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A study on the laser flash photolysis of phenothiazine and its *N*-alkyl derivatives

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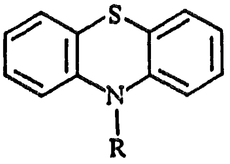
Abstract

Photophysical and photochemical properties of phenothiazine and *N*-alkylphenothiazines (alkyl ≡ methyl, ethyl, isobutyl, phenyl, benzyl) in acetonitrile were studied by means of nanosecond laser flash photolysis. Transient absorption measurements showed that the excited triplet state, radical cation, neutral radical, dimeric radical cation and dimeric dication were formed during the photolysis. The kinetics of the formation and conversion of the transient species was investigated. The deprotonation of the phenothiazine radical cation ($PTH^{\cdot +}$) to give the neutral radical $PT^{\cdot}$ was prevented by the presence of tetracyanoethylene (TCNE). The mechanism of the interaction of phenothiazines and TCNE is discussed.

Keywords: Excited triplet state; Laser flash photolysis; Phenothiazine derivatives; Radical cation; TCNE

1. Introduction

Photo-ionization processes play a major role in photobiology and photoelectrochemistry, e.g. the well-known photochemical reaction in chloroplast during photosynthesis [1] and the mechanism of the action of some conductive coating agents [2]. Recently the study of photo-ionization processes has become an important domain in photochemistry. Phenothiazine and its derivatives were studied as electron donors in electron transfer reactions owing to their low ionization potentials [3,4]. The presence of two heteroatoms in the phenothiazines leads to a total number of π electrons greater than $4n+2$. The resulting non-pairing of bonding and antibonding orbitals facilitates ionization [5]. In addition to the easy formation of stable radical cations by the removal of one electron from the highest occupied molecular orbital (HOMO) in the ground state, the phenothiazines exhibit important photoredox properties and are important in the model system for the storage of light energy [6]. In earlier photochemical studies, phenothiazine was ionized by 347.1 nm photons in methanol and aqueous sodium lauryl sulphate micellar solution [7]. The effect of alkyl chain length on the photo-ionization of *N*-alkylphenothiazines and sulphonated alkylphenothiazines in anionic alkyl sulphate and cationic alkyl trimethyl ammonium bromide micelles has also been studied [8]. In the present paper we report on the photophysical and photochemical behaviour of phenothiazine (PTH) and its *N*-alkyl derivatives (PTR; R ≡ methyl (PTMe), ethyl (PTEt), isobutyl (PTiB), phenyl (PTPh), benzyl (PTBz)) under laser flash photolysis.



(R ≡ H, CH_3, $MeCH_2$, Me_2CHCH_2, Ph, $PhCH_2$)

2. Experimental details

PTH was obtained from a commercial source and recrystallized from aqueous ethanol. PTMe, PTEt, PTiB, PTPh and PTBz were synthesized according to the literature [9]. All solutions were prepared just before measurement and deaerated by bubbling with high purity nitrogen (99.99%)

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for 20 min. All experiments were carried out at room temperature.

Laser flash photolysis experiments were performed using an excimer laser which provides a 248 nm (KrF) pulse with a duration of 20 ns. The maximum energy was 50 mJ per pulse. The source of analysing light was 500 W xenon lamp; its intensity was increased about 100 times during the detection of the transient absorption. The laser and analysing light beams passed perpendicularly through a quartz cell with an optical path length of 10 mm. The transmitted light entered a monochromator equipped with an 1P28 photomultiplier. The signals were collected using a 100 MHz transient recorder processed with a Sun 486 personal computer.

