The kinetics of the E-Z-E isomerisation and liquid-crystalline properties of selected azobenzene derivatives investigated by the prism of the ester group inversion

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Two new groups of azobenzene ester derivatives were synthesised: alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates and 4-[4-(nonyloxy)phenyl]diazenyl]phenyl alkanoates. All 35 presented homologues are mesogenic. Moreover, some of the above-mentioned compounds exhibit rich liquid-crystalline polymorphism likewise tetramorphism. During this investigation by the use of polarising optical microscopy, differential scanning calorimetry and X-Ray studies, six types of mesophases were detected: nematic, smectics (A, C, I, F) and G. Furthermore, due to the presence of the photosensitive azo moiety, the E-Z isomerisation reaction is possible. This process, which is initiated by the UV irradiation, causes significant changes in the UV-Vis absorption spectra of investigated compounds. However, the photoisomerisation is a reversible process and in the dark the thermal relaxation of Z isomer takes place. Based on the achieved data, the kinetic constants of the isomerisation and relaxation processes were calculated. It shows that conversion of the ester bond makes some changes in the optical properties. The shift of about 7 nm of the absorbance maximum was observed. Surprisingly, the inversion of the ester group has significant influence on the liquid-crystalline polymorphism replacing one mesophase (for benzoates) into four (for alkanoates).

**Keywords:** liquid crystals; azobenzene; UV-Vis spectroscopy; DSC calorimetry; photochromism; smectics

1. Introduction

Azobenzene derivatives are a well-known group of materials. Due to their N=N double bond, they are susceptible to the influence of light.[1] Therefore, irradiation of a suitable wavelength causes split of the chemical bond between the nitrogen atoms. This process leads to the geometrical reconstruction of the molecule. The return to the basic form is possible by use of light of different wavelengths.[2] This mechanism of molecular reorientation caused by multiple E-Z-E transitions is commonly described in literature as a photoisomerisation.[3–7] The ultraviolet irradiation, which corresponds to the \( \pi \rightarrow \pi^* \) excitation of azo group, causes the transformation of the rod-like E isomer into a bent Z configuration. This Z isomer is energetically less stable than the E and the return to the basic state is possible in two different ways. The back transition can be induced by the visible light in the range 400–550 nm. These wavelengths correspond to the \( n \rightarrow \pi^* \) transition. The second mechanism can be observed in the dark and is called the thermal relaxation. Because of the above-described optical properties, the azobenzene derivatives can be applied in many branches of modern technologies.[8–12]

The azobenzene compounds are very interesting materials because of their photosensitivity but also due to rich liquid-crystalline polymorphism. Such type of molecules with azo moiety are well known in literature since the 1930s,[13–15] when the enhanced development of the mesogens studies was intensified. The increasing number of papers in the LC branch contributed to the creation of versatile classification of the liquid-crystalline phases.[16–18] Nevertheless, the new mesophases were still discovered, which confirms the validity of the data about the novel banana-shaped molecules.[19,20] Therefore, the main aim of modern liquid crystals research is designing new materials characterised by the rich polymorphism.[21,22]

By introducing various linking groups [23] (like azo, Schiff bases,[24] thioester [25] and ester [26,27]), we can influence the type of the mesophase. Among the ester derivatives, the alkyl 4-[4-(alkyloxy)phenyl]diazenyl] benzoates (see Figure 1A) and 4-[4-(alkyloxy)phenyl] diazenyl]phenyl alkanoates (see Figure 1B) constitute a large group of compounds. In the benzoates series, methyl \((m = 1)\), propyl \((m = 3)\),[28] ethyl \((m = 2)\) [29] as well as several butoxy \((n = 4)\) and hexyloxy \((n = 6)\) [30] homologues were already published. Meanwhile, in the alkanoates class, the methoxy to hexyloxy homologues from \( m = 1 \) to \( m = 7 \) are yet to be described in the literature.[31–33] The derivatives with the short alkyll...
chain were mostly synthesised. A few dodecyloxy derivatives with middle and longer alkyl chain should be considered as exceptions. Therefore, in this article we pay attention to the nonyloxy azobenzene homologues, where extremely rich polymorphism was expected. Furthermore, in this article the synthesis of newazo and ester groups containing rod-like mesogens is presented. By the use of the polarising optical microscopy (POM) and the differential scanning calorimetry (DSC), the liquid-crystalline phase sequences and the phase transition parameters were investigated. Furthermore, the photoisomerisation rate constants for selected samples were calculated. The above-mentioned data give an insight into the interaction of the light with the investigated azobenzene derivatives. Moreover, we defined the influence of the ester group inversion on mesomorphic and optical properties of the materials.

