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COMPLEXES OF 9-PROPYLFLUORENYL ION PAIRS WITH TERTIARY POLYAMINES IN APOLAR SOLVENTS

G. HELARY, L. LEFEVRE-JENOT, M. FONTANILLE,

Laboratoire de Recherches sur les Macromolécules de l'Université Paris-Nord (E.R.A. 607), 93430 Villetaneuse (France)

and J. SMID

Chemistry Department, College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210 (U.S.A.)

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Summary

The complexation of tetramethylethylenediamine (TMEDA), hexamethyltriethylenetetramine (HMTT) and tetramethyltetraazacyclotetradecane (TMTCT) with ion pairs of 9-(n-propyl)fluorenyllithium (PFl^-, Li^+) and n-butyl-9-(n-propyl)fluorenylmagnesium (BuPFlMg) in cyclohexane was studied by optical spectroscopy. The results can be explained in terms of externally complexed tight ion pairs and ligand-separated ion pairs, the latter complexes being much less soluble. With HMTT and PFl^-, Li^+, the only complexes formed are $(PFl^-, Li^+)_2$ HMTT (λ_m 357 nm) and PFl^-, HMTT, Li^+ (λ_m 383 nm). The reaction of PFl^-, Li^+, TMEDA with TMTCT to form the loose ion pair complex PFl^-, TMTCT, Li^+ has a rate constant in toluene of 250 M^{-1} sec^{-1}. With the magnesium compound, the amines form only a loose ion pair complex, e.g., $BuMg^+$, TMEDA, PFl^- (λ_m 382 nm).

Introduction

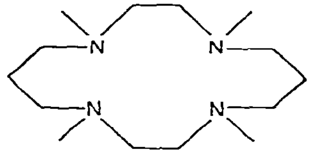
Oxygen- and nitrogen-containing ligands (glymes, polyamines, crown ethers, cryptands) are effective chelating agents for alkali and alkaline earth cations, and their role as anion activators in reactions such as anionic polymerization in hydrocarbon or ethereal solvents, metallation reactions involving organometallic reactions, etc., is well established [1,2]. This activation usually results from a breakdown of unreactive ion pair aggregates or from a stretching of the interionic ion pair bond as the ligand complexes with the cation.

We have recently been concerned with the organolithium-initiated polymerization of monomers in cyclohexane in the presence of tertiary polyamines such as tetramethyltetraazacyclotetradecane. This cyclic polyamine is a powerful lithium cation binder which strongly accelerates the propagation of polystyryllithium [3]. To obtain more information on the role of such tertiary amines in modifying ion pair structures we studied their complex formation with 9-(n-propyl)fluorenyllithium in cyclohexane as solvent. Previous studies have demonstrated that cation binding ligands added to fluorenyl or other carbanion salts lead to different kinds of ligand-complexed ion pairs (e.g., externally solvated tight ion pairs or ligand-separated ion pairs) which can often be detected spectrophotometrically [1,4]. The use of 9-(n-propyl)fluorenyllithium in our studies was prompted by an earlier observation that in toluene the optical spectrum of this salt shows distinctly different absorption bands for the dimeric aggregate $(PFl^-, Li^+)_2$ and the monomeric species PFl^-, Li^+ [5]. Also, externally solvated and separated ion pairs can be detected spectrophotometrically.

Most studies on ion pair solvation complexes have been concerned with oxygen-containing ligands (glymes, crown ethers). However, considerable information is available on complexes of organolithium compounds with tertiary polyamines [2,6], and especially studies in the solid state [7,8] have provided interesting insights into the structures of these ion pair complexes. The tertiary polyamines have the distinct advantage of being less reactive with benzyl type carbanions (polystyryllithium) than the linear or cyclic polyethers [3]. The three polyamines included in our present work are tetramethylethylenediamine (TMEDA), hexamethyltriethylenetetramine (HMTT) and tetramethyltetraazacyclotetradecane (TMTCT). Their structures are depicted below. In addition to their interaction with the lithium salt of propylfluorenyl, we also present some preliminary results on complexes with a propylfluorenylmagnesium compound, since one of us has been particularly interested in the anionic polymerization of vinyl monomers with Mg as counterion [9].

TMEDA

HMTT



TMTCT

Experimental

Materials

9-(n-propyl)fluorene was synthesized as described by Shoen et al. [10]. The compound was purified by preparative VPC followed by liquid chromatography using as eluent a hexane/ether mixture (90/10). 9-(n-propyl)fluorenyllithium was prepared under vacuum by adding BuLi to the hydrocarbon in cyclohexane at 50° C. The carbanion salt can be obtained as yellow needles by recrystallization from cyclohexane. Dibutylmagnesium was prepared under vacuum in cyclohexane from dibutylmercury and a magnesium mirror which was obtained under high vacuum by subliming high purity magnesium turnings.