3. Results and discussion

3.1. *Laser flash photolysis of* N*-alkylphenothiazines*

The transient absorption spectra obtained immediately after the laser pulse are shown in Fig. 1. It is seen that the pattern and wavelength of the transient absorption bands did not change with the alkyl group. This means that the interaction between the *N*-alkyl group and the aromatic heterocycle is weak. The available evidence in the literature suggests that the two bands at 470 and 520 nm are due to the excited triplet state PTR^{*3} [10,11] and the radical cation $PTR^{\cdot +}$ [12,13] respectively. The assignment of the triplet

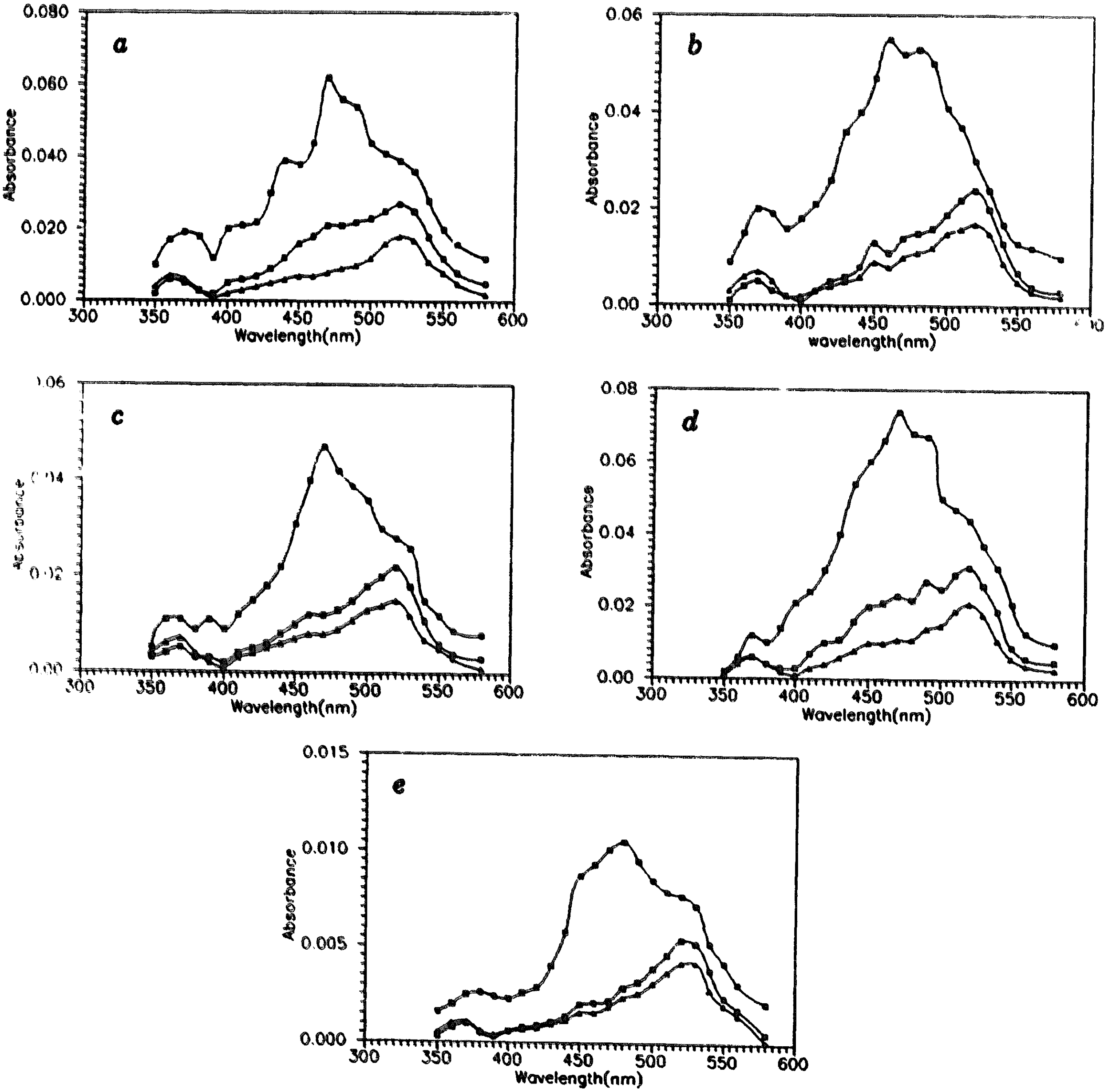

Fig. 1. Transient absorption spectra from laser flash photolysis of 10^{-4} mol l^{-1} of (a) PTMe, (b) PTEt, (c) PTiB, (d) PTBz and (e) PTPh in acetonitrile after 0.1 μs (■), 1 μs (□) and 10 μs (▲).

