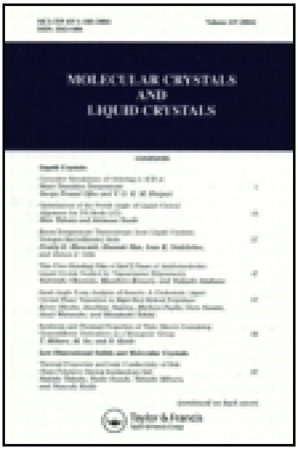

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mesomorphic Poly(aryl ester)/Poly(benzyl ether) Dendrimers/co-Dendrimers with C_{60} as the Core

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Version of record first published: 03 Aug 2009

To cite this article: Natalia Yevlampieva, Nikolai Beljaev, Peter Lavrenko & Robert Deschenaux (2009): Mesomorphic Poly(aryl ester)/Poly(benzyl ether) Dendrimers/co-Dendrimers with C_{60} as the Core, Molecular Crystals and Liquid Crystals, 506:1, 34-46

To link to this article: http://dx.doi.org/10.1080/15421400902841429

Mol. Cryst. Liq. Cryst., Vol. 506, pp. 34–46, 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902841429

Mesomorphic Poly(aryl ester)/Poly(benzyl ether) Dendrimers/co-Dendrimers with C_{60} as the Core

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Structure-properties relations of liquid crystalline fullerene-containing poly(aryl ester)/poly(benzyl ether) dendritic compounds with variation of C_{60} linkage type have been analyzed based on experimental data on their total polarity and electro–optical Kerr effect in benzene solutions. There was established that fulleropyrrolidine as the core of dendrimer strongly restricts rotational freedom of dendrons, in contrast to methanofullerene. A conclusion that not only terminal mesogenic groups and dendrons' generation number, but a manner of C_{60} incorporation into the dendritic matrix also influences on the mesomorphic behavior of these multicomponent hybrid-type liquid crystalline compounds had been made.

INTRODUCTION

Fullerene-containing poly(aryl ester)/poly(benzyl ether) dendrimers bearing terminal mesogenic groups is a promising area of research in material science due to perceived advantages of combining the properties of fullerenes and polyesters/polyethers with those of liquid crystals. The incorporation of fullerene C_{60} as electron-acceptor into the electron-donor liquid crystalline polymer matrix of special architecture opens the door to a rich variety of new geometrical shapes and molecular ordering, that leads to novel optical and electronic properties of the material which cannot be obtainable with simple structure liquid crystals (LC). The mesogenic species of poly(aryl ester)/poly(benzyl ether) dendrimers have been found convenient

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fragments for stimulating of self-organization and formation of well organized molecular assemblies that is important for producing of thin specially organized photosensitive films and conducting materials. The synthesis of mesomorphic fullerene-containing poly(aryl ester)/poly(benzyl ether) dendrimers has initiated research activity in the fields of plastic solar cells [1], organic light emitting diodes [2], photoactive dyads, and polyades [3,4].

Two approaches have been reported recently for the design of fullerene-containing poly(aryl ester) or poly(aryl ester)/poly(benzyl ether) dendritic thermotropic liquid crystals [5,6]. First approach, based on the addition of liquid crystalline addends to C_{60} by applying Bingel reaction [7], produces mesomorphic methanofullerenes (Fig. 1a, compound **1**). The second approach is based on 1, 3-dipolar cycloaddition reaction of addends with fullerene [8] and leads to mesomorphic fulleropyrrolidines (Fig. 1a, compound **2**).