2. Experimental methods
In our research, 4-nitrophenol, ethyl 4-aminobenzoate, 1-bromononane, all alcohols and carboxylic acids used in synthesis, were obtained from commercial sources. All solvents applied were dried over anhydrous magnesium sulphate before use. The progress of the esterification reaction was additionally monitored by thin layer chromatography (TLC).

2.1. Synthesis of alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates
The main route of the synthesis of the alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates is shown in Figure 2A. Compound (3) was synthesised according

Figure 2. (colour online) Synthesis scheme of: (A) alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates. (B) 4-[4-(nonyloxy)phenyl]diazenyl]phenyl alkanoates.
to the procedure described previously.[35] All final compounds of A-n series were synthesised by esterification of the 4-[4-(nonyloxy)phenyl]diazenyl]benzoic acid (3) with appropriate alcohol (from methanol to octadecanol) and with the use of DCC (N,N'-dicyclohexylcarbodiimid) and DMAP (4-dimethylaminopyridine). The reactions were carried out in dry dichloromethane at room temperature for 24 hours. After solvent evaporation, the resulting precipitates were purified by the use of the gel chromatography. The stationary phase was the silica gel (pore size 60 Å) while the mobile phase constituted the dichloromethane. After the evaporation of the eluent, the obtained products were recrystallised from hexane. Yield: 41–70%. All NMR spectra and elemental analysis of alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates are given in the supplementary data.

2.2. Synthesis of 4-[4-(nonyloxy)phenyl]diazenyl]phenyl alkanoates

The synthesis scheme of 4-[4-(nonyloxy)phenyl]diazenyl]phenyl alkanoates is shown in Figure 2B. The preparation of compound (6) was described in detail by Galewski et al. [36]. The above-mentioned phenol (6), the appropriate carboxylic acids, DCC in equimolar amounts and a pinch of DMAP were dissolved in dry dichloromethane. The resulting mixture was stirred at room temperature for 24 hours. Next the solvent was evaporated and the crude product was purified by the use of the gel chromatography applying the conditions described in Section 2.1. Subsequently all the synthesised compounds of B-series were recrystallised from hexane. The NMR spectra and elemental analysis are included in the supplement.

2.3. Characterisation

Chemical structures of all synthesised compounds were confirmed by two methods: elemental analysis (EA) and nuclear magnetic resonance spectroscopy (NMR). The EA measurements were carried out on the Vario EL III elemental analyser. Meanwhile, the NMR spectra were measured with the Bruker Avance III 500 MHz high-resolution spectrometer. Deutetared CDCl$_3$ was applied as solvent.

Phase transitions were investigated by the thermooptical analysis (TOA) with the use of the Olympus polarised light microscope BX61-P (TRF) and Linkam hot stage equipment as in [37]. For all compounds, calorimetric measurements (DSC) in nitrogen atmosphere with the use of the Perkin Elmer 8500 calorimeter were also carried out. The measurement rate of 10 K/min was applied. To confirm the microscopic observations and the calorimetric data, XRD studies in reflection mode for selected substances were conducted. The samples were prepared as drops on heating plate and next performed by the Bruker D8 GADDS system with additional Linkam heating stage.

Optical properties of selected compounds were characterised by UV-Vis spectroscopy method. It allows one to define the optical sensitivity of the materials. Furthermore, the obtained spectrum enables one to choose the alternative light (UV) for the isomerisation process. Therefore, for the irradiation of samples, a mercury lamp as a source of the UV light of $\lambda = 365$ nm was applied. All measurements were conducted with the help of a UV-Visible spectrophotometer (Varian Cary500 instrument).