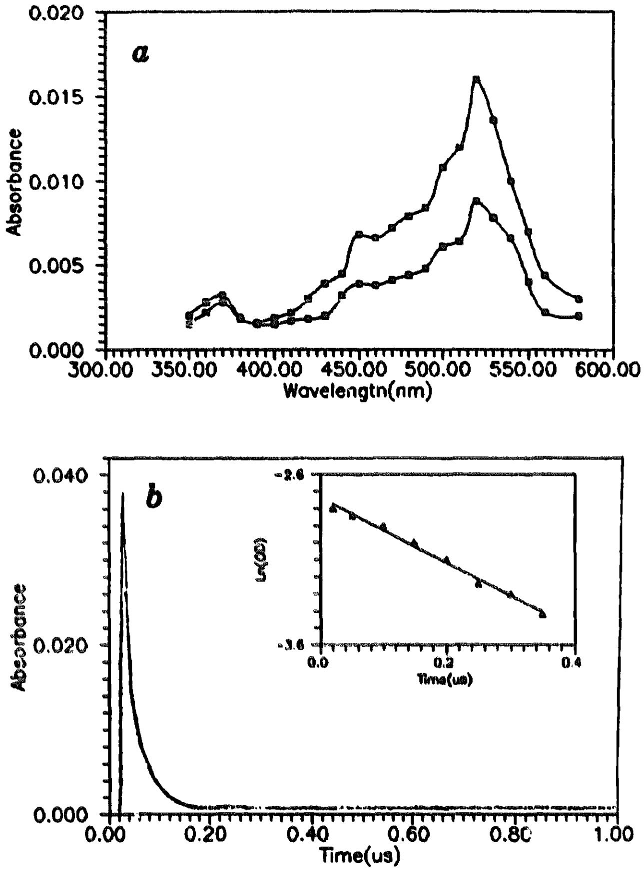

Fig. 2. (a) Transient absorption spectra from laser flash photolysis of 10^{-4} mol l^{-1} of PTMe in acetonitrile saturated with oxygen after 0.1 μs (■) and 10 μs (□). (b) Time profile of transient absorption at 470 nm (excluding concentration of 520 nm band). Inset: plot of ln(optical density) vs. time for first-order kinetics.

state is further supported by the fact that the 470 nm absorption disappeared when the solution was saturated with oxygen, as shown in Fig. 2a. Excluding the contribution of the 520 nm band, the decay curve of the excited triplet state of PTMe is shown in Fig. 2b.

The rate constants of the first-order decay of the excited triplet states were computed (Table 1). They include radiative and non-radiative transitions to the ground state.

The excited triplet states can also be quenched by their ground states. The rate constants k_q were obtained by plotting k_{obs} vs. the concentration of ground states; k_q for PTMe was 1.1×10^{10} l mol^{-1} s^{-1}.

The weak absorption observed at 450 nm could also be due to the radical cation of the phenothiazines, because the absorptions at 450 and 520 nm always appeared simultaneously under the experimental conditions.

The absorption band with a maximum at 370 nm (Fig. 1) was assigned to the dimeric dication $(PTR)_2^{2+}$ and/or the dimeric radical cation $(PTR)_2^{\bullet+}$ on account of the following reasoning. Firstly, it was observed that the decay of the spectrum of $PTR^{\bullet+}$ did not fit first-order kinetics but a mixed decay mechanism. The radical cation $PTR^{\bullet+}$ can be converted to its parent rapidly by geminate ion pair recombination in the first-order reaction (1) and can interact with $PTR^{\bullet+}$ to form $(PTR)_2^{2+}$ in the second-order reaction (2) as well as with its parent to form the dimeric radical cation $(PTR)_2^{\bullet+}$ in the pseudo-first-order reaction (3). Secondly, the 370 nm absorption band was intensified slowly. This indicated that the formation of the signal carrier was a slow process. Thirdly, the formation of $(PTR)_2^{2+}$ and $(PTR)_2^{\bullet+}$ was assisted by the solvent acetonitrile with a large dielectric constant, which could reduce the repulsion between the two associated cations.

