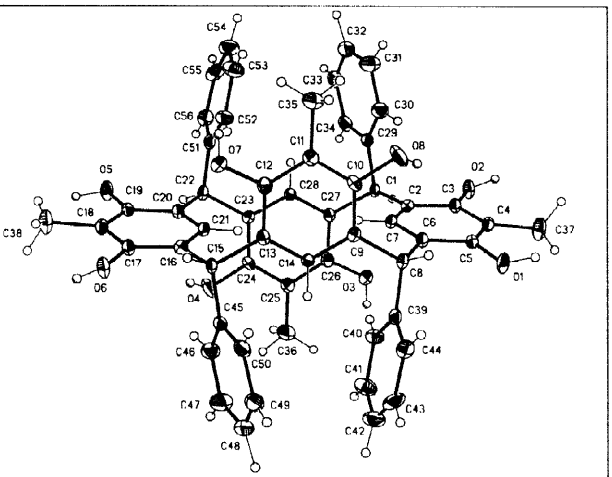


ORTEP view with atomic labeling of **1**

Room temperature COSY, NOESY, HMQC, HMBC (see Tables 1 and 2 for the assignments) and low temperature NMR spectra of **1** can be interpreted in terms of equilibrium of two major conformers (**1a** $\rightleftarrows$**1b**) as depicted in figure 1. The proton at δ 5.62 (table 1) was assigned to benzylic hydrogens, the aromatic signals of the methyl resorcinol moiety appears at δ 6.20 and the δ 5.36 signal assigned to the aromatic hydrogens coplanar and orthogonal to the ansa cycle, respectively. The signal at δ 6.65 (8H) and δ 6.86 (12H)

were attributed to the phenyl protons. Two signals for the benzylic methyl groups were observed at δ 2.10 and 1.92.

