The effect of inversion of the ester group on the mesophase behaviour of some azo/ester compounds

Magdi M. Naoum*, Abdelgawad A. Fahmi, Nagwa H.S. Ahmed and Gamal R. Saad

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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Five homologous series of 4-substituted phenyl 4′-(4″-alkoxy phenylazo) benzoates (I\(_{n-2}\)) were prepared in which, within each homologous series, the length of the terminal alkoxy group varies between 8, 10, 12, 14 and 16 carbons, while the other terminal substituent, X, is a polar group that alternatively changed from CH\(_3\), CH\(_2\), H, Br, and CN groups. Compounds prepared were characterised by infrared, mass, and H\(^1\)-NMR spectroscopy and their mesophase behaviour investigated by differential scanning calorimetry (DSC) and polarised light microscopy (PLM). The results were discussed in terms of mesomeric and polarisability effects. Only for the lower group of compounds, I\(_{16-2}\) that showed a nematic phase, the nematic-to-isotropic transition temperatures (\(T_N-I\)) were successfully correlated to the polarisability anisotropy of bonds to the substituent X. A comparative study was made between the investigated compounds and two previously prepared isomeric groups. In the first group of isomers, 4-(4″-alkoxy phenylazo) phenyl 4″-substituted benzoates (II\(_{n-2}\)), the ester groups are inverted. While in the second, 4-(4″-substituted phenylazo) phenyl 4″-alkoxy benzoates (III\(_{n-2}\)), two modifications were made, inversion of the COO group, and exchange of the two wing substituents.

Keywords: phenylazo phenyl benzoates; mesophase behaviour; inversion of ester group; polarisability anisotropy

1. Introduction

In terms of molecular structures, liquid crystals can be classified as monomers and oligomers, depending on the number of mesogenic cores linked by the flexible spacers. The simplest oligomer is known as the dimer in which two mesogenic units are linked by a single flexible spacer. Many series of dimeric liquid crystals have been reported,[1–5] all of these compounds may be termed symmetric, with identical mesogenic moieties, or non-symmetric dimers, with different mesogenic units. In both cases, the specific interactions between the two mesogenic groups do lead to a significant variation in the mesophase behaviour of such materials. However, non-symmetric dimers exhibited liquid crystalline behaviour, not commonly found on the symmetric dimers, such as intercalated and interdigitated phases.

The great majority of liquid crystalline materials are aromatic in nature and of a general formula X–Ar–A–B–Ar–Y, where X and Y represent a range of terminal substituents such as alkyl, alkoxy, carboxy, nitro and cyano groups; Ar represents aromatic rings that may be two or more rings; A–B represents a linkage unit in the core structure, for example, CH=\(\equiv\)N, N=CH, N=N, N=NO, COO, OOC,[6–9] etc. Aromatic esters are known [10] to be thermally stable and relatively resistant to hydrolysis; in addition, conjugation interactions between the terminal substituent and the ester group, through the intervening benzene rings, do lead to double bond character. On the other hand, azo benzene derivatives were among the first recognised groups of liquid crystalline molecules [11]; in addition, azo compounds are thermally very stable and are attractive from the point of view of studying photo-induced effects.[12]

Based on their outstanding characteristics, both azo and ester groups represent fragments to design and synthesise new structures, giving stable mesophases often with very interesting polymorphism. Thus, an obvious choice for our present investigation seemed to be three-ring molecules connected with these two stable linkages. In a calamitic liquid crystal, terminal substituents attract and repel one another; in addition, they, via mesomeric interactions, affect the polarisability of the benzene rings to which they are attached. As a consequence, the stability of the mesophase in liquid crystals depends mainly on the anisotropy of such intermolecular forces, which accordingly depends on the polarity of the group and its orientation with respect to the ring. Finally, extension of a terminal \(n\)-alkyl chain substituent, in a homologous series, gives rise to a gradient in the liquid crystal transition temperatures.[13,14] A number of homologous series with ester and azo central linkages have been synthesised having different terminal groups.[15–22]

*Corresponding author. Email: magdinaoum@yahoo.co.uk

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The goal of the present work is to prepare a series of model compounds of the type 4-substituted phenyl 4′-alkoxy phenylazo-4′-benzoates (I_{n_a-e}), in which the ester groups (OOC) in the previously investigated isomeric derivatives,[23] namely, 4-(4′-alkoxy phenylazo) phenyl-4′-substituted benzoates (II_{n_a-e}), are inverted in the present investigation to COO. As expected, inversion of the ester group in a compound of type II, results in an isomer that would react mesomerically in a different way and consequently affect their mesophase behaviour differently. Comparison will be extended to another mesomeric modification,[24] III_{n_a-e}, made by inverting the ester group as well as exchanging the two wing substituents.