Table 1
Rate constants (k) and half-times ($t_{1/2}$) for decay of excited triplet states of phenothiazines

Compound [a]	k (s^{-1})	$t_{1/2}$ (s)
PTH	3.1×10^7	2.2×10^{-8}
PTMe	2.9×10^6	2.4×10^{-7}
PTEt	1.6×10^6	4.4×10^{-7}
PTiB	1.8×10^6	3.9×10^{-7}
PTBz	2.5×10^6	2.8×10^{-7}
PTPh	2.4×10^6	2.9×10^{-7}

[a] Concentration 10^{-4} mol l^{-1}.

$$PTR^{\bullet+} + e^- \text{ (solvent)} \longrightarrow PTR \tag{1}$$

$$2PTR^{\bullet+} \longrightarrow (PTR)_2^{2+} \tag{2}$$

$$PTR^{\bullet+} + PTR \longrightarrow (PTR)_2^{\bullet+} \tag{3}$$

3.2. Laser flash photolysis of phenothiazine

Fig. 3 shows the transient absorption spectra of phenothiazine in acetonitrile saturated with nitrogen. Four absorption bands were observed. The absorptions at 520 and 450 nm resulted from the corresponding radical cation $PTH^{\bullet+}$ and the absorption at 470 nm from the excited triplet state. In addition to the similar transient absorption spectra of PTR, a new absorption band at 390 nm was observed (Fig. 3).

In comparison with the spectra of $PTR^{\bullet+}$ it is note worthy that the decay of the 520 nm absorption of $PTH^{\bullet+}$ was faster

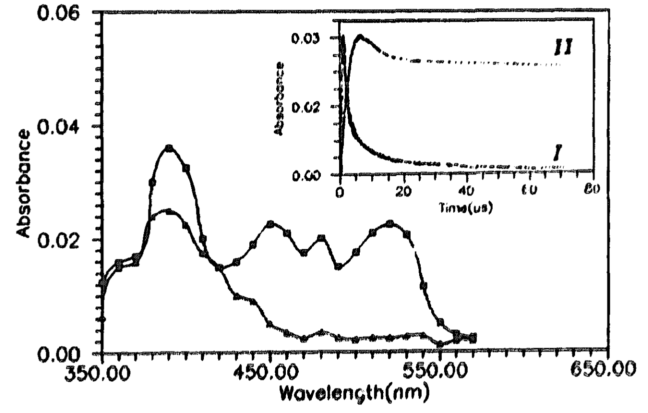

Fig. 3. Transient absorption spectra from laser flash photolysis of 10^{-4} mol l^{-1} of PTH in acetonitrile after 0.1 μs (■) and 10 μs (▲). Inset: time profiles of transient absorption at 520 nm (I) and 390 nm (II).

