

Solvent Effects on the UV-Visible Absorption Spectra of Some New 3-Methyl-5-(Phenylamino)-4-((4-Phenylazo-Phenyl)Azo)-2-Substituted Thiophene Dyes

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Abstract: The preparation of 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes 4a-d, having different polar groups at the second position, was described through hetero-cyclization of the precursor 4-mercapto-4-(phenylamino)-3-((4-phenylazo-phenyl)azo)but-3-en-2-one (3) with various α -chlorinated reagents. The absorption spectra of the synthesized thiophene dyes were studied in three solvents (MeOH, CHCl₃, and DMF) to correlate the effect of solvent polarity as well as chemical structures on absorption in the UV-vis region. The absorption maximum (λ_{max}) changed from 486 to 502 nm in methanol, from 502 to 512 nm in chloroform, and from 626 to 654 nm in DMF. The benzoyl group's introduction in the second position of the thiophene ring brings the absorption maxima to higher values (bathochromic shift).

Keywords: 4-(phenylazo)aniline; chloroacetone; bis-azo thiophene; UV-visible absorption; solvent effect.

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1. Introduction

Azo dyes constitute 70% of dye chemistry, and their relative significance may increase in the future [1-11]. The widespread study of azo dyes is due to various chemical structures and application methods [12-20]. Numerous azo dyes were applied for dyeing natural fibers (cotton, silk, and wool) and synthetic fibers (polyesters, polyamides, acrylics, and viscose rayon) [21-25]. They are widely used to dye leather, plastics, paper, cosmetics, and foods [26,27]. Besides, some bis-azo dyes containing a conjugated group (phenol and/or nitro-phenol moiety) display green luminescence [28-31]. Several heterocyclic azo dyes were introduced on the market to generate azo disperse dyestuffs based on different heteroaromatic diazo or coupling components [32,33]. Azo dyes derived from nitrogen and/or sulfur heterocyclic ring systems were used in printing, laser technology, electronic photography, and solar energy [34-39]. Thiophene-based sensitizers are attractive because of their intrinsic conjugation of electrons that promotes the charge transfer process [40]. Furthermore, thiophene compounds are excellent fluorescent materials with high photo-luminescent performance [41-44]. Heterocyclic azo dyes were recently reported as an attractive research topic for chemists [45] and dyes manufacturers [46]. Especially, thiophene-based azo dyes have gained great interest since they are used in dye-sensitized solar cells (DSSCs) and semiconducting compounds [47-52]. The present paper describes the synthesis of 2-substituted-3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes by cyclization the precursor 2-acetyl-2-(4-

phenylazo-phenyl)thioacetanilide with four chlorinated reagents ($\text{CH}_3\text{COCH}_2\text{Cl}$, PhCOCH_2Cl , $\text{ClCH}_2\text{COOEt}$ and/or ClCH_2CN).

2. Materials and Methods

The ultraviolet-visible absorption spectra were measured on a Shimadzu 1700 spectrophotometer in the region 200–600 nm. The IR spectra were obtained on the Thermo Scientific Nicolet iS10 FTIR spectrometer. ^1H NMR spectra were measured in $\text{DMSO}-d_6$ as a solvent at 500 MHz on JEOL's spectrometer. Perkin-Elmer 2400 analyzer has been used to determine the elemental analyses.

2.1. Preparation of 4-mercapto-4-(phenylamino)-3-((4-phenylazo-phenyl)azo)but-3-en-2-one (3).

A well-stirred solution of 4-(phenylazo)aniline (3.94 g, 0.02 mol) in concentrated HCl (6 mL) was cooled at 0–5°C. Then sodium nitrite solution was added (1.40 g in 10 mL water). The diazonium solution that was obtained was added drop by drop to a cold suspension of 2-acetyl-3-oxo-*N*-phenyl butane thioamide (2) (4.70 g, 0.02 mol) and sodium acetate (6.00 g) in 50 mL ethanol. The reaction components were stirred for 2 hours at 0–5°C. The crude bis-azo dye 3 was collected, dried, and recrystallized from ethanol.