3. Results and discussion

3.1. Mesogenic properties of A-n series

In this series all compounds possess one liquid-crystalline SmA mesophase. For homologues with short and middle alkyl chain, Iso–SmA phase transition is enantiotropic, while for the substances with longer chain, monotropic and visible only during the cooling mode. The first three derivatives (methyl, ethyl and propyl esters) possess significantly higher melting points than the other homologues (see Figure 3). Despite this fact, these compounds still show mesomorphic behaviour. The temperatures of the phase transition of longer homologues do not exceed 95° (see Table 1). From the undecyl derivative, very clearly the even–odd effect for melting temperatures is visible. The melting points and the crystallisation temperatures for esters with even carbon atoms number in alkyl chain are always a few degrees Celsius higher than for odd homologues. During the microscopic observations, characteristic textures of smectic A were observed (see Figure 4A). Moreover, the above-described mesophase was by the XRD measurements (see Figure 5) additionally investigated. Measured smectic layer thickness corresponds to the length of the undecyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoate molecule. For derivatives with $n = 16$ and $n = 18$, the liquid-crystalline mesophase was only observed for very fast cooling rate (about 50 K/min) of the samples. For this reason, the temperatures of the recrystallisation are higher than the temperatures of Iso–SmA phase transition. This phenomenon is caused by the presence of the even–odd effect. An unexpected result was the solid phase polymorphism, which occurred in seven compounds of the A series. The second crystal form (see Figure 4B) is observed during cooling (for derivatives with $n = 1, 6, 7, 10$) or
during heating (for compounds with \( n = 4, 8, 11 \)). In both cases, the phase transitions are visible during microscopic observations as well as in the DSC measurements.

### 3.2. Mesogenic properties of B-n series

In this group of substances, five type of mesophases were detected: nematic, smectics (SmC, SmI, SmF) and G. Six out sixteen synthesised homologues possess even four liquid-crystalline phases. Nematic (see Figure 6A) was only observed for alkanoates with \( n = 1-13 \). In this series the first non-nematic appears in the butanoate homologue (B-3) and it is G (see Figure 6B). The above-mentioned G is observed in the next five compounds (to 4-[4-(alkyloxy)phenyl] diazenyl)phenyl octanoate). On the other hand, the lamellar smectic C phase (see Figure 6C and D)

**Table 1. Phase transition temperatures (°C) and enthalpies (kJ/mol) for alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates (A-n series).**

| Homologue | CrII | Crystallisation | Melting | SmA | Iso |
|-----------|------|----------------|---------|-----|-----|
| 1         | 99.7 | 109.3 [38.93]  | 119.3 [51.26] | 123.5 [7.63] |     |
| 2         | 92.8 [42.66] | 99.2 [46.59] | 106.9 [7.24] |     |
| 3         | 80.1 [33.15] | 86.5 [36.66] | 100.0 [6.72] |     |
| 4         | 81.8 | 68.3 [33.25] | 83.9 [39.47] | 89.9 [7.76] |     |
| 5         | 65.9 [37.90] | 74.5 [41.82] | 91.8 [8.15] |     |
| 6         | 58.1 | 62.2 [36.48] | 77.7 [41.27] | 88.0 [7.90] |     |
| 7         | 73.5 | 68.6 [20.90] | 75.0 [40.31] | 90.3 [7.97] |     |
| 8         | 68.1 [2.11] | 67.3 [22.30] | 81.1 [17.32] | 89.6 [7.71] |     |
| 9         | 67.8 [24.02] | 80.6 [20.99] | 84.6 [7.57] |     |
| 10        | 55.8 [17.33] | 69.8 [28.49] | 76.1 [49.25] | 83.9 [8.31] |     |
| 11        | 67.8 | 64.6 [28.31] | 75.9 [46.11] | 82.9 [8.93] |     |
| 12        | 77.6 [62.82] | 86.3 [74.29] | (82.1) [8.65] |     |
| 13        | 59.7 [26.20] | 73.9 [51.26] | 84.8 [8.35] |     |
| 14        | 79.3 [64.77] | 88.0 [80.88] | (82.8) [8.44] |     |
| 15        | 62.5 [66.47] | 82.2 [77.37] | (78.6) [9.41] |     |
| 16        | 82.1 [84.10] | 88.9 [87.90] | (76.0) [9.00] |     |
| 17        | 60.7 [67.29] | 84.4 [81.69] | (76.9) [9.00] |     |
| 18        | 86.1 [90.99] | 91.2 [90.97] | (73.0) |     |