These new prepared compounds (I_{n_a-e}) will be chemically characterised and investigated for their mesophase behaviour, and compared with their two previously prepared groups of isomers (II_{n_a-e} and III_{n_a-e}).

2. Experimental

Chemicals were of very pure grades and purchased from the following Companies: Fluka, Buchs, Switzerland; MP Biomedicals, Inc., Illkirch, France; BDH, Poole, England; Aldrich, Wisconsin, USA; and E. Merck, Darmstadt, Germany.

Infrared absorption spectra were measured with a Perkin-Elmer B25 spectrophotometer (Perkin-Elmer, Inc., Shelton, CT, USA), and 1H-NMR spectra with a Varian EM 350L (Oxford, UK).

Calorimetric measurements were carried out using a differential scanning calorimeter, PL-DSC, of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al. [25] DSC investigation was carried out for small samples (2-3 mg) placed in sealed aluminium pans. All measurements were achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and type of mesophase was identified for all compounds prepared with a standard polarised light microscope PLM (Wild, Germany) attached to a home-made hot-stage.

Thermogravimetric (TG) analysis was carried out using Shimadzu TGA-50H Thermal Analyzer under nitrogen at 10°C/min. The experiments were conducted from room temperature up to 500°C, and the reference material was a-alumina. The sample weights for all the experiments were taken in the range of 3-4 mg.

The purity of the prepared samples was checked with thin-layer chromatography (TLC) using TLC sheets coated with silica gel and CH\(_2\)Cl\(_2\)/CH\(_3\)OH (9:1) as eluent, whereby only one spot was detected by a UV-lamp.

2.1 Preparation of materials

The azo/esters (I_{n_a-e}) were prepared according to the following scheme:
2.1.1. Preparation of ethyl-4-hydroxyphenylazo benzoate (A)

Ethyl 4-amino benzoate (0.001 mole) was dissolved in concentrated hydrochloric acid and cooled in ice-salt bath to 0°C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.003 mole) was added drop-wise with stirring. During the addition, the temperatures did not exceed 2°C. After complete addition, the cold mixture was added drop-wise to an ice-cold solution of phenol (0.001 mole) in sodium hydroxide (0.003 mole). The mixture was further stirred at 0°C for 1 hour then acidified with dilute hydrochloric acid. The solid separated was filtered and crystallised twice from ethanol. The product was TLC pure and gave melting point 160.3°C that agreed with that reported in the literature.[26]

2.1.2. Preparation of ethyl 4-n-alkoxy phenylazo benzoates (Bn)

These homologues (n = 8–16 carbons) were prepared by the method described previously.[20] Ethyl-4-hydroxyphenylazo benzoate (0.001 mol) was dissolved in alcoholic KOH (0.02 mol), and slightly excess amount of 1-bromo-n-alkane (0.0012 mol) was added drop-wise while stirring. Stirring was continued at room temperature for 2 days. The solid separated was filtered off, the solution evaporated, and the residue crystallised twice from ethanol. The products were TLC pure and give melting point 160.3°C that agreed with that reported in the literature.[27]

2.1.3. Preparation of 4-n-alkoxy phenylazo benzoic acids (An)

The esters (Bn) were hydrolysed to the corresponding acids by refluxing in aqueous ethanolic potassium hydroxide for 24 hours to give the corresponding acids. Again, the products after crystallisation from ethanol were TLC pure and gave transition temperatures that agree with those reported in the literature. [26,28,29]

2.1.4. Preparation of 4-substituted phenyl-4′-n-alkoxy phenylazo benzoates (Ina.e)

Molar equivalents of 4-n-alkoxy phenylazo benzoic acid (An) and 4-substituted phenol (0.001 mole each) were dissolved in 25 ml of dry methylene chloride. To the resulting mixture, dicyclohexylcarbodiimide (DCC, 0.002 mole) and few crystals of 4-(dimethylamino) pyridine (DMAP), as a catalyst, were added and the mixture stirred at room temperature for 3 days. The solid separated was filtered off, the solution evaporated, and the residue crystallised twice from ethanol. The products obtained were TLC pure, with yields between 41.5% and 61 %, and gave transition temperatures as given in Table 1.