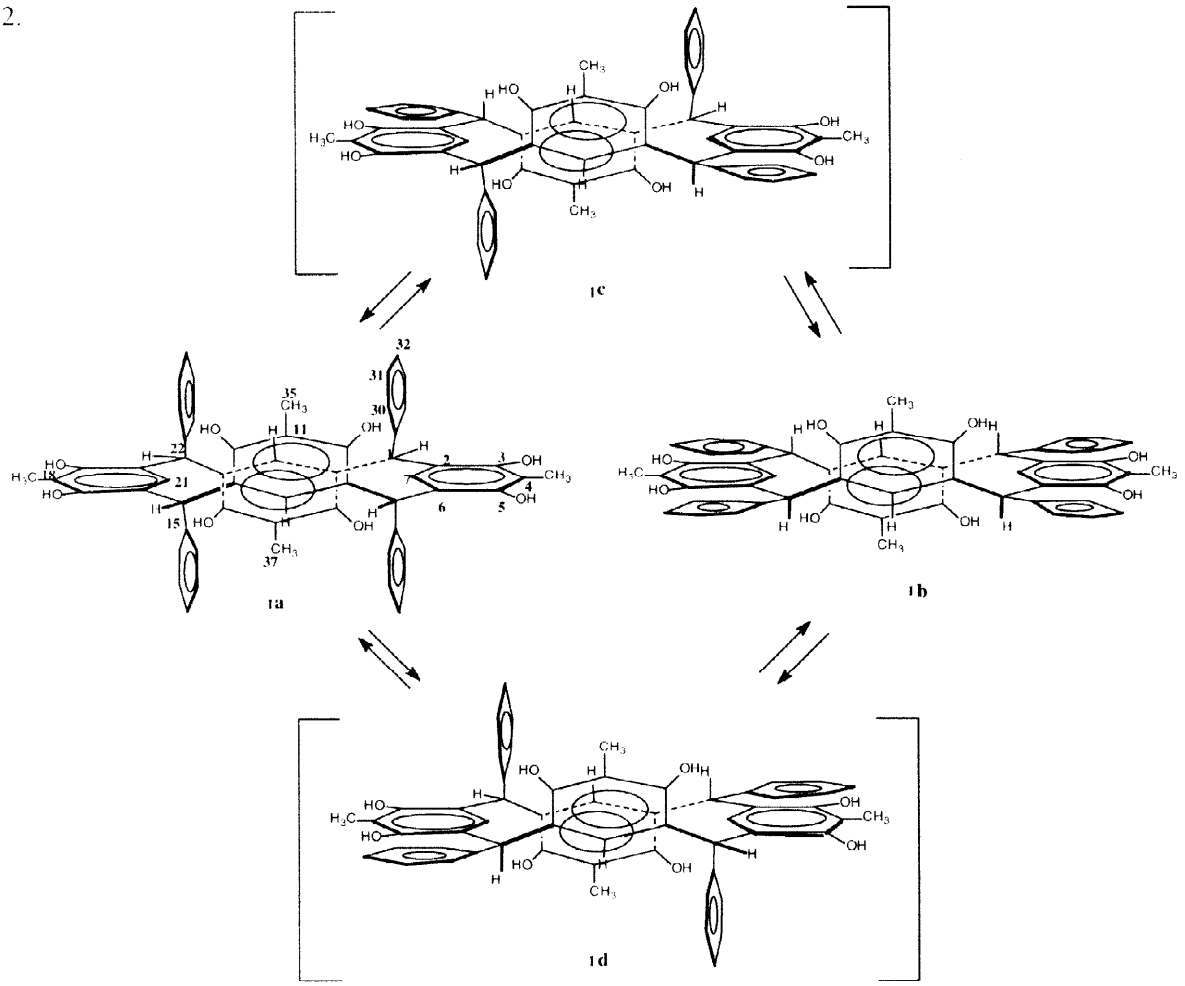


Figure 1

Furthermore, all these assignments are in agreement for two conformations, **1a** and **1b** with the following observations: a) the magnetic equivalency of the benzylic hydrogens oriented equatorially and axially in the ansa chain, b) the observed NOE (NOESY) between H-30 and the methyl groups, orthogonal to the ansa chain, and the benzenic hydrogens of the resorcinol moiety, and c) a NOESY crosspeak between the H-1 and the phenolic hydrogens.

Table 1. ^{1}H NMR spectral data for **1**

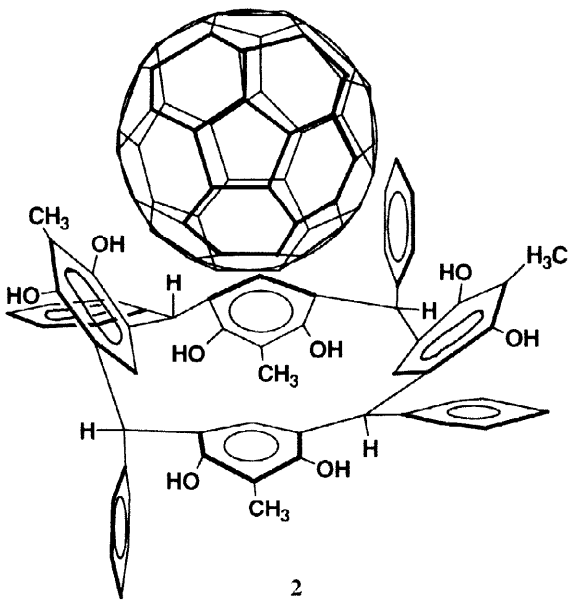
H	1	7	14	30	31,32	37($C\underline{H}_3$)	35($C\underline{H}_3$)	3($O\underline{H}$)	10($O\underline{H}$)
δ	5.62	6.20	5.36	6.65	6.86	2.10	1.92	7.49	7.06

Table 2. ^{13}C NMR Chemical shifts for **1**

C	1	2	3	4	7	9	10	11	14	29	30	31	32	35	37
δ	43.56	122.59	150.56	111.06	125.78	121.88	150.32	110..53	127.86	143.08	129.02	126..92	124.54	9.18	9.64

Room temperature ^{13}C CP-MAS NMR (figure 2, plot A) indicates the presence of two conformers (**1a** and **1b**), since two non-equivalent methine groups (at δ_c 43.83 and δ_c 45.38) are observed. This is confirmed by low temperature (-90 °C) NMR spectra of **1** in deuterated acetone, where the methine and methyl signals are solved for each conformers.

Crystallization of the metacyclophane **1** at –20 °C and the X-ray crystallographic determination of this solid at –50 °C allowed us to trap and analyse only conformer **1a**, which is depicted in figure 1.