Orange solid, yield = 63%, m.p. = 134–135°C. IR (KBr): 3435 (NH), 1648 (C=O), 1595 (C=N), 1525 cm^{-1} (N=N). ^1H NMR: 2.19 (s, 1H, SH), 2.48 (s, 3H, CH_3), 7.44–8.10 (m, 14H, Ar-H), 12.16 ppm (s, 1H, NH). Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_5\text{OS}$ (401.13); C, 65.82; H, 4.77; N, 17.44. Found; C, 65.88; H, 4.74; N, 17.49%.

2.2. Preparation of 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes 4a-d.

To a suspension of thiol derivatives 3 (0.40 g, 0.001 mol) in sodium ethoxide solution (prepared from 0.05 g Na metal and 20 mL dry ethanol), 0.001 mol of each appropriate chlorinated reagent (namely; $\text{CH}_3\text{COCH}_2\text{Cl}$, PhCOCH_2Cl , $\text{ClCH}_2\text{COOEt}$ and/or ClCH_2CN) was added. The reaction components were refluxed for 2 hours and then cooled to 30°C. The solid that formed upon the addition of ice-cold water and neutralized by dilute HCl was collected and washed with water. The solid obtained in each case was recrystallized from ethanol to give the targeted thiophene derivatives 4a-d.

2.2.1. 2-Acetyl-3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene (4a).

Red solid, yield = 82%, m.p. = 215–217°C. IR: 3386 (N-H), 1637 cm^{-1} (C=O). ^1H NMR: 2.56 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 7.33–8.05 (m, 14H, Ar-H), 14.29 ppm (s, 1H, NH). Anal. Calcd. for $\text{C}_{25}\text{H}_{21}\text{N}_5\text{OS}$ (439.15): C, 68.32; H, 4.82; N, 15.93%. Found; C, 68.20; H, 4.86; N, 15.98%.

2.2.2. 2-Benzoyl-3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene (4b).

Reddish brown solid, yield = 73%, m.p. = 183–184°C. IR: 3443 (N-H), 1622 cm^{-1} (C=O). ^1H NMR: 2.22 (s, 3H, CH_3), 7.28–7.99 (m, 19H, Ar-H), 14.18 ppm (s, 1H, NH). Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{N}_5\text{OS}$ (501.16): C, 71.83; H, 4.62; N, 13.96%. Found; C, 71.91; H, 4.60; N, 13.88%.

2.2.3. 2-Ethoxycarbonyl-3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene (4c).

Dark red solid, yield = 75%, m.p. = 150-151°C. IR: 3423 (N-H), 1704 cm⁻¹ (C=O ester). ¹H NMR: 1.23 (t, *J* = 7.20 Hz, 3H, CH₃), 2.21 (s, 3H, CH₃), 4.33 (q, *J* = 7.20 Hz, 2H, CH₂), 7.03-7.96 (m, 14H, Ar-H), 14.44 ppm (s, 1H, NH). Anal. Calcd. for C₂₆H₂₃N₅O₂S (469.16); C, 66.51; H, 4.94; N, 14.91%. Found; C, 66.66; H, 4.86; N, 14.82%.