Notes: *Because of the overlapping peaks the enthalpy of crystallisation of both crystalline forms is given. **The specified melting enthalpy also includes the energy of SmA–Iso transition due to overlapping peaks. *The common enthalpy of phase transitions CrI–CrII and melting are given. #Temperature is estimated because of the complex peak.
appeared in the B-4 compound (pentanoate derivative) and was present in all homologues with longer alkyl chain (up to \(n = 19\)). A similar dependence is shown for the smectic I phase in Table 2 (for the texture, see Figure 6E). However, the above-described mesophase appeared only in the B-8 (nonanoate derivative). The smectic F phase (see Figure 6F) was present in the medium chain length derivatives (from \(n = 6\) to \(n = 11\)).

The first two acetate and propanoate compounds in contrast to the other homologues have melting point above the 90°C and exhibit only one nematic phase. Meanwhile, the butyl derivative (\(n = 3\)) is the first in the B-\(n\) series, which possesses G mesophase. The next compound of this group, 4-[4-(nonyloxy)phenyl]diazenyl]phenyl pentanoate, already has three phases: SmC, G and nematic, like the previous two homologues. It has a liquid-crystalline behaviour similar to that of its predecessor hexanoate derivative (B-5), but its phase transition temperatures are slightly higher.

In the group of homologues with middle alkyl chain (from \(n = 6\) to \(n = 11\)), a very interesting liquid-crystalline polymorphism was observed. Compounds B-6 and B-7 have identical sequence of mesophases: nematic, smectic C, smectic F and G. Even the phase transition temperatures of the above-described substances are similar. Another homologue B-8 ((4-[4-(nonyloxy)phenyl]diazenyl]phenyl nonanoate) also has four liquid-crystalline phases. However, the G phase disappeared and in its place smectic F appeared. Moreover, the mesomorphic behaviour of B-8 compound was studied by the use of the XRD measurements. The typical patterns of three detected smectic phases are shown in Figure 7. During the cooling from nematic, the smectic C mesophase first appeared. Next, at about 80°C, smectic I was detected and characterised by the presence of two signals.

| Homologue | Crystallisation | Melting \(^{°C}\) | G | SmF | SmI | SmC | N | Iso |
|-----------|----------------|-----------------|---|-----|-----|-----|---|-----|
| 1         | 77.5 [36.96]   | 98.4 [40.33]    |   |     |     |     |   |     |
| 2         | 78.5 [35.28]   | 96.4 [37.85]    |   |     |     |     |   |     |
| 3         | 60.5 [25.29]   | 87.3 [36.58]    | 79.3 [7.93] |     |     |     |   |     |
| 4         | 51.2 [23.41]   | 79.8 [27.81]    | 82.2 [8.80]* |     |     |     |   |     |
| 5         | 54.0 [29.54]   | 81.9 [35.56]    | 80.5 [4.02] |     |     |     |   |     |
| 6         | 53.0 [25.42]   | 74.7 [27.87]    | 77.8 [3.76]* | 78.5 [3.76]* |     |     |   |     |
| 7         | 61.9 [15.28]   | 80.6 [34.00]    | 75.9 [2.61]* | 80.4 [2.61]* |     |     |   |     |
| 8         | 64.1 [11.57]   | 74.3 [29.50]    | 79.9 [0.00] | 82.0 [2.83] | 84.7 [8.80]* | 105.7 [1.53] |   |     |
| 9         | 65.8 [33.71]   | 82.0 [36.68]    | 77.7 [0.00] | 79.5 [2.33] | 86.7 [2.98] | 107.5 [1.50] |   |     |
| 10        | 68.1 [38.32]   | 82.2 [38.78]    | 77.9 [0.00] | 80.5 [1.97] | 90.6 [3.88] | 104.6 [1.69] |   |     |
| 11        | 68.4 [41.46]   | 83.2 [40.94]    | 74.1 [0.00] | 79.7 [1.92] | 91.5 [3.38] | 104.7 [1.88] |   |     |
| 12        | 73.5 [44.07]   | 87.3 [46.62]    | 79.9 [0.00] | 82.0 [2.83] | 87.0 [3.49] | 101.1 [3.05] | 105.4 [2.55] |   |
| 13        | 80.2 [50.89]   | 91.3 [53.45]    | 80.5 [1.97] | 85.7 [4.02] | 98.0 [3.40] | 103.5 [2.99] |   |     |
| 14        | 84.2 [61.06]*  | 93.2 [59.86]    | 88.1 [6.00]* | 88.1 [6.00]* | 89.7 [5.97] | 101.9 [12.86] |   |     |
| 15        | 84.8 [52.48]   | 92.9 [57.87]    | 88.1 [6.00]* | 89.7 [5.97] | 91.1 [8.47] | 101.4 [14.51] |   |     |
| 16        | 81.3 [55.21]   | 83.9 [80.16]    | 88.1 [6.00]* | 89.7 [5.97] | 91.1 [8.47] | 101.4 [14.51] |   |     |