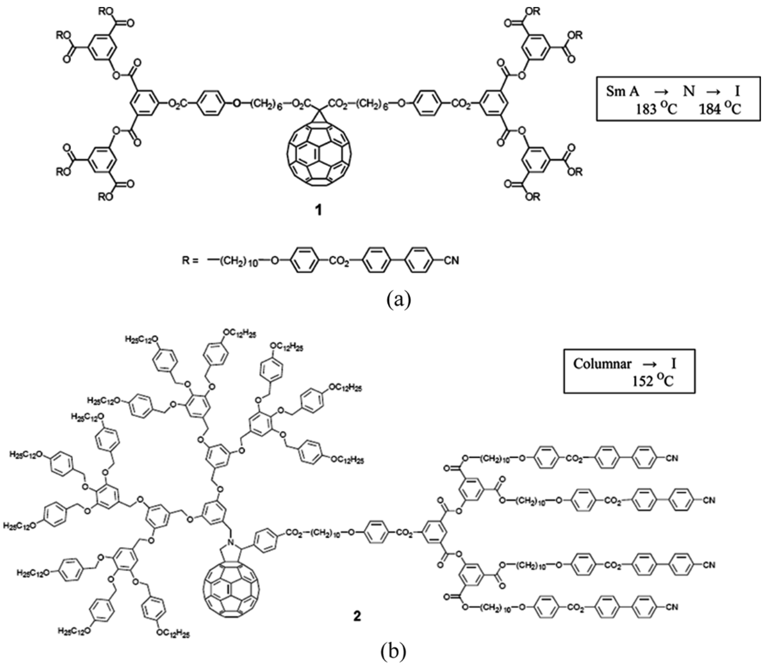
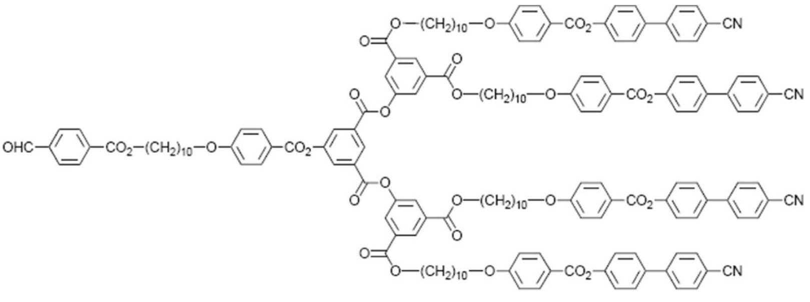
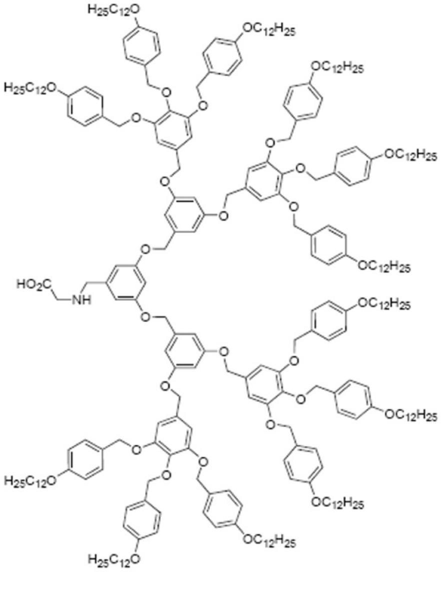


FIGURE 1 Chemical structure of fullerene-containing poly(aryl ester) dendrimer **1**, poly(aryl ester)/poly(benzyl ether) co-dendrimer **2** with the data on their phase transition temperatures [5,10]; **R** is mesogenic end-group **(a)**; and chemical structure of compounds **D1** (the second generation) and **D2** (the third generation) analogues to dendrons of **1** and **2** (**b**).



D1



D2

FIGURE 1 Continued.

Methanofullerene **1** and fulleropyrrolidine **2** have significantly different thermotropic liquid crystalline properties in spite of their similar molecular shape and dimensions. The phase transition temperatures of **1** and **2** are presented in Fig. 1a. Compound **1,** containing two poly(aryl ester) dendrons **D1** bearing cyanobiphenyl mesogenic end-groups (Fig. 1b), demonstrates a smectic A and a short range nematic phase; however, co-dendrimer **2**, combining poly(aryl ester) dendron **D1** with poly(benzyl ether) dendron **D2** (Fig. 1b), possesses a rectangular columnar phase. A glass transition temperature was not defected in either compounds.

The influence of the dendrons' generation number and the number of mesogenic groups on the mesomorphic behavior of fullerene-containing poly(aryl ester)/poly(benzyl ether) dendrimers/co-dendrimers have been studied earlier [5,9,10]. Because the previous studies have been performed for methanofullerene- and fulleropyrroline-derivatives' series separately, the influence of chemical linkage type between fullerene C_{60} and polyester/polyether dendrons on mesomorphic ordering of fullerene-containing dedritic structure compounds has been out of discussions and has not been yet analyzed. Taking into account a strong electron-accepting nature of C_{60} and its possible transformation under chemical modification, the investigation of structure-properties relations of the hybrid multicomponent compounds had been continued with the purpose to clear the role of chemical binding of fullerene on their molecular properties and mesomorphic behavior.