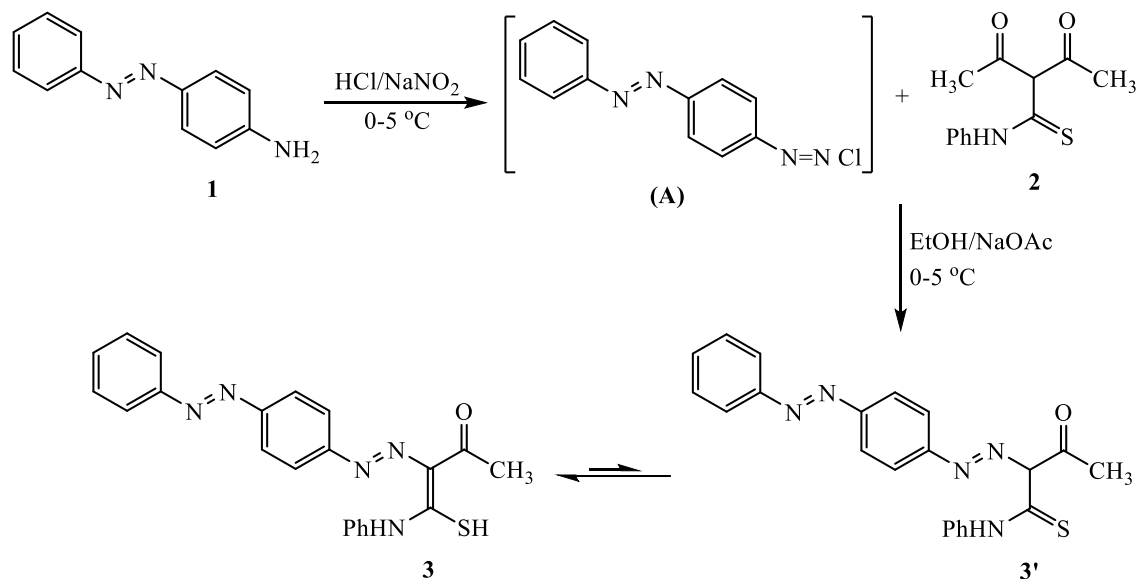
2.2.4. 2-Cyano-3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene (4d).

Dark red solid, yield = 88%, m.p. = 209-211°C. IR: 3394 (N-H), 2203 cm⁻¹ (C≡N). ¹H NMR: 2.44 (s, 3H, CH₃), 7.36-8.04 (m, 14H, Ar-H), 14.27 ppm (s, 1H, NH). Anal. Calcd. for C₂₄H₁₈N₆S (422.13): C, 68.23; H, 4.29; N, 19.89%. Found; C, 68.12; H, 4.27; N, 19.87%.

3. Results and Discussion

3.1. Synthesis and characterization of bis-azo thiophene dyes 4a-d.

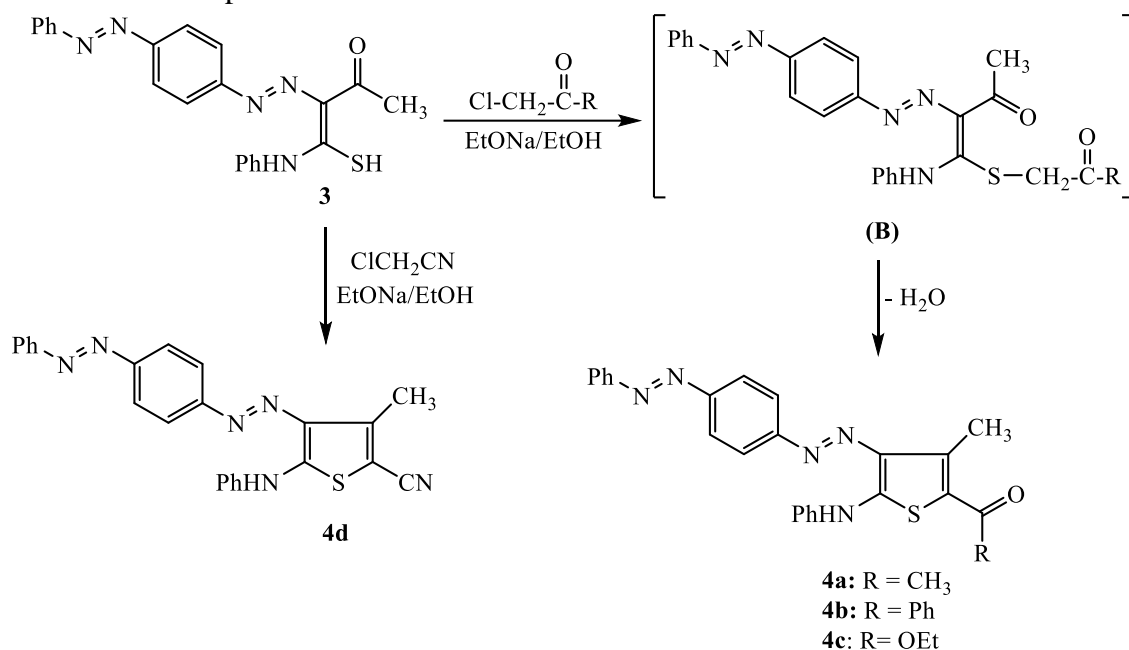
4-(Phenylazo)aniline (1) has been easily diazotized by the action of nitrous acid (sodium nitrite and HCl) at 0-5°C to form the corresponding diazonium intermediate (A). *In situ* coupling of the freshly obtained diazonium salt (A) with 2-acetyl-3-oxo-*N*-phenyl butane thioamide (2) to furnish the coupling product, 4-mercapto-4-(phenylamino)-3-((4-phenylazo-phenyl)azo)but-3-en-2-one (3) (Scheme 1). The coupling process was performed in ethanol and sodium acetate and accompanied by loss of acetyl group (Japp-Klingemann reaction).



