

Photometric and Fluorimetric Study of the Acid–Base Behavior of 2,2'-Diquinolyl and 2,2',2''-Terpyridyl

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A photometric and fluorimetric study of the acid–base behavior of 2,2'-diquinolyl and 2,2',2''-terpyridyl was performed. In sulfuric acid medium, the doubly charged 2,2'-diquinolynium ion undergoes the first dissociation at $H_0 = 0.20 \pm 0.09$, as determined by fluorimetry ($\lambda_{\text{ex}} = 336$ nm, $\lambda_{\text{em}} = 424$ nm). Photometric titration is less accurate because of the overlapping of the absorption spectra. The second dissociation constant of 2,2'-diquinolyl was determined by fluorimetric titration ($\lambda_{\text{ex}} = 336$ nm, $\lambda_{\text{em}} = 420$ nm), obtaining a value of 3.67 ± 0.03 . The triply charged 2,2',2''-terpyridyl molecule was found to undergo the first dissociation at $H_0 = -7.17 \pm 0.04$, as determined by fluorimetric titration ($\lambda_{\text{ex}} = 316$ nm, $\lambda_{\text{em}} = 350$ nm), in aqueous sulfuric acid medium. Photometric titration ($\lambda = 335$ nm) was performed in the presence of 6.5% ethanol because of the low solubility of the compound in water. In this ethanolic:water medium, a value of the dissociation constant at $H_0 = -7.39 \pm 0.03$ was calculated. The second dissociation constant was determined to be 2.81 ± 0.12 by photometric titration at 285 nm, and values of 4.03 ± 0.26 and 4.16 ± 0.20 were found for the third dissociation constant by photometric titrations at 320 and 295 nm, in 10% ethanol, in close agreement with previously reported values. The fluorimetric titration profile obtained by exciting at 274 nm and measuring the fluorescence emission at 350 nm, in the zone between $H_0 = -3$ and $\text{pH} = 10$, is complicated by the several equilibria involved.

KEY WORDS: Acid–base behavior; photometry; fluorimetry; 2,2'-diquinolyl; 2,2',2''-terpyridyl.

INTRODUCTION

Polyazine ligands such as the *o*-phenanthrolines, *o*-polypyridyls, and diquinolyls have been used for the spectrophotometric determination of a variety of metal ions. They also have the potential for luminescent determination of metal ions with great sensitivity.⁽¹⁾

Before one can take full advantage of the analytical methodology to be derived from the measurement of absorption or fluorescence, it is in order to understand, as

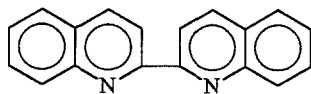
completely as possible, the factors that affect luminescence emission. The dissociation constants of the various protonated forms of the ligand and the stability constants of the metal complexes are adequate to describe quantitatively the competition between protons and metal ions for the ligand.

The determination of dissociation constants of compounds with a low solubility in water can be done by means of a fluorimetric titration, by following the changes on the emission spectra of the compound in study with the pH. 2,2'-Diquinolyl is a compound slightly soluble in water, which shows an intense fluorescence in aqueous solution in acid medium. As far as we know, dissociation constant values for this compound have been not reported in the literature, except for a report in a journal of difficult access.⁽²⁾

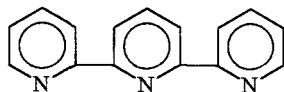
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2,2'-Diquinolyl



2,2',2''-Terpyridyl

Scheme I. Structures of 2,2'-diquinolyl and 2,2',2''-terpyridyl.

The dissociation constants of doubly and single protonated 2,2',2''-terpyridyl have been reported to be 2.64 ± 0.07 and 4.33 ± 0.03 by Martin and Lissfelt⁽³⁾ and redetermined by Nakamoto⁽⁴⁾ as 2.59 and 4.16. Later,⁽⁵⁾ the luminescence characteristics of 2,2',2''-terpyridyl were established and this compound was used for the fluorimetric determination of iron⁽⁶⁾ and iridium.⁽⁷⁾ No reference about the fluorescence emission of the dication at around 370 nm and of the dissociation constant of the triply charged 2,2',2''-terpyridyl has been reported in the literature.