The dibutylmagnesium was analyzed by titration with carbazole as described elsewhere [11]. n-Butyl-9-(n-propyl)fluorenylmagnesium was obtained by reacting dibutylmagnesium and propylfluorene in the presence of complexing amines (see Discussion).

Benzene, toluene and cyclohexane were distilled from sodium or potassium mirrors, then treated with polystyryllithium to remove impurities capable of destroying carbanionic species. TMEDA was obtained by vacuum distillation from a BuLi/TMEDA solution, while HMTT (Aldrich) and TMTCT (Strem) were purified by sublimation under high vacuum.

Spectrophotometric measurements

Experiments were carried out in all glass-enclosed vessels to which optical cells were attached. Spectra were obtained on a Varian-Cary 118 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WP 60 spectrometer using the FT system.

Results and discussion

I. Ligand complexes with 9-(n-propyl)fluorenyllithium (PFl^-, Li^+)

Dimeric aggregates. In cyclohexane, PFl^-, Li^+ gives a concentration-independent (5×10^{-4} *M*—4×10^{-6} *M*) absorption band centered at 368 nm. Hence, contrary to findings in toluene [5], no dissociation of the $(PFl^-, Li^+)_2$ dimer into the monomeric species PFl^-, Li^+ (λ_m 353 nm in toluene, probably about 345 nm in cyclohexane [5]) was observed. This result is consistent with that of Exner et al. [12], who reported a concentration-independent absorption maximum, λ_m 368 nm, for 9-(2-hexyl)fluorenyllithium in cyclohexane. The poorer solvating properties of this solvent as compared to toluene increases the ion pair aggregation constant enough to prevent any appreciable dissociation of the dimer into PFl^-, Li^+ above 4×10^{-6} *M*. The structure of the dimer has been described as a species with the two lithium ions sandwiched in between the two nearly planar fluorenyl rings [5,12].

Complexes with TMEDA. At ratios r = TMEDA/PFl^-, Li^+ of unity or two, the 368 nm absorption band is replaced by a similar band at 355 nm (359 nm in toluene as solvent). This hypsochromic shift resembles that observed for the dimeric aggregate on addition of small amounts of diethyl ether, tetrahydropyran or tetrahydrofuran [5,12]. A TMEDA-complexed tight ion pair of 1 : 1 stoichiometry is formed. Whether the interaction of TMEDA with the dimer breaks down the aggregate could not be ascertained, since the monomeric and dimeric form probably have the same absorption band. (For example, THP addition to PFl^-, Li^+ in toluene produces the 359 nm etherate independent of whether PFl^-, Li^+ dimer (368 nm) or the monomeric form (353 nm) is the starting species [5]). At $r = 0.5$ (one N atom per Li ion) the spectrum shows a considerable shoulder at 368 nm, suggesting a mixture of the non-solvated dimer and the 1 : 1 PFl^-, Li^+ ... TMEDA complex.

Solid PFl^-, Li^+, obtained on evaporation of cyclohexane, can be solubilized in pure TMEDA, but on standing precipitation occurs. When the precipitate is filtered, washed with cyclohexane, and dissolved in toluene, a single absorption band at 359 nm is found, indicative of the presence of the PFl^-, Li^+/TMEDA complex. However, the ^{1}H NMR spectrum shows a 1 : 2 stoichiometry of this complex.

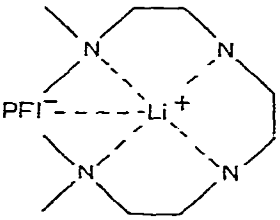
It is known that TMEDA, although an excellent chelating agent for organolithium reagents [2], is a poor solvent separating agent [4,13]. The eight bulky methyl groups severaly hinder the formation of a cage of two TMEDA molecules in which the four N atoms are in the correct juxtaposition for a close interaction with the Li^+ cation. Hence, even in pure TMEDA fluorenyllithium is basically a 1 : 1 externally complexed tight ion pair with a small fraction (~0.05) of loose ion pairs visible in the optical spectrum. It is frequently found that ligand-separated ion pairs have a much lower solubility than the corresponding externally solvated tight ion pairs [14]. The observed precipitation of PFl^-, Li^+ in pure TMEDA most likely involves the 1 : 2 loose ion pair complex. When dissolved in toluene, the complex, because of its low stability, releases one molecule of TMEDA to produce the 1 : 1 complex absorbing at 359 nm.

$$PFl^-, TMEDA, Li^+, TMEDA \rightarrow PFl^-, Li^+, TMEDA + TMEDA \qquad (1)$$

Stable complexes with 2 TMEDA molecules per organolithium have been reported in the solid state for carbanions which favor loose ion pair formation, e.g., $(C_6H_5)_2CH^-$, Li^+ and $(C_6H_5)_3C^-$, Li^+ (see ref. 2, page 4). For ethylene diamine (EDA) the stability of the loose ion pair complex in solution is much higher. For example, small quantities of this amine added to fluorenyllithium in diethyl ether can convert the tight ion pair into an EDA-separated ion pair [13]. However, in this system slow precipitation occurs at carbanion concentrations above 10^{-3} *M*.