The present article reports experimental and calculated data on the dipole-dependent electrooptical molecular properties of compounds **1** and **2** with the different manner of covalent C_{60} binding (Fig. 1a). Permanent dipole moment values and electrooptical Kerr effect of **1** and **2** were measured in benzene solutions. The same molecular properties of dendrons **D1** and **D2** (Fig. 1b) as the individual compounds have been studied also. Intramolecular dipole organization of different types was detected for the multicomponent compounds **1** and **2** which was consistant with their mesomorphic properties.

EXPERIMENTAL

Dendrons **D1, D2,** co-dendrimer **2**, and dendrimer **1** have been synthesized as described earlier [5,6]. The dielectric, elecro–optical, and hydrodynamic properties of **1, 2, D1**, and **D2** have been investigated in dilute benzene solutions. Quantum chemical modeling has been used for the comparative analysis of electrooptical characteristics of dendritic molecules. Semiempirical quantum chemical method PM3 in the framework of HyperChem program has been applied for the molecular parameters calculation [11].

The permanent dipole moment values μ of compounds have been determined by the Guggenheim–Smith method [12]. This method is derived from the experimental determination of the dielectric permittivity increment $(\varepsilon - \varepsilon_o)/c$, where $(\varepsilon - \varepsilon_o)$ is the difference between the dielectric permittivity of the solution and solvent, and from the determination of the squared refractive index increment $(n^2 - n_o^2)/c$, where n and n_o are the refractive indices of the solution and solvent, respectively, and c is the solute concentration. Dielectric permittivity measurements were performed at 21°C by a resonance technique at a frequency of 700 kHz using a standard capacity meter E12-1 and cylindrical titanium capacitor having its own capacity of 92.86 pF. Refractive indices n were determined using Abbe refractometer IRF-23 with the line 578 nm corresponding to the wavelength of Hg at the same temperature. The dipole moments μ were calculated according to Eq. (1):

$$\mu^2 = 27\,\mathrm{kT\ M}[(\varepsilon - \varepsilon_o)/c - (n^2 - n_o^2)/c]/[4\pi N_A(\varepsilon_o^2 + 2)^2]. \qquad (1)$$

Here M is molecular mass, k is Boltsmann constant, T is absolute temperature, and N_A is Avogadro's number.

Linear concentration dependencies of $(\varepsilon - \varepsilon_o)$ (Fig. 2) and $(n^2 - n_o^2)$ (Fig. 3) for solutions of all compounds under investigation were observed. The increments $(\varepsilon - \varepsilon_o)/c$ and $(n^2 - n_o^2)/c$ were determined from the slopes of the curves presented in Figs. 2 and 3, and are reported in Table 1.

Electrooptical properties of the compounds have been studied by Kerr-effect method in radio frequency rectangular pulsed electric field [13] and characterized by specific electrooptical Kerr constant K and

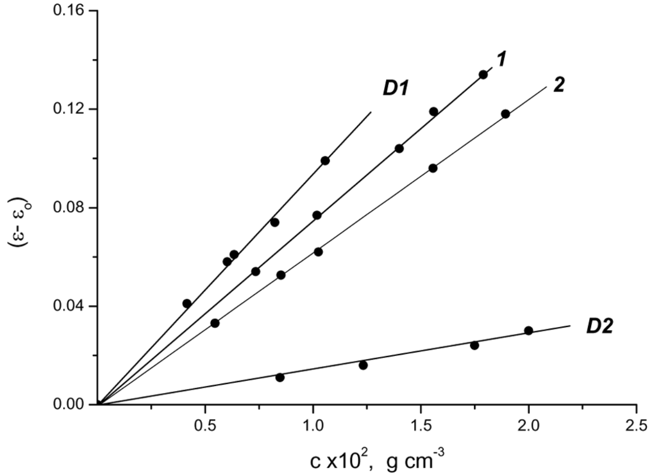


FIGURE 2 Variation of $(\varepsilon - \varepsilon_o)$ as a function of solute concentration c for compounds **1, 2, D1,** and **D2** in benzene.