Note: *Enthalpy given for two phase transitions because of overlapping of peaks.
first signal is narrow, diffused and located in a high-angle area. The second signal is perpendicular to normal layer and disappears in the temperature range of smectic F phase. The DSC diagram of compound B-8 shows Figure 8. During the cooling mode six anomalies are visible, which correspond to the phase transitions. At 105.5°C the transition from the isotropic to the nematic phase takes place. Next, the peak at about 97°C corresponds to the transition N-SmC. Then, at 82°C, smectic I phase occurs. The SmC-SmI transition is present on the relevant diagram in the form of the peak with enthalpy equal to 2.83 kJ/mol. SmI phase is very narrow and at 79.9°C is replaced by smectic F. This phase transition is a second-order type phase transition, so it is not detectable in the DSC method. At 64°C occurs crystallisation, observed in the DSC diagram in the form of a large peak with enthalpy of about 11 kJ/mol. Furthermore, at a slightly lower temperature, a second similar peak is seen indicating the formation of a second crystalline form. Moreover, the next three homologues (B-9, B-10 and B-11) show similar liquid-crystalline phase sequence as shown by the above-described B-8 compound.

The group of compounds with the longest alkyl chain (from \( n = 13 \) to \( n = 19 \)) of the B-\( n \) series constitutes five compounds. B-13 as the last homologue has a very narrow nematic phase. Starting from the B-15 only two smectic mesophases, SmC and SmI, were observed. Also, the melting points of the above-mentioned compounds (see Table 2) are relatively higher and exceed 80°C.

Figure 9 shows the mesogenic behaviour of a full series of 4-[4-(nonyloxy)phenyl]-diazenyl]-phenyl alkanoates. On the first sight the plenteous liquid-crystalline mesomorphism is strongly marked. Already the first derivative possesses nematic phase, which narrows with an increasing number of carbon.
atoms in alkyl chain. Next, the homologue B-3 besides the above-mentioned nematic phase has also G mesophase. An interesting sequence of the liquid-crystalline phase is that this is observed in compounds B-4 and B-5, which possess three mesophases: nematic, smectic C and G. However, the richest polymorphism characterised the derivatives with middle alkyl chain length (from \( n = 6 \) to \( n = 11 \)). In the group of the above-described substances, five different mesophases were detected. Smectic F like nematic tends to narrow with the length of the alkyl chain.

3.3. Photoisomerisation studies
Synthesised molecules show similar absorption spectra. It is the consequence of their molecular structure. The only difference is the position of the ester group. The photoisomerisation studies were carried out on
the compounds dissolved in the dichloromethane. The concentrations of the pure solutions containing the \( E \) isomer were following: \( 2.65 \times 10^{-5} \) mol/dm\(^3\) for the A-6 compound and \( 1.37 \times 10^{-5} \) mol/dm\(^3\) for B-6. The obtained results of the UV-Vis absorption spectra are presented in Figures 10 and 11. Figure 10 corresponds to the A-6 compound, whereas Figure 11 refers to the B-6 compound.