Scheme 1. Formation of the thiocarbamoyl compound 3.

The reaction of thiol compound 3 with various chlorinated reagents (namely; chloroacetone, phenacyl chloride, ethyl chloroacetate, and chloroacetonitrile) was achieved in boiling ethyl alcohol and sodium ethoxide to give the corresponding 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes 4a-d (Scheme 2). The suggested mechanism for preparing these bis-azo thiophene dyes involves initial alkylation of thiol compound 3 with each alpha-chlorinated reagent to form the thioether intermediate of the type B followed by *in situ* cyclization that proceeds by the elimination of water molecule from the methylene and carbonyl groups. The structures of bis-azo thiophene dyes 4a-d were established by their elemental and spectral analyses. The IR spectra of the synthesized bis-azo thiophene

dyes 4a-d showed the absorption of N-H function in the range 3443-3386 cm^{-1} . The absorption of the carbonyl group of 2-benzoylthiophene dye 4b was identified at lower wavenumber (1622 cm^{-1}) due to high conjugation with benzene thiophene rings. The carbonyl group of 2-acetylthiophene dye 4a was observed at a slightly higher frequency (1637 cm^{-1}) because of conjugation with the thiophene ring. The characteristic absorption of the carbonyl group of 2-ethoxy-carbonyl thiophene dye 4c was observed at a higher wavenumber (1704 cm^{-1}). The ^1H NMR spectrum of bis-azo thiophene dye 4a (as an example) displayed two singlet signals at δ 2.56 and 2.65 ppm for the methyl protons group (thiophene- CH_3 and COCH_3 , respectively). The aromatic protons resonate as multiplet in the region δ 7.33-8.05 ppm. The singlet at δ 14.29 ppm referred to the proton of the N-H function.



Scheme 2. Formation of bis-azo thiophene dyes 4a-d.