In this paper, the two dissociation constants of protonated 2,2'-diquinolyl and the three dissociation constants of protonated 2,2',2''-terpyridyl are determined by fluorimetric and photometric titrations, and the results obtained are discussed. The possibility of the origin of the emission from various conformational isomers in the case of 2,2',2''-terpyridyl is discussed.⁽⁸⁾

EXPERIMENTAL

Instrumental

Fluorescence spectra were recorded on a Perkin-Elmer MPF-2A fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission spectrum and whose output was corrected for instrumental response by means of a rhodamine-B quantum counter. The instrument is equipped with an Osram BO 150-W xenon lamp, an R-508 photomultiplier, and a Perkin Elmer 056 recorder. The excitation and emission slits were maintained at 8 and 6 nm, respectively. Analysis of the data for calculation of the pK_a values

was performed by the method of Stenstrom and Goldsmith.^(9,10) A Beckman Model 25 spectrophotometer and an Orion 801 pH meter with a Corning silver-silver chloride-glass combination electrode were also used.

Reagents

2,2'-Diquinolyl was obtained from Merck and recrystallized before use. Solutions of which fluorescence spectra were taken were 10^{-6} M in concentration and had their pH adjusted with sulfuric acid and sodium hydroxide solutions. For photometric titration in very concentrated sulfuric acid, a 10^{-5} M aqueous solution was used.

2,2',2''-Terpyridyl was obtained from Merck and recrystallized before used. Solutions of which fluorescence spectra were taken were 2×10^{-6} M in concentration and had their pH adjusted with sulfuric acid and sodium hydroxide solutions. For photometric titration in very concentrated sulfuric acid, a 3.25×10^{-5} M aqueous solution, in the presence of 6.5% ethanol, was used, and for titration between $H_0/pH = -3$ and 10, a 5×10^{-5} M aqueous solution in the presence of 10% ethanol was used. Jorgenson and Hartter's corrected Hammett acidity scale was employed to calibrate the concentrated sulfuric acid solutions.⁽¹¹⁾ Doubly distilled and demineralized water was used throughout.

RESULTS AND DISCUSSION

Acid-Base Behavior of 2,2'-Diquinolyl

The doubly charged 2,2'-diquinolium cation is capable of undergoing two successive protolytic dissociations. The dissociation constants are related to the dication \rightleftharpoons monocation equilibrium (pK_1) and the monocation \rightleftharpoons neutral molecule equilibrium (pK_2). The first path entails dissociation of the double-protonated species at the nitrogen group to form the singly charged molecule. The second dissociation gives rise to the neutral species (Scheme I). The fluorescence of this compound in moderate acid medium is due to the emission from the single protonated species. When the acidity is further increased, the fluorescence intensity decreases because of the formation of the nonfluorescent doubly charged cation. Also, on going from acidic pH to neutral pH, the fluorescence intensity of the compound decreases to practically zero, because of the second dissociation equilibrium giving rise to the nonfluorescent neutral species.

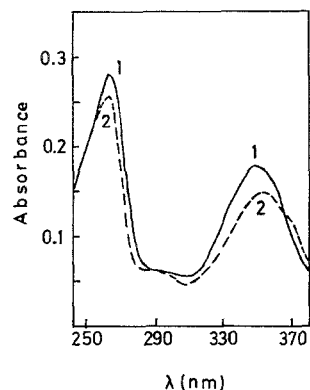


Fig. 1. Absorption spectra of the doubly (1) and singly (2) charged protonated diquinolyl species. $[R] = 1.0 \times 10^{-5} M$.

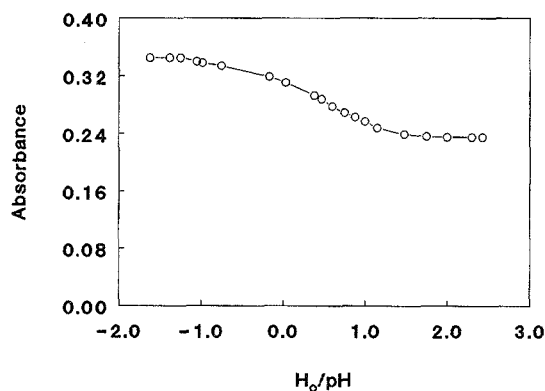


Fig. 2. Absorbance vs H_0/pH for $1.0 \times 10^{-5} M$ 2,2'-diquinolyl in sulfuric acid medium, at an analytical wavelength of 262 nm.