3. Results and discussion

3.1. Confirmation of molecular structure

The molecular formulae of the newly prepared azo/ester homologues (Ina.e) were confirmed via elemental analyses, FT-IR and 1H-NMR (Supplemental data). Elemental analyses were found to be in agreement, within permissible limits, with the proposed formulae. H1-NMR data showed expected integrated aliphatic-aromatic ratios in all compounds investigated. Mass spectra indicated exact molecular masses for the whole molecular structures and expected fragmentation.

Since almost identical infrared absorption spectra were observed for all the members of each of the five homologous series (Ina.e), the absorption bands of compounds in series Ina.e, with their assignments are given. The nearly identical infrared absorption spectra observed for the five homologous series investigated (Ina.e–I16a.e) revealed that neither the length of the alkoxy chain, C8–C16, in any of the homologous series, nor the substituent X in any group of derivatives bearing the same alkoxy chain, has a significant effect on the position of infrared absorption bands.

3.2. Mesophase behaviour of compounds investigated

Since the mesophase stability of a liquid crystalline compound depends mainly upon intermolecular attractions in which molecular polarity plays a significant role, it has been shown [7] that within one series of compounds, e.g. I8a.e, the dipole moments of its individuals are determined by the nature of the substituent. A change in the extent of conjugation alters the polarisability and resultant dipole moment of the molecule. It has also been shown [11] that the dipole moments of all members of a homologous series are virtually identical, irrespective of the length of the alkoxy chain. This result is supported by the fact that the alkoxy groups have similar polarity regardless of their length, and, at the same time, do not affect the degree of conjugative interaction between the alkoxy oxygen and the ester carbonyl, as is confirmed by infrared measurements. Transition temperatures and enthalpies measured
Table 1. Transition temperatures (°C) (and transition enthalpies in kJ/mol) of 4-substituted phenyl 4’-(4”-alkoxy phenylazo) benzoates (I\textsubscript{n-a-e}).

| Compound | n  | X   | T\textsubscript{Cr-A} | T\textsubscript{Cr-N} | T\textsubscript{A-N} | T\textsubscript{A-I} | T\textsubscript{N-I} |
|----------|----|-----|------------------------|-----------------------|---------------------|---------------------|---------------------|
| I8\textsubscript{a} | CH\textsubscript{3}O | – | 131 (55.5) | – | – | 228 (2.5) |
| I8\textsubscript{b} | CH\textsubscript{3} | 109 (24.5) | – | 134 (1.9) | – | 230 (1.3) |
| I8\textsubscript{c} | H | 120 (44.0) | – | 139 (1.5) | – | 153 (1.1) |
| I8\textsubscript{d} | Br | – | 136 (24.2) | – | – | 213 (1.3) |
| I8\textsubscript{e} | CN | – | 131 (39.0) | – | – | 251 (0.64) |
| I10\textsubscript{a} | CH\textsubscript{3}O | 120 (23.7) | – | 145 (2.3) | – | 220 (1.7) |
| I10\textsubscript{b} | CH\textsubscript{3} | 101 (28.0) | – | 172 (3.6) | – | 212 (2.2) |
| I10\textsubscript{c} | H | 95 (32.4) | – | – | 145 (1.9) | – |
| I10\textsubscript{d} | Br | 101 (53.5) | – | – | 146 (4.2) | – |
| I10\textsubscript{e} | CN | 91 (56.5) | – | – | 148 (2.9) | – |
| I12\textsubscript{a} | CH\textsubscript{3}O | 113 (46.9) | – | 156 (2.4) | – | 209.5 (1.1) |
| I12\textsubscript{b} | CH\textsubscript{3} | 90 (20.5) | – | 176 (1.3) | – | 188 (1.2) |
| I12\textsubscript{c} | H | 127 (27.3) | – | – | 143 (1.4) | – |
| I12\textsubscript{d} | Br | 121 (50.0) | – | – | 146 (2.0) | – |
| I12\textsubscript{e} | CN | 106 (55.5) | – | – | 160 (1.4) | – |
| I14\textsubscript{a} | CH\textsubscript{3}O | 114 (48.5) | – | 164 (2.3) | – | 191 (1.2) |
| I14\textsubscript{b} | CH\textsubscript{3} | 101.5 (4.0) | – | – | 172 (2.3) | – |
| I14\textsubscript{c} | H | 114 (34.2) | – | – | 136 (3.5) | – |
| I14\textsubscript{d} | Br | 106 (29.3) | – | – | 160 (2.6) | – |
| I14\textsubscript{e} | CN | 112 (26.0) | – | – | 184 (1.3) | – |
| I16\textsubscript{a} | CH\textsubscript{3}O | 118 (27.8) | – | – | 173 (1.5) | – |
| I16\textsubscript{b} | CH\textsubscript{3} | 102 (75.6) | – | – | 163 (3.4) | – |
| I16\textsubscript{c} | H | 111 (49.0) | – | – | 137 (4.3) | – |
| I16\textsubscript{d} | Br | 104 (28.1) | – | – | 168 (2.8) | – |
| I16\textsubscript{e} | CN | 115 (56.3) | – | – | 203 (2.2) | – |