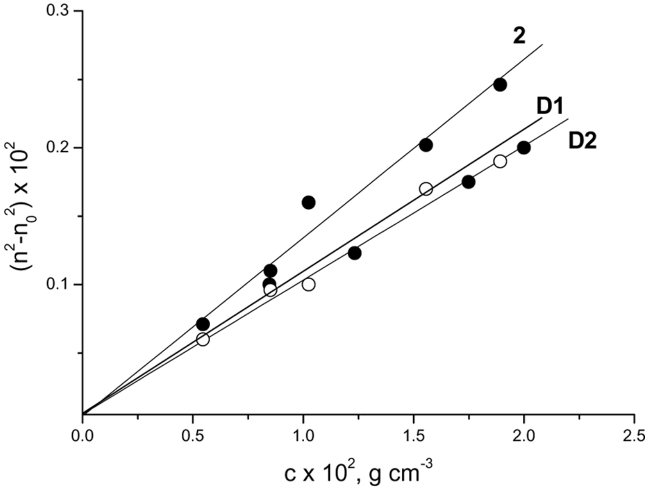


FIGURE 3 Variation of $(n^2 - n_o^2)$ as a function of the solute concentration for **2, D1,** and **D2** in benzene.

molar electrooptcal Kerr constant K_M which are connected with each other by Eq. (2)

$$K_M = \frac{6n_0MK}{(n_0^2+2)^2(\varepsilon_0+2)^2}, \tag{2}$$

where $K = \left(\frac{\Delta n - \Delta n_0}{E^2 c}\right)_{c\to 0}$; $(\Delta n - \Delta n_o)$ is the difference between optical birefringence of solution with the solute concentration c and optical birefringence of solvent, respectively; E is the electric field strength; the subscript $c \to 0$ is symbolizing K value determination at the infinite dilution condition. The others parameters of Eq. (2) have been explained above.

The optical birefringence in solutions of **1, 2, D1**, and **D2** under the treatment of the rectangular pulsed electric field have been measured with the impulse duration of 1 ms in the voltage range 100–1000 V at 21°C. A compensatory technique with the photoelectric registration of optical birefringence value was applied. A thin mica plate compensator having its own optical phase difference $0.01 \times 2\pi$ was used. A glass cell with the titanium semicylindrical electrodes of 2 cm in light path length and with the gap between electrodes of 0.05 cm was employed. He-Ne laser (1.5 mW power) operating at 632.8 nm was used as the light source.

The variation of optical birefringence value Δn as a function of E^2 for different concentrations of **1** are shown in Fig. 4. No deviation from Kerr low (according to which, optical birefringence Δn is proportional

TABLE 1 Molecular Weight (M), Hydrodynamic Diameter (d), Permanent Dipole Moment (μ), Specific Dielectric Polarization (μ^2/M), and Molar Kerr Constant (K_M) of Samples **1, 2, D1**, and **D2**

Compound	M*	d Å	μ Debye	$(\varepsilon - \varepsilon_o)/c$ $cm^3 \cdot g^{-1}$	$(n^2 - n_o^2)/c$ $cm^3 \cdot g^{-1}$	$K_{M,\ exp} \cdot 10^8\,cm^5 \cdot (300\,V)^{-2} \cdot mol^{-1}$	$K_{M,\ cal} \cdot 10^8\,cm^5 \cdot (300\,V)^{-2} \cdot mol^{-1}$
1	5878	44 ± 5	18.6 ± 0.8	7.6 ± 0.2	0.15 ± 0.01	12.5	11.4
2	7679	45 ± 5	19.2 ± 0.8	6.2 ± 0.2	0.13 ± 0.01	11.4	1.8
D1	2733	33 ± 4	14.2 ± 0.9	9.4 ± 0.3	0.10 ± 0.01	3.6	3.7
D2	4228	34 ± 5	6.4 ± 0.5	1.3 ± 0.1	0.09 ± 0.01	0.46	–

*Molecular mass M corresponds to structural formula.

