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New cyclopentadiene derivatives as novel pH indicators

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Abstract

(Triphenylphosphoranylidene)cyclopenta-1,3-dienes with stabilized zwitterionic resonance structures showed the application feasibility as new pH indicators. In terms of absorption intensity occurring from the acid–base reactions, (triphenylphosphoranylidene)cyclopenta-1,3-dienes displayed strong colors with high extinction coefficients in the alkali pH range. Resonance structures of (triphenylphosphoranylidene)cyclopenta-1,3-dienes in alkali media stabilize anionic ions. Three derivatives of (triphenylphosphoranylidene)cyclopenta-1,3-dienes **1a–c**, are used as pH indicators in the range 10–12. For these compounds color change in the pH range 10–12 was extremely sharp, clear and reversible. But there are not many indicators in the pH range 10–14.
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1. Introduction

Many chemical analyses are performed by titration, a procedure in which a reagent in a solution of known concentration, called the standard solution, is allowed to react with a sample containing an unknown quantity of the substance to be analyzed. The point at which equivalent quantities of the reactant are present, exactly the equivalent point, is usually detected through the addition of an indicator to the solution being titrated [1–4].

Many dyes have been used as pH indicators by the reversible action of acid and base, and this behavior led to the concept of acid–base indicators, although there are not many indicators in the pH range 10–14 [1,2]. In this work, three derivatives of (triphenylphosphoranylidene)cyclopenta-1,3-dienes, that are recently synthesized [5,6], are used as pH indicators in the pH range 10–12. For these compounds color change in the pH range 10–12 was extremely sharp and clear (Table 1). For comparison purposes, commonly used pH indicators and the newly introduced indicators, in the pH range 10–14, are listed in Table 1 [1]. In terms of transition ranges and color changes (triphenylphosphoranylidene)cyclopenta-1,3-dienes exhibited quite acceptable properties to be used as indicators.

2. Experimental

2.1. Chemicals and instrumentation

All organic solvents used in the present investigation were of spectral grade (Merck) products. The measurements of pH were carried out using pH-meter, model 713, digital pH-Messgerate, accurate to ±0.005 units. The electrode system was calibrated using Merck standard buffer solutions of pH 4.0, 7.0 and 9.0. The absorption spectra in the UV and visible regions were recorded by a Shimadzu multispec-1501 UV/vis recording spectrophotometer.

2.2. Methods

The measured pH values were corrected using the relation $pH^* = pH(R)-\delta$, where pH* is the corrected reading and pH(R) is the meter reading obtained in water–ethanol

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Table 1
Position of new indicators among commonly used pH indicators in the pH range 10–14

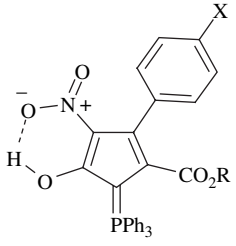
pH (transition range)	Indicators	Color change	Composition of indicator (%)
9.4–12	Alizarin (Red)	Brown orange–violet	0.1 (in water)
10.2–11.8	Alizarin	Brownish red–violet	0.5 (in 96% ethanol)
10.2–12.1	Alizarin Yellow	Pale yellow–brownish red	0.1 (in water)
10.2–11.5	Compound **1a**	Yellow–red	0.16 (in 70% ethanol)
10.7–12	Compound **1b**	Yellowish white–red	0.1 (in 70% ethanol)
10.8–12	Compound **1c**	Yellowish white–red	0.16 (in 70% ethanol)
11.5–13	Alkali Blue	Blue–pink violet	0.1 (in 90% ethanol)
11.6–13	Epsilon Blue	Orange–violet	0.1 (in water)
11.7–14	Indigo Carmine	Blue–yellow	0.25 (in 50% ethanol)
12–14	Acid Fuchsine	Red–colorless	0.1 (in water)

(30:70) solvent mixture [7–9]. In this report pH values are corrected. The (triphenylphosphoranylidene)cyclopenta-1,3-dienes were reproduced and characterized as mentioned in Ref. [5]. To determine the transition range for color change of the indicators, the measurement of absorption was carried out at 493 nm, 509 nm, and 495 nm for compounds **1a**, **1b**, **1c**, respectively, during the addition of dilute alkali solution (NaOH). The distinct maximum of its absorption spectrum is shifted both bathochromically and – to a less extent – hyperchromically with any increase of the pH value [10].