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A comparative study of the solid state ^{13}C CP-MAS NMR spectra of **1,** with that of the 1:C_{60} complex (figure 2, plot B) implies a major conformational change for **1**. The presence of four non-equivalent signals for the benzylic methines, and the presence of two magnetically equivalent methyls suggested a conic conformation related to the intermediates **1c** and **1d** (figure 1) which could be derived from rotation of conformations **1a** and **1b** to a favorable topologic convex space for the fullerene.

Additional support for conformation **2** was obtained from the observation of an upfield shift of the ^{13}C NMR signal ((δ142.43), Δδ=1.1), presumably arising from the interactions of the four phenyls rings in **1** with six of the eigth phenolic groups. This interaction could occur through a combination of σ-π, HO-π, and π-π interactions.

Complexation of **1** with two equivalents of C-60 again evokes a conformational change in the metacyclophane. From ^{13}C solid-state CP-MAS NMR spectrum (figure 2, plot C) four signals at δ_c 7-14 for

the non-equivalent benzylic methyls were observed. The splitting of the signals of the benzylic methines (at δ_c 35-44) and non-equivalency of the aromatic hydrogens of the methyl resorcinol residues indicate a chair-like conformation. In this case, where the resorcinol residues do not lay in the plane, thus forming two convex spaces above and below the ansa cycle, the C_{60} is electrostatically bonded, such is as shown in **3**.

The low field shift of C_{60} (δ_c 143.50) in the complex 1:2C_{60} compared with that of C_{60} in the complex 1:C_{60} (δ_c 142.43) could be attributed to weaker electrostatic interactions, probably due to larger distances between the methyl and the phenolic groups and the C_{60}.

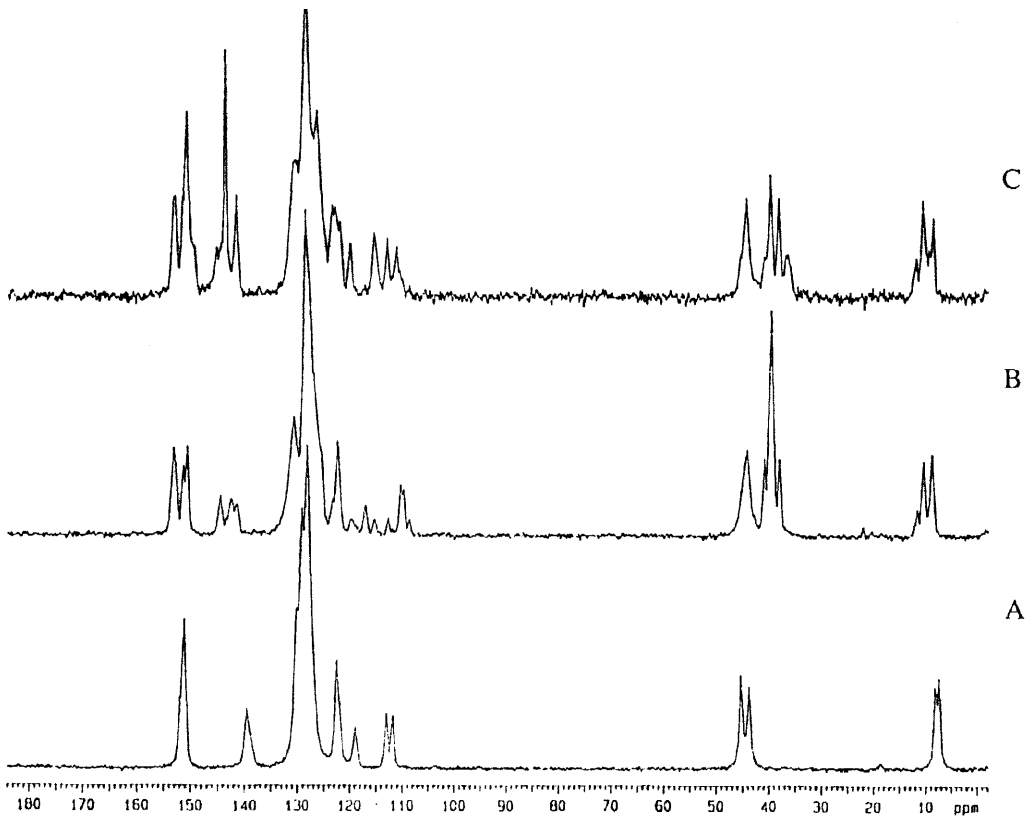
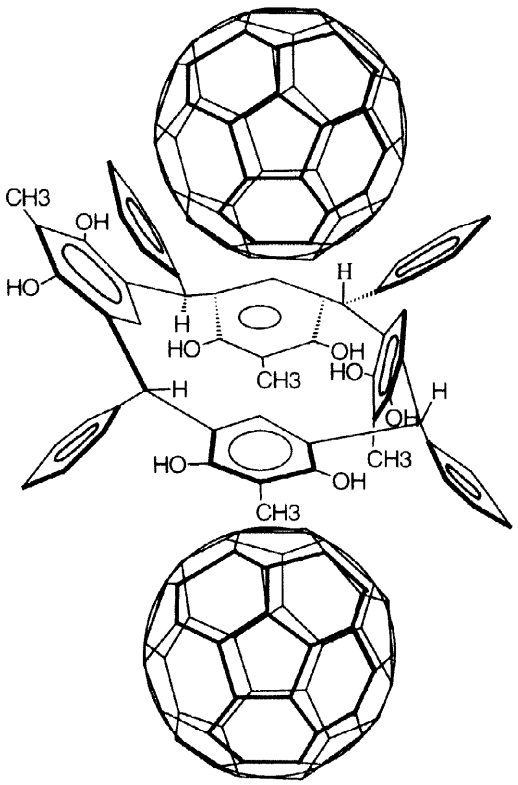