Notes: Cr–A denotes transition from solid to the SmA phase. Cr–N denotes transition from solid to the N phase. A–N denotes transition from SmA to the N phase. A–I denotes transition from SmA to the isotropic phase. N–I denotes transition from Nematic to the isotropic phase.

by DSC, and phases identified by polarised light microscopy (PLM), for compounds I\textsubscript{n-a-e} are summarised in Table 1. It is obvious that the enthalpy values of the various transitions agree well with the existing related literature values.[30] Corresponding data for compounds II\textsubscript{n-a-e} and III\textsubscript{n-a-e} are given elsewhere.[23,24] The synthesised compound of the present work, showed to display pronounced thermal stability, when heated. Thus, when the samples were subjected to repeated heating/cooling cycles, the DSC profiles exhibited similar behaviours. Figure 1 presents, as examples, the DSC curves of compounds I8\textsubscript{c} and I16\textsubscript{c}.

The thermal stability of these compounds was also confirmed by TG analysis. Figure 2 shows the TG curves and their differentials (DTG) of the compounds I8\textsubscript{a} and I10\textsubscript{a}, as examples. As seen from the figure, the curves exhibit typical profiles and the thermal degradation occurs in one step. The I8\textsubscript{a} compound starts to decompose at ca. 260°C with a maximum rate loss (T\textsubscript{max}) at ca. 340°C. For I10\textsubscript{a}, the initial temperature at which thermal degradation begins is ca. 300°C with T\textsubscript{max} 380°C. This indicates a good thermal stability for the investigated compounds, above the isotropic temperatures.

In order to put the data in Table 1 in a more deductible way, the effect of increasing alkoxy-chain length, through a homologous series, on their phase behaviour, transition temperatures are plotted individually, for each homologous series, against the length of the alkoxy group (n) in Figure 3.

As can be seen from Table 1 and Figure 3, dependent on the substituent X, the nematic-to-isotropic transition temperatures (T\textsubscript{N-I}) decrease gradually for un-substituted and electron-donating substituted analogues (X = H, CH\textsubscript{3}O and CH\textsubscript{3}) and sharply for electron-withdrawing substituted ones (X = Br and CN), with the increase of the alkoxy-chain length (n). This pattern of behaviour is in accordance with that shown by Gray [31] and Imrie and Taylor,[32] in which the nematic-to-
isotropic transition temperatures fall with increasing alkoxy-chain length, and if the homologous series also exhibits the smectic phase, then the smectic-nematic, or smectic-to-isotropic transition temperatures rise steeply at first and then more gradually as the alkoxy chain lengthens. All compounds with terminal alkoxy group with 8 carbon atoms present enantiotropic nematic phases, with characteristic Schlieren textures, and smectic A phases (Figure 4a and b). The un-substituted and electron-withdrawing substituted compounds bearing alkoxy chains with 10–16 carbons do not show the nematic phase, i.e. they are purely smectogenic, possessing the SmA phase as the only mesophase observed (Figure 4c and d). These may be attributed to the difference in the type of molecular interactions taking place within these individual molecules. In the bromo- and cyano-substituted derivatives, it seems that quadrupole interactions play an important role in phase behaviour.[4,5]