3. Results and discussion

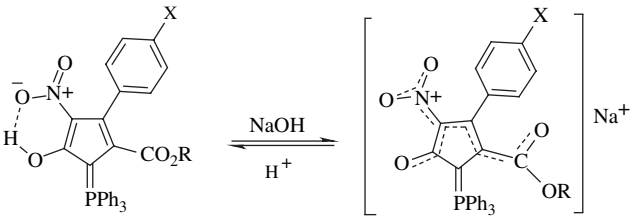
A new and efficient synthesis of highly functionalized (triphenylphosphoranylidene)cyclopenta-1,3-dienes with zwitterionic resonance structures has recently been reported [5] (Scheme 1). Compounds **1a–c** have been synthesized and purified at least 95%. (Triphenylphosphoranylidene)cyclopenta-1,3-dienes showed the application feasibility as new pH indicators. The absorption intensity occurring from the acid–base reactions of compounds **1a–c** displayed quite strong colors in the alkali pH range.

From the UV/vis absorption spectra based on the varying basicity, a pH-dependent reversible equilibrium between (triphenylphosphoranylidene)cyclopenta-1,3-dienes (I-H) and its deprotonated form (I^-) has been established in a mixture of sodium hydroxide and EtOH/H_2O (70:30) system. The negative charge is stabilized by NO_2 and CO_2R substitutions on



1	X	R
a	H	CH_3
b	NO_2	CH_3
c	Cl	CH_2CH_3

Scheme 1. (Triphenylphosphoranylidene)cyclopenta-1,3-dienes **1a–c**.



Scheme 2. Resonance structure of (triphenylphosphoranylidene)cyclopenta-1,3-dienes.

cyclopentadiene by resonance (Scheme 2), also electronic withdrawing groups on phenylene moiety ($X = NO_2$ and Cl in compounds **1b** and **1c**, respectively) are effective by induction effects. The high electrophilic effects of $X = NO_2$ (compound **1b**) cause more stability of negative charge and also sharp change in color of cyclopenta-1,3-diene **1b** during alkali titration (Table 1 and Figs. 2, 4).

In addition, this corresponding color development at the transition point was attributable to the resonance structures, for example, in methyl 4-hydroxy-3-nitro-2-phenyl-5-(1,1,1-triphenyl-λ^5-phosphoranylidene) cyclopenta-1,3-diene-1-carboxylate **1a** showed yellow at λ_{max} 358 nm but with alkali addition this indicator showed strong red at λ_{max} 493 nm with high extinction coefficient in the pH range 10.2–11.5. Methyl 4-hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl-λ^5-phosphoranylidene) cyclopenta-1,3-diene-1-carboxylate **1b** is yellowish white at λ_{max} 355 nm and during alkali addition, this indicator showed strong red at λ_{max} 509 nm with high extinction coefficient in the pH range 10.7–12. Ethyl 2-(4-chlorophenyl)-4-hydroxy-3-nitro-5-(1,1,1-triphenyl-λ^5-phosphoranylidene) cyclopenta-1,3-diene-1-carboxylate **1c** also showed yellowish white at λ_{max} 356 nm and strong red at λ_{max} 495 nm with high extinction coefficient in the pH range 10.8–12.

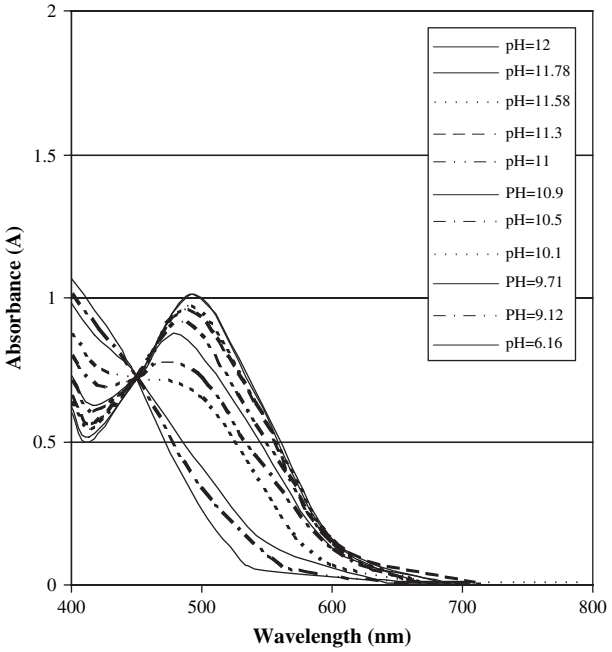


Fig. 1. UV/vis spectra of dye **1a** at different pH values ($c = 0.16$ g/l).