Figure 2. (A) ^{13}C CP-MAS NMR of **1**. (B) ^{13}C CP-MAS NMR of 1:C_{60}: (C) ^{13}C CP-MAS NMR of 1:2C_{60}. All the spectra were taken at room temperature.

IR spectroscopy (KBr) of complex **2** indicates that the intermolecular hydrogen bonding normally present at 3532 cm^{-1} in the parent compound is partially disrupted and shifted to 3467 cm^{-1}. The same effect was observed for complex **3** indicated by a shift to 3473 cm^{-1}.

In summary ^{13}C CP-MAS analysis and low temperature ^{13}C NMR allowed to establish the presence of two conformers (**1a** and **1b**) for the methacyclophane **1**. Incidentally, low temperature X-ray analysis of the solid obtained at –20°C indicated the unique presence of the conformer **1a**. Two different host-guest

interactions of **1** and C_{60} were observed, depending on the reaction conditions. A 1:1 complex **2** was obtained in shorther reaction times, and the methacyclophane undergoes a major conformational change to adopt a convex area to host the fullerene. 1:2/C_{60} complex **3** was obtained in longer reaction times and again, a conformational change of the methacyclophane was deduced by comparative ^{13}C-CP-MAS NMR analysis. Host-guest interactions cause remarkable conformational changes in the host.



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Experimental Section

General Remarks.

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H- and ^{13}C- NMR spectra were collected on a Varian Unity 500 operating at 500 and 125 MHz, respectively. For both ^{1}H and ^{13}C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me_4Si 0.00 ppm) used as an internal standard. The ^{13}C CP-MAS NMR spectra were collected on a Bruker spectrometer at 125 MHz for carbon-13. Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville. FAB^+ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystalographic data were collected at –50 °C on a Siemens P/4 diffractometer.