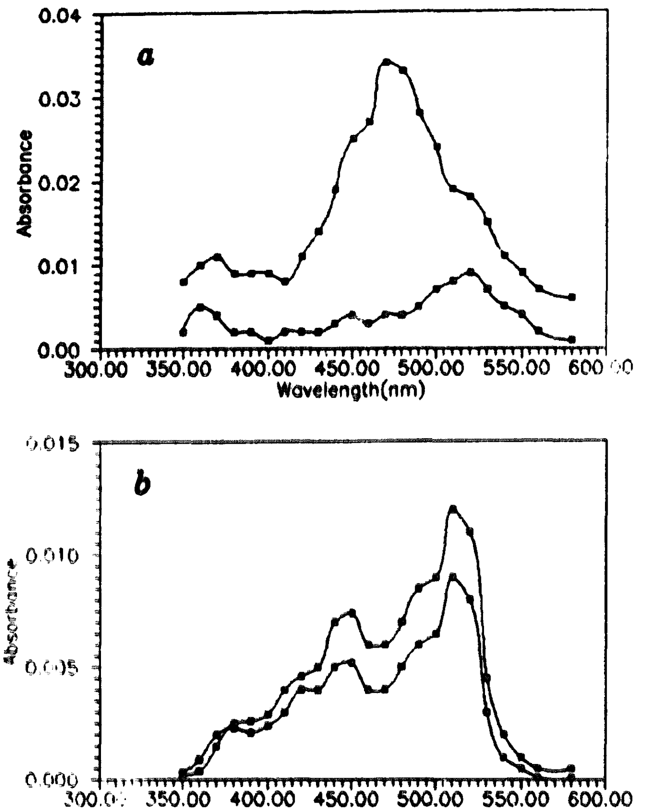

Fig. 4. Transient absorption spectra from laser flash photolysis of 10^{-4} mol l^{-1} of (a) PTMe and (b) PTH in acetonitrile containing 10^{-4} mol l^{-1} of TCNE after 0.1 μs (■) and 10 μs (□).

than that of PTR$^{\bullet+}$. This indicated that PTH$^{\bullet+}$ was less stable. On the other hand, the absorption of the excited triplet state of PTH was not so obvious as that of PTR under the same conditions. By resolution of the composite spectra, the decay kinetic parameters of PTH^{*3} were obtained (Table 1). From the data listed in Table 1 it is apparent that the rate of decay of PTH^{*3} was faster than that of PTR^{*3}.

It has been reported by Iwaoka et al. [13] that the absorption at 390 nm arises from a charge transfer complex of PTH and O_2 [PTH···O_2] in the flash photolysis of PTH in aerated ethanol. In our experiment, however, no oxygen was present in the system under nitrogen protection, so the [PTH···O_2] complex can be ruled out. Therefore the band at 390 nm could be due to the neutral radical PT$^{\bullet}$ formed by the deprotonation of PTH$^{\bullet+}$ according to Eq. (4), the same as that reported by Alkaitis et al. [7] from results in alcoholic solution.

$$PTH^{\bullet+} \xrightarrow{-H^+} PT^{\bullet} \qquad (4)$$

The PT$^{\bullet}$ radical is known to be very stable and can exist for hours or days in solution [12–14]. It was observed that the absorption at 390 nm was very long-lived in our experiments. When the solvent acetonitrile containing water was used, the deprotonation process became faster, because H_2O acted as a Brönsted base. The decay of the PT$^{\bullet}$ radical followed mixed decay kinetics, suggesting that the radical decayed by more than one pathway.

3.3. Interaction between phenothiazines and tetracyanoethylene (TCNE)

TCNE is a compound of high electron affinity which is strongly deficient in electrons. In the study of photoinduced electron transfer, TCNE is often used as an electron acceptor. TCNE can form charge transfer complexes (CTCs) [15] or electron donor–acceptor complexes (EDAs) [16] with many electron donors such as arenes [17] and aromatic hydrocarbons [18]. It has been reported that TCNE can form a CTC with 2-polyvinylphenothiazine in acetonitrile [19].

For 248 nm laser flash photolysis of PTMe and PTH (10^{-4} mol l^{-1}) in acetonitrile containing 10^{-4} mol l^{-1} of TCNE saturated with N_2 the transient absorption spectra are shown in Fig. 4.

Compared with the transient absorption spectra of PTMe (Fig. 1a), little difference was observed in Fig. 4a. However, there is a large difference between Figs. 4b and 3 for PTH. The marked change is that no absorption band at 390 nm and a strong absorption band at 520 nm were observed (Fig. 4b). This implies that the neutral radical PT$^{\bullet}$ was not formed. Interestingly, it was observed that the absorption at 390 nm appeared and the 520 nm absorption disappeared upon adding Et_3N to the PTH–TCNE system (Fig. 5).