3.2. UV-visible spectra of thiophene dyes 4a-d.

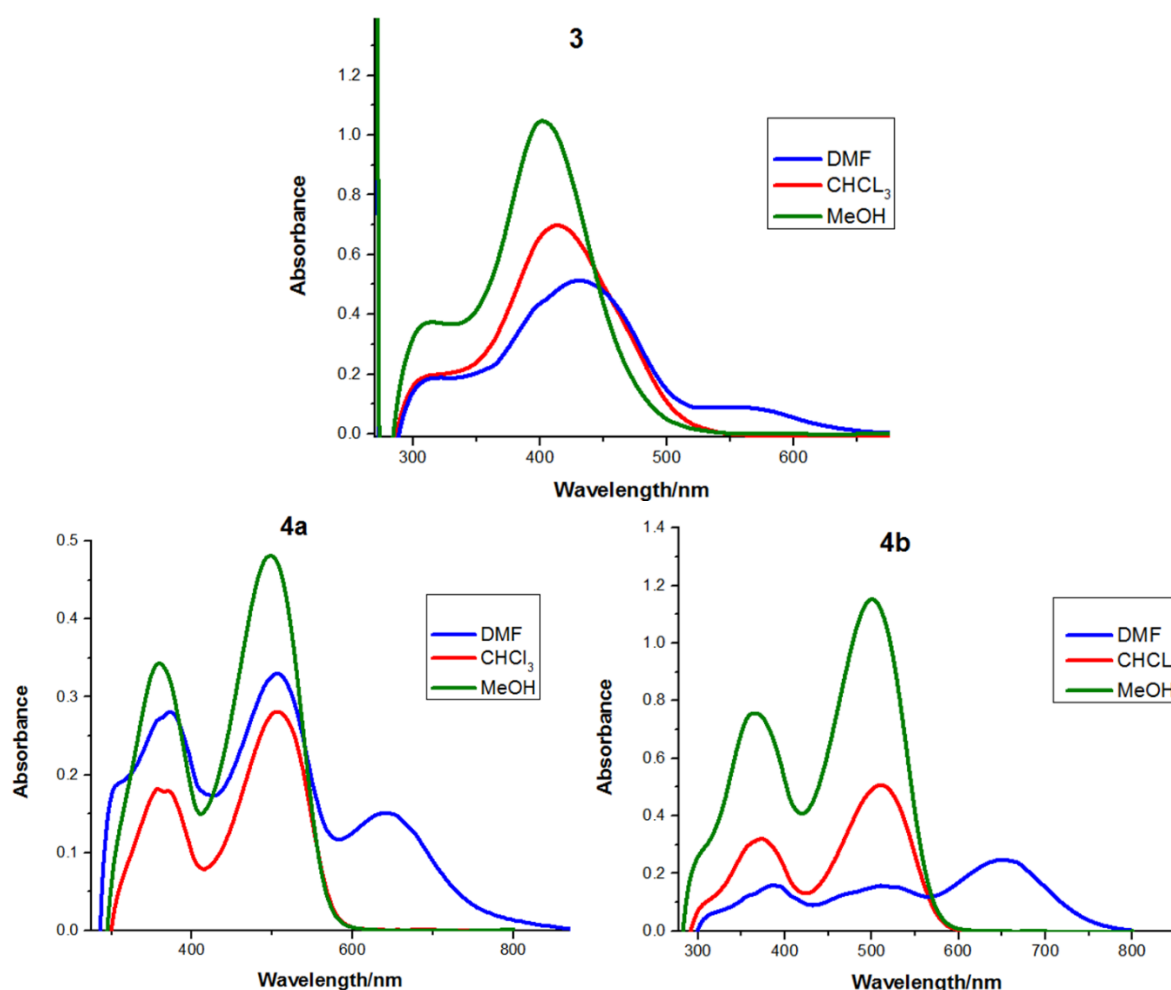
The absorption maxima (UV-visible spectra) of 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes 4a-d was explored using three types of solvents (MeOH, CHCl_3 , and DMF) with different polarities. In general, different colors of the synthesized bis-azo thiophene dyes result from either alternation of the substituent that occupies position number two at the thiophene ring. The color of the synthesized bis-azo thiophene dyes changed from orange to reddish-brown. The absorption spectra of dye solution were examined to estimate the color. The wavelength at maximum absorption of the synthesized 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)thiophene dyes 4a-d were measured in three solvents with diverse polarity (dimethylformamide, chloroform, and methanol). The absorption maximum (λ_{max}) of the constructed bis-azo thiophene dyes in DMF (table 1) changed from 626 to 654 nm. They displayed a tight range (500-512 nm) in chloroform and (478-502) nm in methanol. Among the four bis-azo thiophene dyes 4a-d under investigation, the relationship between the change of absorption maxima, and polarities of the solvents and substituents, the following can be summarized:

- (a) In DMF, the absorption λ_{max} values were higher than their conforming values in chloroform and methanol for the four bis-azo thiophene dyes 4a, 4b, 4c, and 4d.