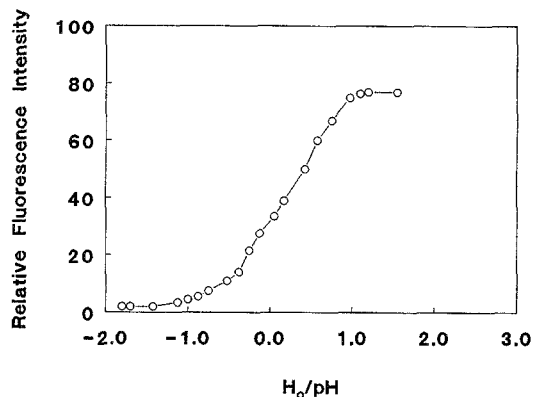


Fig. 3. Dependence on H_0/pH of the fluorescence intensity for $1.0 \times 10^{-5} M$ 2,2'-diquinolyl (at the emission maximum of 424 nm). Excitation at 366 nm, the isosbestic point in the absorption spectra of the double and singly charged cationic species.

In concentrated sulfuric medium, the double-charged cation presents absorption maxima at 263 and 350 nm. The single-charged species presents a small decrease in the absorbance and maxima slightly different

with respect to those of the double-charged species, at 262 and 352 nm. The two species are in equilibrium, showing an isosbestic point at around 366 nm. The absorption spectra of the double and singly charged molecules are shown in Fig. 1.

Although 2,2'-diquinolyl is a compound slightly soluble in water, the diquinolinium cation is more soluble than the neutral species. A $10^{-5} M$ solution of this compound was prepared in sulfuric acid medium and photometric titration was performed in the acidity range between and $H_0 = -2$ and pH 1. The changes in the absorbance at 262 nm in this acidity range are presented in Fig. 2. A pK_1 value of 0.38 ± 0.05 was obtained for the first dissociation constant of the double-charged cation.

Fluorimetric titration was also performed in this acidity zone, to calculate the first dissociation constant more accurately, because the observed changes in the emission spectrum are more pronounced than the changes in the absorption spectrum. Exciting at 366 nm, the isosbestic point of the absorption spectra of the two species in equilibrium, fluorimetric titration was made between $H_0 = -2$ and pH 1, by adding different concentrations of sulfuric acid. The double-charged cation is nonfluorescent and the singly charged species presents an intense broad fluorescence band at around 424 nm. The titration curve obtained by monitoring the fluorescence emission at 424 nm is shown in Fig. 3. A pK_1 value of 0.20 ± 0.09 was obtained, around 0.2 unit lower than the value found in photometric titration. The differences between the pK_1 values of diquinolyl measured by absorption and by fluorescence are probably due to the overlap of the absorption spectra. The value obtained by fluorimetric titration is more accurate than the photometric value.

In spite of the low solubility of 2,2'-diquinolyl in aqueous solution, we attempted to follow the changes in the absorption spectra on going from pH 1 to pH 7, to evaluate the value of the second dissociation constant. For that, a $10^{-5} M$ solution was prepared in 5% (v/v) ethanol:water medium. The absorbance of that solution was very low. The neutral species presents maxima at 255 and at 326 nm and the singly charged species presents maxima at 260 and 355 nm, but the changes produced on titration were very small to allow estimation of the pK_2 by photometry.

To calculate the second dissociation constant, fluorimetric titration was also performed. Excitation was effected at the isosbestic point of the absorption spectra of the singly charged cation and the neutral species. To define this isosbestic point, a $10^{-4} M$ solution of 2,2'-diquinolyl was prepared in 50% (v/v) ethanol:water me-

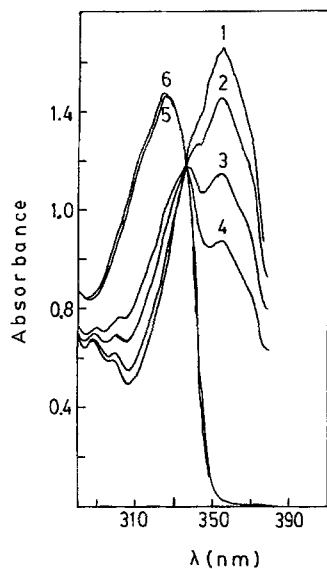


Fig. 4. Absorption spectra of 1.0×10^{-4} M 2,2'-diquinolyl in 50% (v/v) ethanol:water medium, at different pH values. (1) pH 1.95; (2) pH 2.20; (3) pH 2.55; (4) pH 2.90; (5) pH 6.0; (6) pH 7.0.