Generally, the thermal stability of the smectic mesophase is determined by the intermolecular attraction operating between the sides of adjacent molecules. Thus, in the bromo and cyano homologues of series I, the mesomeric interactions between the alkoxy oxygen and the ester carbonyl via the phenylazo group, in one side of the molecule, are augmented by the inductive electron-withdrawing power of the bromo or cyano group, on the other side of molecule. Similarly, in the cyano homologues of series II, the interactions between the alkoxy oxygen and the phenylazo group, in one side of the molecule, are augmented by the inductive electron-withdrawing power of the cyano group, on the other side of molecule. Again, the mesomeric interaction between the alkoxy oxygen and the ester carbonyl, on one side of the molecule, is again augmented by the conjugative interaction between the ester oxygen and the CN group via the phenylazo benzene group, on the other side of the molecule of group III (i.e., IIIc), see Figure 5. That is, in all three cases, this should increase the polarity of the mesogenic portion as a whole, and consequently stabilise the mesophase. This inference is in accordance with the experimental results (Table 1, refs. [23,24]); the cyano analogues (in series I, II and III) have the highest clearing (Tc) temperatures.

Conversely, there are opposing effects on each side of the molecules (I, II and III) of the methoxy (Ia, Ib or IIIa) and methyl (Ib, IIb or IIIb) analogues (Figure 6). Accordingly, they are expected to possess lower dipolar character that would lead to derivatives with lower Tc values.

For the purpose of comparison, the effect of increasing alkoxy chain length on the mesophase stability of compounds of series I, II and III is plotted collectively in Figure 7. As can be deduced from this figure, the mesophase stability (clearing temperature) decreases in order differs according to the nature of these substituents. In summary:

Figure 1. DSC curves for I8c and I16c: (1) first heating cycle and (2) first cooling cycle.

Figure 2. TG and DTG curves of the I8a and I10a recorded under nitrogen at a heating rate of 10°C/min.

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For $X = \text{CH}_3\text{O}, \ I_{8a} > \ II_{8a} \approx \ I_{8a}$.

For $X = \text{CH}_3, \ I_{8b} > \ III_{8b} > \ II_{8b}$.

For $X = \text{H}, \ III_{8c} > \ I_{8c} = \ II_{8c}$.

For $X = \text{Br}, \ III_{8d} > \ I_{8d} = \ II_{8d}, \ III_{8d}$ is a chloro-derivative.

For $X = \text{CN}, \ III_{8e} > \ I_{8e} > \ II_{8e}$.

For $X = \text{CN}, \ III_{10e} > \ I_{10e} > \ II_{10e}.$

Figure 3. Dependence of transition temperatures of compounds $I_{n_{a-e}}$ on the alkoxy chain length ($n$).
For $X = \text{CH}_3\text{O}$,

$$III_{12a} > I_{12a} > II_{12a}.\quad (3) n = 12$$

For $X = \text{CH}_3$,

$$II_{12b} > III_{12b} > II_{12b}.$$

For $X = \text{H}$,

$$III_{12c} > I_{12c} > II_{12c}$$.  

For $X = \text{Br}$,

$$III_{12d} > II_{12d} > I_{12d}, \quad \text{III}_{12d} \text{ is a chloro-derivative}.$$

For $X = \text{CN}$,

$$III_{12e} > II_{12e} > I_{12e}.$$

For $X = \text{CH}_3\text{O}$,

$$III_{14a} > I_{14a}, \quad \text{III}_{14a} \text{ is not available}.$$

For $X = \text{CH}_3$,

$$III_{14b} > I_{14b}, \quad \text{III}_{14b} \text{ is not available}.$$

For $X = \text{H}$,

$$II_{14c} \quad \text{and} \quad III_{14c} \text{ are not available}.$$

For $X = \text{Br}$,

$$III_{14d} > II_{14d}, \quad \text{III}_{14d} \text{ is a chloro-derivative}.$
For $X = \text{CN}$, $\text{III}_{14_e} > \text{I}_{14_e}$, $\text{II}_{14_e}$ is not available.