Matacyclophane (1). It was synthesized according to a procedure previously reported.[17] by treatment of 2.0 g (16.1 mmol) of 2-methylresorcinol and 1.8 ml (16.1 mmol) of benzaldehyde. The solid residue was washed successively with methanol and dichloromethane. To afford 2.68 g (72 %) of **1**. mp > 350 °C. IR (KBr): 3532, 3027, 2923, 1607, 1476, 1449, 1320, 1237. 1192, 1093, 1028, 916, 754, 703,575 cm^{-1} ^1H NMR (DMSO-d) δ 6.86(m, 12H), 6.65(m, 8H), 6.19 (s, 2H) 5.36(s, 2H), 5.62(s, 2H) 2.10 (s, 6H), 1.92 (s, 6H). ^{13}C NMR (DMSO-d) δ 9.18($\underline{C}H_3$), 9.64($\underline{C}H_3$), 43.56($\underline{C}$H-Ph), 110.53($\underline{C}$-CH_3), 111.06 ($\underline{C}$-CH_3), 121.88 ($\underline{C}$-CH-Ph), 122.59($\underline{C}$-CH-Ph), 124.54(Ph), 125.78 (Ar-H), 126.92 (Ph-H),129.02(Ph-H), 127.86(Ar-H), 143.08(PhC-ipso), 150.32(Ar-OH), 150.56(Ar-OH). Anal. Calcd for $C_{56}H_{51}O_8$: C, 79.15; H, 5.65; O, 15.07. found; C,79.12; H, 5.62; O, 15.09. CP-MAS spectrum ^{13}C CP-MAS NMR Chemical shifts for conformer **1a** and **1b** 7.50($\underline{C}H_3$), 8.17($\underline{C}H_3$), 43.83($\underline{C}$H-Ph), 45.38 ($\underline{C}$H-Ph), 113.01($\underline{C}$-CH_3), 118.94 ($\underline{C}$-CH-Ph), 122.52 ($\underline{C}$-CH-Ph), 124-130 (Ph), 139.61($\underline{C}$ ipso), 151.85 ($\underline{C}$-OH), 151.95 ($\underline{C}$-OH). Ms m/z, %: 848 (20), 847(5), 771(2). Anal. Calcd for $C_{56}H_{51}O_8$: C, 79.15; H, 5.65; O, 15.07. found; C,79.12; H, 5.62; O, 15.09.

In order to get the X-ray crystallographic analysis a sample of **1** was recrystallized from DMSO.

Complex: Metacyclophane 1: 1C60 (2). A DMSO solution of **1** (117 mg, 0.138 mmol) was added to a benzene solution of C_{60} (100 mg, 0.138 mmol), and the mixture stirred vigorously at 80°C for 3.5 days. After this period, a brown precipitated was formed. The solid was filtered from the colorless solution and washed with benzene affording 153 mg of compound **2**. Elemental analysis results were consistent with a 1:1 stoichiometry. IR (KBr): 3467, 3370, 3025, 2917, 1603, 1475, 1430, 1317, 1213, 1182, 1099, 1015, 948, 754, 704, 575, 252 cm^{-1} . ^{13}C CP-MAS NMR Chemical shifts 8.95, 10,58 ($\underline{C}H_3$), 11.74 ($\underline{C}H_3$), 38.09; 39.64 ($\underline{C}$H-Ph), 40.98-44.28 ($\underline{C}$H-Ph), 109.67-110.32($\underline{C}$-CH_3), 116.99 ($\underline{C}$-CH-Ph), 122.26, 123.27 ($\underline{C}$-CH-Ph), 125-130 (Ph), 141.29($\underline{C}$ ipso), 150.58 ($\underline{C}$-OH), 151.36 ($\underline{C}$-OH). Anal. Calcd. for $C_{56}H_{48}O_8$. C_{60}.5DMSO.H_2O. C, 76.51; H, 4.04. Found: C, 76.85; H, 4.35.

Complex: Metacyclophane 1:2C60 (3). A DMSO solution of **1** (117 mg, 0.138 mmol) was added to a benzene solution of C_{60} (100 mg, 0.138 mmol), and the mixture stirred vigorously at 80°C for 7 days. After usual work-up a new complex **3** was formed. The elemental analysis showed two molecules of C_{60} with one of macrocycle **1**. IR (KBr): 3473, 3298, 2921, 1601, 1476, 1430, 1182, 1102, 1012, 952, 757, 703, 576, 528 cm^{-1} .^{13}C CP-MAS NMR Chemical shifts 8.67; 9.46 ($\underline{C}H_3$), 10.71; 12.0 ($\underline{C}H_3$), 36.547; 38.22 ($\underline{C}$H-Ph), 39.82; 44.44 ($\underline{C}$H-Ph), 111.11; 112.77 ($\underline{C}$-CH_3), 114.75; 115.28($\underline{C}$-CH_3), 119.85-121.86 ($\underline{C}$-CH-Ph), 122.68-123.39 ($\underline{C}$-CH-Ph), 126-130 (Ph), 141.45($\underline{C}$ ipso), 149.28 ($\underline{C}$-OH), 153.14 ($\underline{C}$-OH). Anal. Calcd. for $C_{56}H_{48}O_8$.2C_{60}.4DMSO.2H_2O. C, 83.76; H, 2.88. Found: C, 83.69; H, 2.16.

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