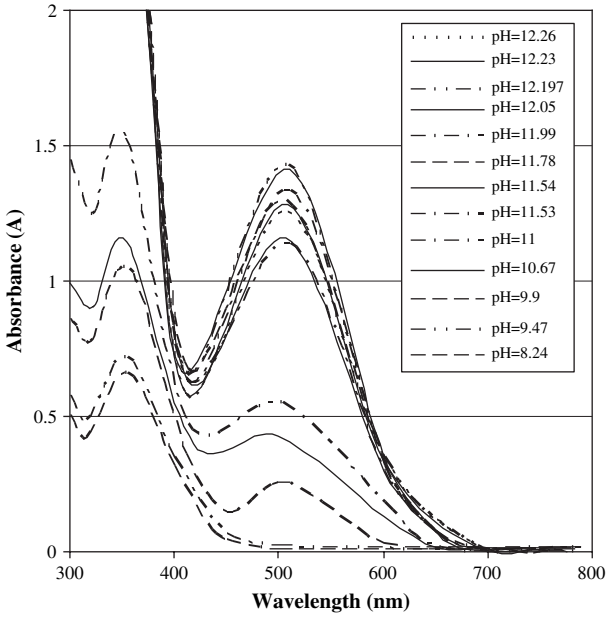


Fig. 2. UV/vis spectra of dye **1b** at different pH values ($c = 0.1$ g/l).

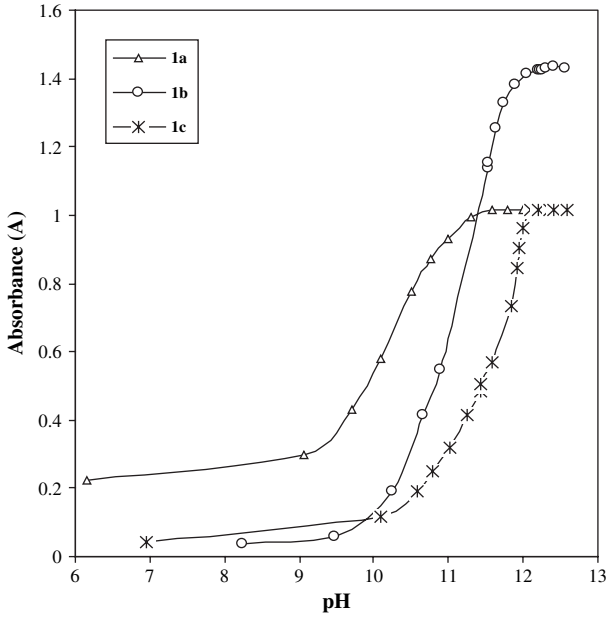


Fig. 4. Effect of pH on the maximum absorption intensity transition for dyes **1a–c** on the wavelength: 493 nm, 509 nm, 495 nm, respectively.

Color changes are reversible and the compounds **1a–c** are stable in acidic and alkaline conditions. Consequently, (triphenylphosphoranylidene)cyclopenta-1,3-dienes **1a–c** could be considered to be used as new pH indicators. The results are shown in Figs. 1–4. The position of new indicators among commonly used pH indicators in the pH range 10–14 is shown in Table 1. The UV/vis absorption spectra of compounds **1a**, **1b**, and **1c** are shown in Figs. 1, 2 and 3. These compounds have excellent indicator properties within the alkaline-pH range.

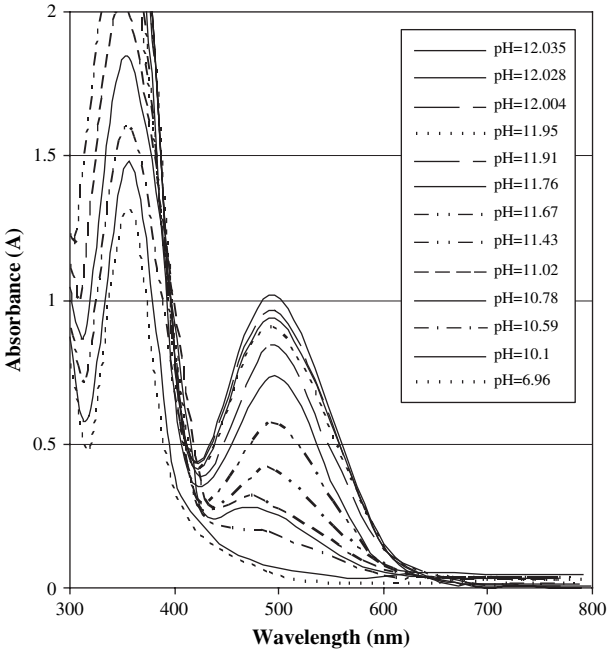


Fig. 3. UV/vis spectra of dye **1c** at different pH values ($c = 0.16$ g/l).

An additional interesting subeffect is that anionic cyclopentadiene systems behave as an electron donor substitute for *p*-NO_2- (and *p*-Cl-)phenylene moiety in compound **1b** (and **1c**) and produce an electron donor–acceptor system, therefore the second absorption is observed in UV area by increasing the pH.

4. Conclusion

Many dyes have been used as pH indicators but there are not many indicators in the pH range 10–14 [1]. Stabilized zwitterionic cyclopentadienes **1a–c** can be used as pH indicators as they show sharp, clear and reversible change in the pH range 10–12. A few drops of each one in 100 ml solution will turn to strong red color in the mentioned pH range.

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