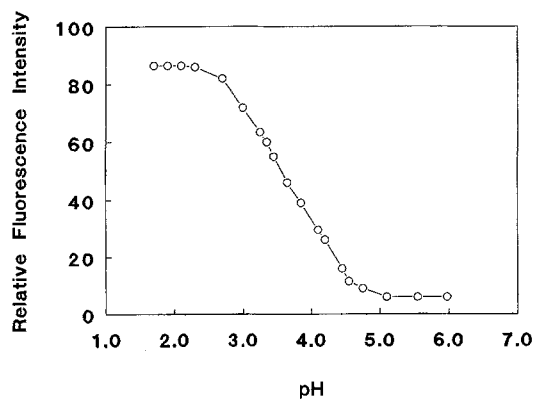


Fig. 5. Dependence on pH of the fluorescence intensity of 1.0×10^{-6} M 2,2'-diquinolyl (at the emission maximum of 420 nm). Excitation at 336 nm, the isosbestic point in the absorption spectra of the singly charged cation and the neutral species.

dium, and the pH was changed by the addition of sulfuric acid. The neutral species presents a maximum in the visible zone at 326 nm, which changes to higher wavelengths on protonation. The isosbestic point is clearly situated at 336 nm and the singly charged species presents a maximum at 355 nm (Fig. 4).

Exciting at 336 nm, the changes of the fluorescence emission with the pH were monitored at 420 nm. The fluorimetric titration curve is presented in Fig. 5. The fluorescence decreases with pH on going from the singly protonated species to the neutral form. In its neutral

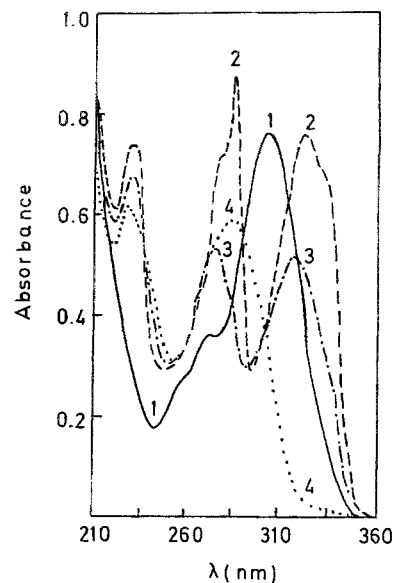


Fig. 6. Absorption spectra of the triply (1), doubly (2), and singly (3) charged protonated 2,2',2''-terpyridyl and of the neutral species (4). $[R] = 3.25 \times 10^{-5}$ M.

form, 2,2'-diquinolyl presents a small displacement to lower wavelengths, and the emission maximum is finally located at around 416 nm. The singly protonated species emission is located at 420 nm when excited at 336 nm. The titration curve obtained allowed the calculation of a value of 3.67 ± 0.03 for the pK_2 dissociation constant of 2,2'-diquinolyl.

Acid-Base Behavior of 2,2',2''-Terpyridyl

2,2',2''-Terpyridyl (Scheme I) is a molecule capable of being protonated at the three nitrogen atoms, giving rise to single, doubly, and triply charged species. The dissociation constants are related to the trication \rightleftharpoons dication equilibria (pK_1), the dication \rightleftharpoons monocation equilibria (pK_2), and the monocation \rightleftharpoons neutral molecule equilibria (pK_3).

Figure 6 shows the absorption curves for the various forms of the base. The RH_3^+ form occurs in very concentrated sulfuric acid medium and presents an absorption maximum at 306 nm. The doubly charged species exists at $pH < 1$ and presents maxima at 288 and 323 nm. The two species are in equilibrium, showing isosbestic points at 292 and 316 nm. The single-charged species presents maxima at 280 and 319 nm and shows isosbestic points at 274 and 304 nm. The neutral species shows an absorption maximum at 287 nm.