Photo-ionization of PTH or PTR via a monophotonic process using an intense excimer laser (248 nm) produced the radical cation PTH$^{\bullet+}$ or PTR$^{\bullet+}$, excited triplet state and solvated electron. The solvated electron can be captured by TCNE to form the corresponding radical anion TCNE$^{\bullet-}$ [18]. In this case the radical cation PTH$^{\bullet+}$ or PTR$^{\bullet+}$ could form a solvent-separated radical ion pair (SSRIP) with TCNE$^{\bullet-}$ (PTR$^{\bullet+}$/TCNE$^{\bullet-}$). It is well known that the SSRIP is more common than the contact radical ion pair (CRIP) in polar solvents such as acetonitrile [19,20]. Back electron transfer between radical ions in the SSRIP is much slower than in the CRIP [21,22]. Thus the absorption band at 520

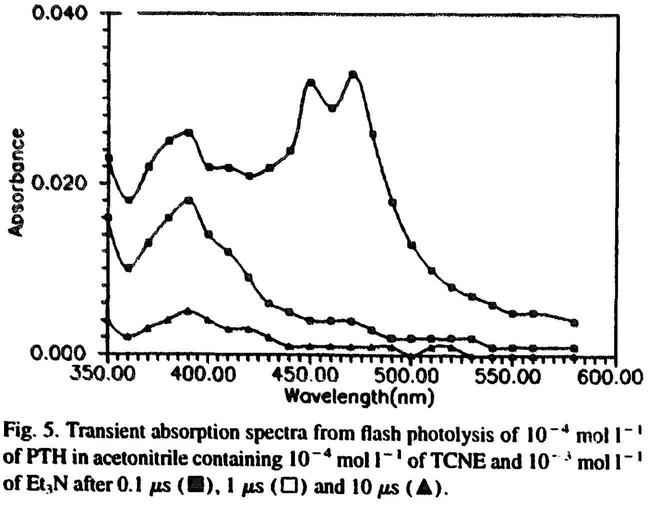

Fig. 5. Transient absorption spectra from flash photolysis of 10^{-4} mol l^{-1} of PTH in acetonitrile containing 10^{-4} mol l^{-1} of TCNE and 10^{-3} mol l^{-1} of Et_3N after 0.1 μs (■), 1 μs (□) and 10 μs (▲).

nm of the radical cation $\mathrm{PTH}^{\bullet+}$ or $\mathrm{PTR}^{\bullet+}$ decayed slowly. Furthermore, the interaction between $\mathrm{PTH}^{\bullet+}$ and $\mathrm{TCNE}^{\bullet-}$ in the SSRIP prevented $\mathrm{PTH}^{\bullet+}$ from deprotonation, resulting in no absorption band at 390 nm. The fact that $\mathrm{Et_3N}$ could abstract a proton from $\mathrm{PTH}^{\bullet+}$ to give a corresponding neutral radical $\mathrm{PT}^{\bullet}$ is the reason why the absorption band at 390 nm appeared again in the presence of $\mathrm{Et_3N}$ (Fig. 5).

The SSRIP also can be produced through a CTC pathway. The excited PTH* or PTR* formed a charge transfer complex with TCNE, followed by electron transfer to yield a geminate radical ion pair or a CRIP [16,23]. The CRIP went to an SSRIP immediately upon fast solvation of the acetonitrile [24,25]. On the other hand, a polar solvent would be favourable for the dissociation of the SSRIP to free-radical ions [26]. Therefore the absorption at 520 nm is also due to the free-radical cation ($\mathrm{PTH}^{\bullet+}$ or $\mathrm{PTR}^{\bullet+}$). Based on experimental observations, the contribution of free-radical cations to the absorption at 520 nm is not important.

4. Conclusions

Laser flash photolysis (248 nm) of phenothiazine and its *N*-alkyl derivatives in acetonitrile leads to the formation of radical cations, excited triplet states, dimeric species and neutral radicals (for PTH). The decay of the excited triplet state follows first-order kinetics. The interaction between $\mathrm{PTH}^{\bullet+}$ and $\mathrm{TCNE}^{\bullet-}$ in the SSRIP can prevent $\mathrm{PTH}^{\bullet+}$ from deprotonation. On the other hand, the deprotonation process occurred readily in the presence of $\mathrm{Et_3N}$. The absorption band at 520 nm is due to the SSRIP and free-radical cation $\mathrm{PTR}^{\bullet+}$ or $\mathrm{PTH}^{\bullet+}$.

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