- (b) DMF created more bathochromic shifts than chloroform and methanol. The highest observed λ_{\max} value was 654 nm in DMF for the bis-azo thiophene dye 4b that substituted with benzoyl group at the second position of thiophene ring.
- (c) In all solvents, the benzoyl group's introduction at the second position of the thiophene ring affects shifting the absorption maxima to higher values (bathochromic shift).
- (d) In all solvents, the cyano group's introduction at the second position of the thiophene ring affects shifting the absorption maxima to lower values (hypsochromic shift).
- (e) The bathochromic effect of the substituent at the second position of thiophene follows the order: CPh (4b: λ_{\max} = 654) > COMe (4b: λ_{\max} = 646) > COOEt (4c: λ_{\max} = 642) > CN (4d: λ_{\max} = 626).
- (f) In chloroform, the absorption maximum (λ_{\max}) of the four bis-azo thiophene dyes 4a, 4b, 4c, and 4d occupy a compact range of wavelengths values (500-512 nm).

Table 1. UV-visible absorption wavelength (λ_{\max} , nm) of bis-azo thiophene dyes 4a-d in DMF, CHCl₃, and MeOH.

Dye No.	DMF	CHCl ₃	MeOH
3	264, 432, ---	264, 414	264, 402
4a	264, 510, 646	662, 508,	258, 500
4b	266, 510, 654	272, 512	262, 502
4c	266, 502, 642	258, 500	262, 478
4d	264, 502, 626	262, 502	258, 486



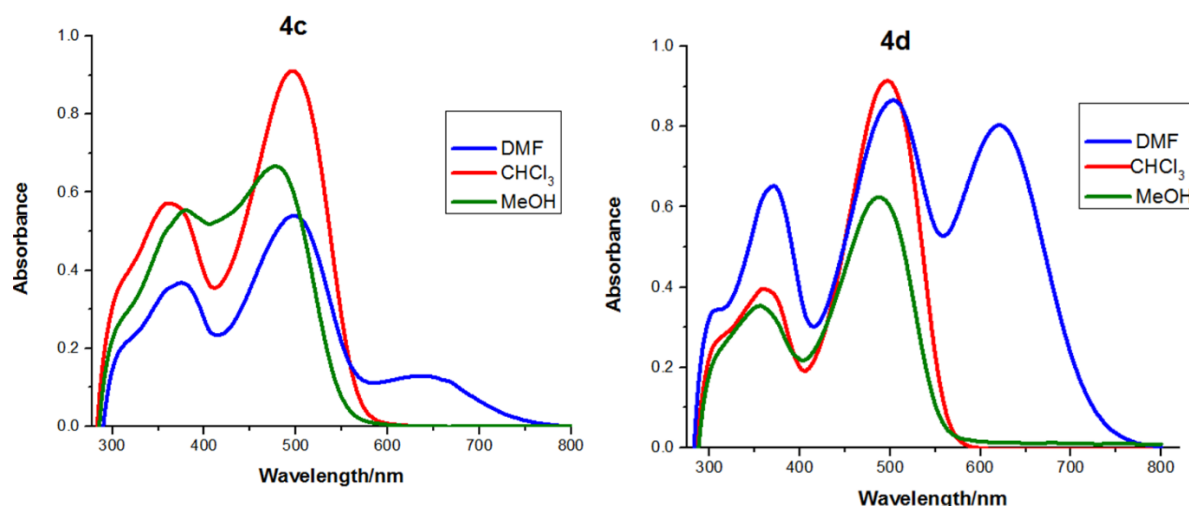


Figure 1. UV-visible spectra of dyes 3 and 4a-d in DMF, CHCl₃ and MeOH.

4. Conclusions

In conclusion, a series of four 3-methyl-5-(phenylamino)-4-((4-phenylazo-phenyl)azo)-2-substitutedthiophene dyes 4a-d was successfully prepared and their absorption spectra were studied in MeOH, CHCl₃, and DMF. The absorption maximum (λ_{max}) changed from 486 to 502 nm in methanol, from 502 to 512 nm in chloroform, and from 626 to 654 nm in DMF. The substituent at the second position of the thiophene ring clearly affecting the absorption maxima to follow this order in DMF: CPh (4b: λ_{max} = 654) > COMe (4b: λ_{max} = 646) > COOEt (4c: λ_{max} = 642) > CN (4d: λ_{max} = 626).

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Conflicts of Interest

The authors declare no conflict of interest.

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