Figure 7 shows the emission profiles of 2,2',2''-terpyridyl in different acidity ranges. The BH_3^+ species

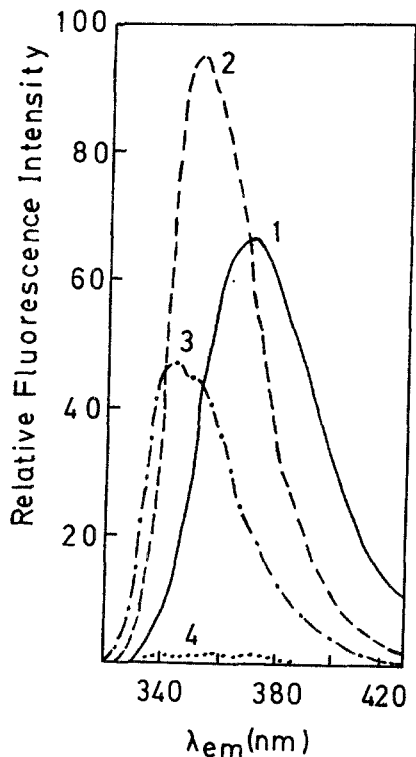


Fig. 7. Emission spectra of the triply (1), doubly (2), and singly (3) charged protonated 2,2',2''-terpyridyl and of the neutral species (4). $[R] = 2 \times 10^{-6} M$.

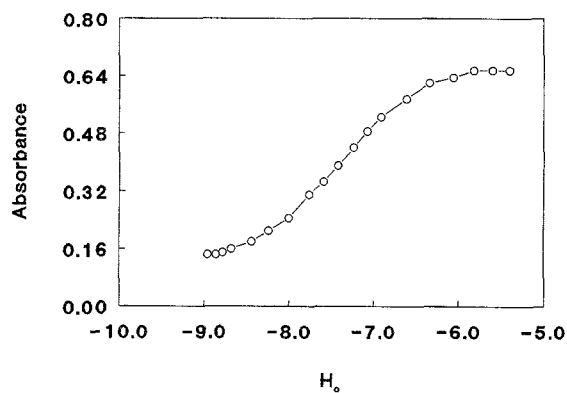


Fig. 8. Absorbance vs H_0 for $3.25 \times 10^{-5} M$ 2,2',2''-terpyridyl (6.5% ethanol) in sulfuric acid medium, at an analytical wavelength of 335 nm.

shows fluorescence emission at 370 nm, BH_2^{2+} at 350 nm, BH^+ at 345 nm, and the neutral species is practically nonfluorescent.

As 2,2',2''-terpyridyl is a compound slightly soluble in water, a $3.25 \times 10^{-5} M$ solution of this compound was prepared by pipetting 0.65 ml of a $5 \times 10^{-4} M$

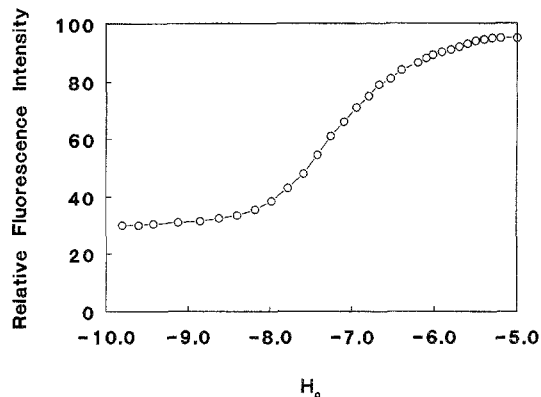


Fig. 9. Dependence on H_0 of the fluorescence intensity for $2.0 \times 10^{-6} M$ 2,2',2''-terpyridine (at the emission maximum of 350 nm). Excitation at 316 nm, the isosbestic point in the absorption spectra of the triply and doubly charged cationic species.

ethanolic terpyridyl stock solution in a 10-ml volumetric flask. A photometric titration was performed in very concentrated sulfuric medium by going to the mark with sulfuric acid solution of different concentrations in the acidity range between $H_0 = -9$ and $H_0 = -5$. In this form, a 6.5% of ethanol was always present in the titration. The changes in absorbance at 335 nm in this acidity range are presented in Fig. 8. A pK_1 value of -7.39 ± 0.03 was obtained for the first dissociation constant of the triply charged cation, in this ethanol aqueous sulfuric acid medium.