(5) $n = 16$

For $X = \text{CH}_3\text{O}$, $\text{III}_{16_a} > \text{I}_{16_a}$, $\text{II}_{16_a}$ is not available.

For $X = \text{CH}_3$, $\text{III}_{16_b} > \text{I}_{16_b}$, $\text{II}_{16_b}$ is not available.

For $X = \text{H}$, $\text{III}_{16_c}$ and $\text{III}_{16_e}$ are not available.

For $X = \text{Br}$, $\text{III}_{16_d} > \text{I}_{16_d}$, $\text{III}_{16_d}$ is a chloro-derivative.

For $X = \text{CN}$, $\text{III}_{16_e} > \text{I}_{16_e}$, $\text{II}_{16_e}$ is not available.

3.3. Clearing temperatures and polarisability

anisotropy of the $\text{C}_{\text{ar}}$-$X$

The relationship derived by van der Veen [33] between the stability of the mesophase, expressed as the clearing temperature, $T_C$, and the anisotropy of polarisability ($\Delta \alpha_X$) of bonds to small compact terminal substituent ($\text{C}_{\text{ar}}$-$X$), has the form:

$$T_C \propto (\Delta \alpha_M + \Delta \alpha_X)^2$$

where $T_C$ is measured in Kelvin. Equation (1) can be put in the form [34]:

$$T_C^{1/2} \propto a (\Delta \alpha_M + \Delta \alpha_X) = a.\Delta \alpha_M + a.\Delta \alpha_X$$

The term $\Delta \alpha_M$ is the polarisability anisotropy of all the molecular structure except the terminal substituent, $X$, and ‘$a$’ is the proportionality constant. Thus, if $T_C^{1/2}$ of any of our investigated compounds, bearing one and the same alkoxy group, $n$, but of varying $X$, is plotted against $\Delta \alpha_X$, a straight line is expected with a slope ‘$a$’ and intercept equals ‘$a.\Delta \alpha_M$’. Where ‘$a$’ is the slope of the $\Delta \alpha_X$-dependency of $T_C^{1/2}$, and ‘$\Delta \alpha_M = \text{intercept/slope}$’ is the polarisability anisotropy of the whole molecular structure except the substituent $X$. The $T_C^{1/2}$ values were plotted, individually, for each series bearing the same alkoxy group ($n$), as a function of the polarisability anisotropy $\Delta \alpha_X$, as calculated previously,[34] and the plots are depicted in Figure 8. As can be seen from Figure 8, fairly linear dependency was observed for $n = 8$, where all the five derivatives showed the nematic phase. For other homologues ($n = 10–14$), some derivatives ($X = \text{H, Br and CN}$) are purely smectogenic, so
their correlations are not perfectly linear (Figure 8b–e). The slope and intercept were calculated for the regression line, in Figure 8a, by the method of least squares, from which $\Delta \alpha_M$ was calculated to be $5.51 \times 10^{-23}$ cm$^3$.

4. Conclusions

Five series of 4-substituted phenyl 4′-(4″-alkoxy phenylazo) benzoates were prepared and their thermal behaviour characterised. Two types of substituent were used, namely, an alkoxy group of varying length and a small compact polar group, X. All the compounds investigated were found to possess high transition temperatures, indicating strong molecular interaction in either the solid or the mesophase. A comparison was made between the present series (Series I) and two other isomeric series, wherein the first the ester group is inverted (Series II) and in the second (Series III), the ester group is inverted and the two wings are exchanged. The study revealed that, independent of $n$, the methoxy and cyano-substituted derivatives in series III are most stable; while for $X = \text{CH}_3$, the stability varies according to $n$. 

Figure 7. Dependence of the clearing temperature ($T_c$) of series I (●), series II (○) and series III (▼) on the alkoxy chain length ($n$).
Disclosure statement
No potential conflict of interest was reported by the authors.

Supplemental data
Supplemental data for this article can be accessed here.

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