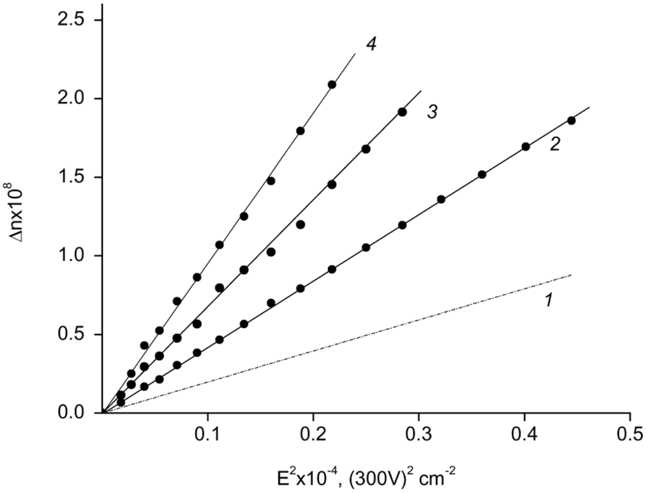


FIGURE 4 Variation of the optical birefringence (Δn) versus E^2 for **2** in benzene at different concentrations: (1) pure solvent, (2) 0.353, (3) 0.635, and (4) $1.057{\cdot}10^{-2}\,g\,cm^{-3}$.

to E^2 in molecular dispersed liquids) was observed in solutions of **1, 2, D1**, and **D2**.

The dependences of $(\Delta n - \Delta n_o/E^2c)$ as a function of solute concentration are shown in Fig. 5. The $(\Delta n - \Delta n_o/E^2c)_{c\to 0}$ values were obtained at c = 0 and used for the calculation of K_M according to Eq. (2).

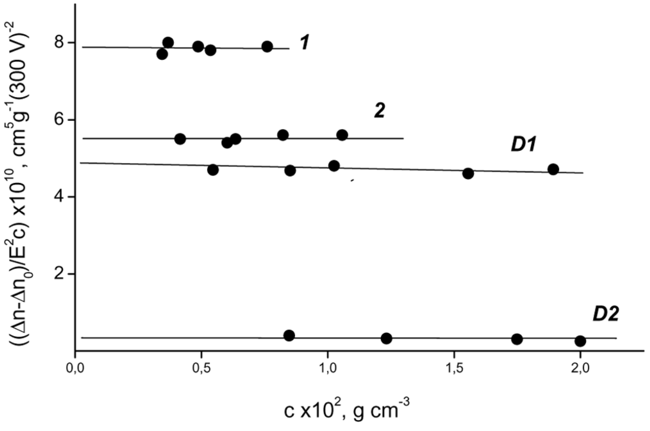


FIGURE 5 Concentration dependence of $(\Delta n - \Delta n_0)/E^2c$ for **1, 2, D1,** and **D2** in benzene.

The hydrodynamic method of translation diffusion [13] has been used for estimation of hydrodynamic dimension of compounds. The translation diffusion coefficients D, experimentally determined in benzene at 25°C, allowed to calculate the hydrodynamic diameters d (Table 1) based on the spherical model for dendritic molecules according to the Stokes–Einstein Eq. (3).

$$d = kT/3\pi\eta_o D, \tag{3}$$

here η_o is viscosity of the solvent.

RESULTS AND DISCUSSION

Table 1 accumulates the experimental data on molecular properties of dendrons **D1, D2**, and compounds **1, 2** received in dilute benzene solutions. As easy to see, all the samples have polar molecules with the large in value permanent dipole moment μ, including compound **D2** which has not polar mesogenic end-groups. Each mesogenic group of **D1** has a permanent dipole moment of 7.2 D according to quantum chemical calculation. The compounds **1** and **2** are characterized practically equal to each other total polarity (see, please, μ value in Table 1) in spite of number of strongly polar mesogenic groups in their content differ twice. Due to dendrons **D1** and **D2** have closed in value hydrodynamic diameters d (within the experimental error), the compounds **1** and **2** are also characterized by similar in value dimensions (Table 1). Incidentally, our hydrodynamic data show that the third generation of poly(benzyl ether) (or dendron **D2)** is more folded in comparison with the second generation of poly(aryl ester) (or dendron **D1)**. The latter leads to the conclusion that nonequivalent mass and polarity distribution in co-dendrimer **2** have a heavier part (sub-unit **D2**) and a more polar part (sub-unit **D1**) of practically equal size, if compared with compound **1**, which is more symmetric due to a full equality of its sub-units (Fig. 1a). This fact points out an importance of structural difference between **1** and **2**, but it cannot be considered as sufficient to explain the experimentally determined difference in mesomorphic behavior of these compounds (Fig. 1). The following analysis of electro-optical properties of **1** and **2** permits us to detect additional specific features in their molecular organization.