Fluorimetric titration was also performed in this acidity zone, to calculate the first dissociation constant. Exciting at 316 nm, the isosbestic point of the absorption spectra of the two species in equilibrium, fluorimetric titration was made between $H_0 = -9$ and $H_0 = -5$, by adding different concentrations of sulfuric acid. The double-charged cation shows emission at 350 nm and the fluorescence intensity of this maximum decreases when the sulfuric acid content of the medium is increased and changes to a new maximum located at 370 nm. The titration curve obtained by monitoring the fluorescence emission at 350 nm is shown in Fig. 9. A pK_1 value of -7.17 ± 0.04 was obtained, around 0.2 unit lower than the value found in the photometric titration. The differences between the values obtained by photometric and fluorimetric titrations are due to the ethanol content present in the medium in the photometric titration. The fluorimetric value is more accurate as it was obtained in pure aqueous medium.

Photometric titration was performed between pH 1 and pH 10 in 10% ethanol. The variation of absorbance with the pH was measured at three wavelengths, 320,

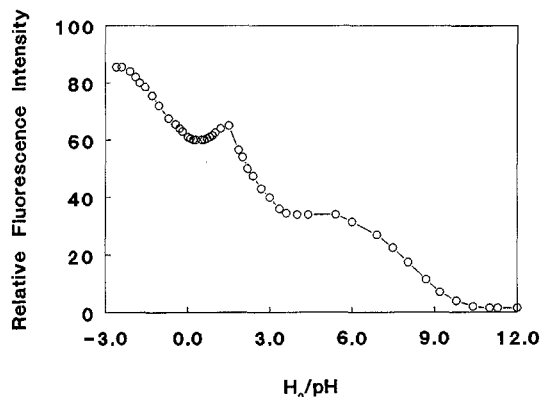


Fig. 10. Dependence on H_0/pH , between $H_0 = -3$ and pH 10, of the fluorescence intensity at 350 nm of $2.0 \times 10^{-6} M$ 2,2',2''-terpyridyl, with excitation at 274 nm.

295, and 280 nm. The titration at 285 nm gave an estimated pK_2 value of 2.81 ± 0.12 . The inflection points of the titrations at 320 and 295 nm allow calculation of the pK_3 . Values of 4.03 ± 0.26 and 4.16 ± 0.20 were obtained. These values are very close to the reported literature values.^(3,4)

Fluorimetric titration was also performed in this acidity range. Excitation was effected at the isosbestic point of the absorption spectra of the singly charged cation and the double-charged species. The isosbestic point is clearly situated at 274 nm.

Exciting at 274 nm, the fluorescence emission was monitored at 350 nm, as a function of the H_0/pH . The fluorimetric titration curve, between $H_0 = -3$ and pH 10, is presented in Fig. 10. Different variation zones can be observed which must be due to more than two species in equilibrium.

It has been suggested that the origin of the fluorescence emission of terpyridyl can be attributed to the existence of various conformational isomers in solution. Nakamoto⁽³⁾ did discuss the possible cis-trans conformers of terpyridyl, and based upon spectrophotometric

studies he assigned the conformation of the basic unprotonated terpyridyl molecule as trans-trans, the monocation as cis-trans, and the dication as cis-cis, in their ground state, although it has been noted that there was a small twist angle about the carbon-carbon bonds connecting the pyridine fragments ($<28^\circ$). Therefore, the geometries are better described as cisoid and transoid, rather than cis or trans.^(4,5,8) Fink and Ohnesorge (4) found evidence for conformational change in the excited state ($^1\pi^*$). According to Chapman *et al.*,⁽⁸⁾ conformational equilibrium of the ligand is observed in solutions of tris (2,2',2''-terpyridyl) europium(III), assuming approximate geometries of cis,cis, cis,trans, or trans,trans, as judged by their fluorescence emission and excitation spectra.

Conclusions

The acid-base behavior of 2,2'-diquinolyl and 2,2',2''-terpyridyl has been investigated by photometry and fluorimetry. The fluorescence and photometric characteristics of the different species, particularly in concentrated sulfuric acid medium, have been described.

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