The initial measurements were carried out on the unexposed materials (irradiation 0 s). The received spectra are shown in Figures 10A and 11A. These spectra are characterised by two absorption peaks with the maximum absorbance at 450 and 360 nm (A-6 compound) and 443 and 352 nm (B-6 compound). First are the low-intensity \( n-\pi^* \) absorption bands in the visible region (450 nm, 443 nm), whereas the second are much higher intensity \( \pi-\pi^* \) absorption bands in ultraviolet area (360 nm, 352 nm). Thus, the ester group inversion causes a shift of the absorption band of the compound of about 7 nm. Furthermore, the graphs show that the UV light (365 nm) corresponds to the energy gap of the \( \pi-\pi^* \) transition. It suggests that such light can cause the conversion from \( E \) to \( Z \) form. Therefore, the materials were irradiated by the UV light for a certain time to induce the photoisomerisation phenomenon. The spectral changes are presented on the same graphs as spectra of pure, unexposed materials (Figures 10A and 11A). The direction of changes were marked on the graphs. It can be observed that, as a result of the irradiation, in both cases the peak intensity of the \( \pi-\pi^* \) transition band successively decreases. It is equivalent to decrease in the amount of the \( E \) isomer. On the other hand the higher intensity of the \( n-\pi^* \) band was observed, which means the increase in the concentration of the \( Z \) isomer. The photoisomerisation process continues until the equilibrium state of the \( E-Z \) mixture is reached.

After irradiation the back transition from \( Z \) to \( E \) form begins. This process, which is called the thermal relaxation, is presented in Figures 10C (A-6 compound) and 11C (B-6 compound). It can be seen that back transition from \( Z \) to \( E \) form is much slower than the isomerisation during the UV irradiation. To define those differences, the kinetics of the isomerisation and the relaxation processes were carried out. The results for the isomerisation process are presented in Figures 10B (A-6 compound) and 11B (B-6 compound), while the values obtained for the relaxation process are shown in Figures 10D (A-6 compound)
and 11D (B-6 compound). Based on these results, it is possible to designate the rate constant \( k \) of mentioned processes. For the isomerisation reaction, it is equal to \( 6.37 \times 10^{-2} \) \( s^{-1} \) (A-6 compound) and \( 8.17 \times 10^{-2} \) \( s^{-1} \) (B-6 compound), whereas the relaxation rate constant is \( 2.85 \times 10^{-5} \) \( s^{-1} \) (A-6 compound) and \( 1.18 \times 10^{-5} \) \( s^{-1} \) (B-6 compound). Calculations were performed with respect to the E isomer. It can be seen that for both compounds the relaxation process is much slower than the photoisomerisation reaction. Furthermore, the obtained values of the rate constants are similar.

4. Conclusions

There were synthesised 35 compounds: 18 derivatives of alkyl 4-[4-(nonyloxy)phenyl]diazenyl]benzoates and 17 homologues of 4-[4-(nonyloxy)phenyl]diazenyl]phenyl alkanoates. Only three of them were previously described in the literature. The presented liquid-crystalline polymorphism was investigated by the use of DSC and POM methods. In the benzoates series, only one mesophase (SmA) was observed while in the alkanoates group five different mesophases occur: N, SmC, SmI, SmF and G. Based on these data, we can draw the conclusion that the inversion of the ester group strongly influences the liquid-crystalline polymorphism.

Furthermore, for selected compounds from A and B series, the photoisomerisation and the relaxation processes in dichloromethane as a solvent were studied. It was shown that by means of light the two-component system can be created in these materials. It consists of two components: E and Z isomers, which have different optical properties. The measurements of the absorption spectra show that the UV light causes the increase of the \( n-\pi^{*} \) band intensity, which corresponds to the increase of Z isomer population. However, this isomer is unstable and after certain time thermal relaxation to the E form is observed. It corresponds to the increase of the \( \pi-\pi^{*} \) band intensity and decrease of the \( n-\pi^{*} \) band maximum. The calculated rate constants show that the isomerisation E–Z is a highly rapid process, whereas the relaxation Z–E takes much longer. It allows us to assume that the investigated materials can be used as an optical short-term memory. Furthermore, it was found that the modification of the ester bond caused a shift of the absorption band of the compound of about 7 nm. However, it does not significantly affect the rate of the discussed reaction.
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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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