Elecrooptical Kerr constant K (K_M) of the substance directly depends on polarity, optical and dielectric anisotropy, and on the structural geometry of its molecules. That is why K_M values may be analyzed for clearing of the intramolecular details of multicomponent compounds constructed by relatively separate sub-units. An existence of long length spacers in the structure of the compounds under consideration permits to select those type sub-units in theirs structure.

It is well known that molar Kerr constant is an additive value in the case when separated fragments of molecule are able to be independent in their orientations under the treatment of external electric field [13]. Because of this, it is possible to estimate the freedom degree of sub-units in multicomponent molecules **1** and **2** by means of comparison of their experimental molar Kerr constants with the corresponding values calculated using the additive scheme. It is self-evident that electrooptical properties of separated molecular sub-units need to be known. But before the calculation, some important remarks need to be taken into consideration in relation to difference in the chemical structure of dendrons **D1** and **D2**.

The total polarity and the dependence on polarity of the electrooptical properties of dendron **D1** are fully related to the structure of the mesogenic end-groups, because the central part of **D1** is a highly symmetric nonpolar unit (Fig. 6). Hence, the electrooptical Kerr effect in solution of dendrimer **1** is also dependent on the structure of the mesogenic groups. $K_{M,\ cal}$ value of single mesogenic group (its chemical structure is presented in Fig. 1a) as well as $K_{M,\ cal}$ values of the model compound corresponding to the central part of **D1** and of the fullerene derivatives analogues to the fullerne-core of compounds **1** and **2** (named **MF** and **FP**, correspondingly, Fig. 7) have been calculated with parameters accumulated in Table 2.

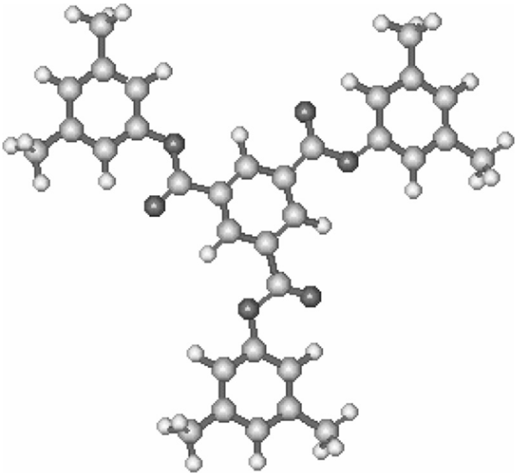
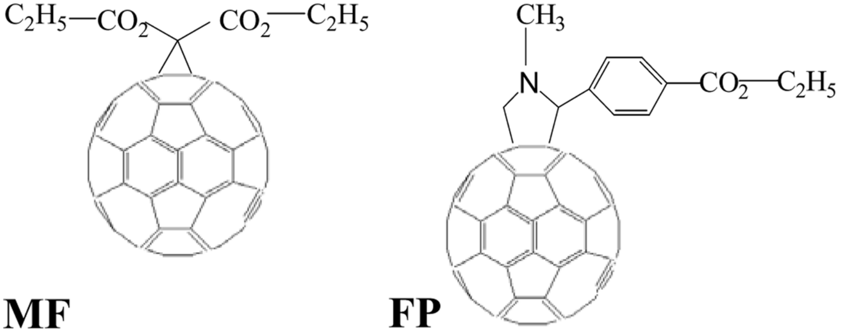


FIGURE 6 Model of the central part of poly(aryl ester) dendron **D1**.



MF **FP**

FIGURE 7 Model compounds **MF** and **FP** analogues to the fullerene-cores of **1** and **2**, correspondingly.

Estimation of molar Kerr constant $K_{M,\ cal}$ according to additive scheme for multicomponent compounds **1** and **2** have been done as a sum (Eq. (4)).

$$K_{M,cal} = \sum_i K_{Mi} W_i, \tag{4}$$

where K_{Mi} is the molar Kerr constant of i-fragment and W_i is its weight fraction value.

The inputs of eight mesogenic groups, **MF**-unit, and two polyaryl ester fragments (Fig. 6) without mesogenes have been taken for calculation of $K_{M,\ cal}$ for compound **1** through Eq. (4). Correspondingly, the

TABLE 2 Dipole Moment (μ), Mean Polarizability Value (b_{mean}), Anisotropy of Optical Polarizability (Δb) Calculated by Quantum Chemical Semiempirical Method PM3 for Fully Optimized Model Compounds Presented in Figs. 6 and 7 and for Compound Analogues to Mesogene, and their Molar Kerr Constants (K_M)

Compound	μ, D	$b_{mean} \times 10^{24}$, cm^3	$\Delta b \times 10^{24}$, cm^3	$K_M \times 10^{10*}$
MF	2.96	78.4	11.54	5.52
FP	1.18	86.9	21.49	19.12
Model of the central part of **D1**	0.01	38.0	47.35	93
Mesogene	7.20	39.4	50.99	220

*$K_M = 2\pi N_A(\theta_1 + \theta_2)$ [13], where $\theta_1 = (45\,kT)^{-1}[(b_1\text{-}b_2)^2 + (b_2\text{-}b_3)^2 + (b_3\text{-}b_1)^2]$ and $\theta_2 = (45\,k^2\,T^2)^{-1}\,[(\mu_1^2\text{-}\mu_2^2)(b_1\text{-}b_2) + (\mu_2^2\text{-}\mu_3^2)(b_2\text{-}b_3) + (\mu_3^2\text{-}\mu_1^2)(b_3\text{-}b_1)]$; here b_i are the main values of optical polarizability tensor, μ_i are the projections of dipole moment in the coordinate system, which abscissa-axis coincides with the principal optical polarizability direction; $i = 1, 2, 3$; $b_{mean} = (b_1 + b_2 + b_3)/3$; $\Delta b = [(b_1\text{-}b_2)^2 + (b_2\text{-}b_3)^2 + (b_3\text{-}b_1)^2]^{\frac{1}{2}}$.

inputs of four mesogenic groups, **D2** (its experimental value K_M was used), polyaryl ester fragments, and **FP** – unit have been taken for calculation of $K_{M,\ cal}$ for compound **2**.

The result of calculation presented in the last column of Table 1 shows very good coincidence between the calculated and experimental values of molar Kerr constant for compound **1**; and at the same time, an absence of coincidence can be declared for compound **2**. This reveals that the rotational freedom of dendrons in compound **2** is significantly restricted by the stiffness induced by the fulleropyrrolidine unit. Furthermore, the fact that the experimental dipole moment value of **2** is practically the sum of the polarities of its both dendrons (see, please, μ column in Table 1) is further evidence of the structural stiffness of **2**. Indeed, this situation is reached because **D1** and **D2** are stiffly linked in **2**, and rotate synchronically in the external pulsed (in the case of Kerr effect study) and in the external sinusoidal (in the case dielectric measurements) electric fields which were used in the framework of this study. Due to their stiffness, the molecules' packing in the mesophase of compound **2** will differ from the process of compounds **1**, having relatively free and mobile sub-units. Molecular stiffness is responsible also for the specific segregation of sub-units detected by X-rays diffraction in the mesophase of compound **2** [10].

CONCLUSION

We have found that not only mesogenic end-groups determine mesomorphic behavior of the considered liquid crystalline fullerene-containing polyester/polyether dendrimers/co-dendrimers, but that the chemical linkage type of C_{60} with the dendritic matrix also plays an important role. Partially, it was shown that fulleropyrrolidine unit as the core of co-dendrimer **2** stiffly binds poly(aryl ester) and poly(benzyl ether) dendrons in comparison with methanofullerene as the core of symmetric structure dendrimer **1**. Polar sub-units of compound **1** are independent in their rotations and orientations in solutions in electric field, when dendritic fullerene derivative **2** has strongly linked and strongly interacting sub-units. This also means an existence of the difference in the scale of sub-units mobility inside of the considered dendritic macromolecules that may be responsible for their ordering type in mesomorphic state.

The molecular asymmetry and relatively rigid linkage of dendron bearing mesogenic groups by fulleropyrrolidine in polyester/polyether yether co-dendrimer can be considered as a fruitful example of a reproducing of anisometry-principle at the level of dendritic structure macromolecules for the design of novel liquid crystalline compounds.

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