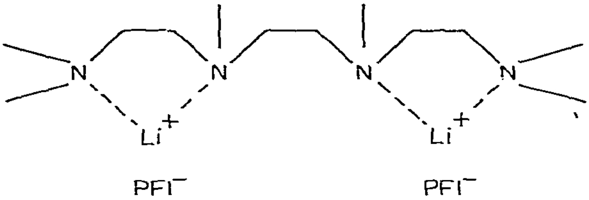
Complexes with HMTT. Spectra of mixtures of 9-PFl^-, Li^+ with the acyclic tetramine HMTT in cyclohexane provide the following information. At a ratio r = HMTT/PFl^-, Li^+ = 0.2, two absorption maxima are found in the spectrum, viz, that of the unsolvated $(PFl^-, Li^+)_2$ dimer (λ 368 nm) and that of the HMTT-complexed tight ion pair PFl^-, Li^+ (357 nm). By increasing r to 0.5 the 368 nm band disappears, leaving only the band at 357 nm. For r = 0.8 again two maxima are visible, at 357 nm and at 383 nm. At r = 1, the 357 nm has nearly disappeared, and at r = 1.5 (excess HMTT), only the 383 nm absorption band remains. For $r > 1$ a precipitate is gradually formed. When this precipitate, after washing with cyclohexane, is dissolved in toluene-d_8, the absorption maximum is at 386 nm and the ^{1}H NMR spectrum integrates to 1 HMTT molecule per PFl^-, Li^+ ion pair.

The above observations suggest that at $r > 1$ the stable species is a 1 : 1 loose ion pair complex (I) (λ_m 383 in cyclohexane, slightly higher in toluene), with



(I)

all four N atoms probably coordinating simultaneously with Li^+ (2). The fact that this is the only complex existing at $r > 1$ (or slightly higher than unity) means that the 357 nm band observed at $r = 0.5$ or $r = 0.2$ cannot be that of a 1 : 1 tight ion pair complex. If so, at these r values we would also have seen an appreciable amount of complex I at 383 nm. Since only one species is observed at $r = 0.5$ (absorbing at 357 nm), it must be the 2 : 1 complex II shown below.



(II)

This complex apparently is considerably more stable than a 1 : 1 complex, and at $r = 0.2$, with PFl^-, Li^+ in considerable excess, only the non-solvated dimer (368 nm) and complex II are found. The latter species derives its stability from the ion pair—ion pair interaction. The stable dimer $(PFl^-, Li^+)_2$ in cyclohexane interacts with HMTT and most likely rearranges to maximize $Li^+ \ldots N$ interactions, but the two ion pairs remain aggregated. This dimer-solvate then interacts with more HMTT to form the 1 : 1 loose ion pair complex.

$$(PFl^-, Li^+)_2\ HMTT + HMTT \rightleftharpoons 2\ PFl^-, HMTT, Li^+ \tag{2}$$

This reaction is reversible, as shown in Figure 1. For example, at $r = 0.6$ the 383 nm band is clearly visible, but this band disappears on addition of PFl^-, Li^+, with complex I changing back into complex II.

The separated ion pair complex I, like the 2 : 1 complex with TMEDA, has a considerably lower solubility than the externally solvated complex II. This can be shown as follows: At $r = 0.8$, the mixture of complexes I and II in cyclohexane at 10^{-5} M total carbanion concentration is homogeneous. On concentrating the solution the ratio I/II as calculated from the optical spectra is not changed. However, above about 4×10^{-5} M precipitation occurs. Figure 2 shows that only complex I (λ_m 383 nm) precipitates, while the concentration of II (λ_m 357 nm) continues to increase.

Complexes with TMTCT. For $r < 1$, two maxima are found in the spectrum, the 368 nm dimer and the 387 nm separated ion pair. Hence, dimer interaction with TMTCT leads directly to the TMTCT-separated ion pair complex, the only stable complex. For $r > 1$ only the 387 nm peak is visible. Precipitation in cyclohexane is quite rapid, and ^1H NMR analysis of the toluene-d_8-solubilized precipitate shows a 1 : 1 stoichiometry.

To assess the complexing power of TMTCT relative to that of TMEDA, we studied the reaction:

$$PFl^-, Li^+, TMEDA + TMTCT \rightarrow PFl^-, TMTCT, Li^+ + TMEDA \tag{3}$$

The change in absorption maximum, 357 → 387 nm makes it possible to measure the rate of this reaction spectrophotometrically. Toluene was used as solvent since precipitation occurs in cyclohexane. Denoting the initial $[PFl^-, Li^+, TMEDA]$ by A_0 and $[PFl^-, TMTCT, Li^+]$ at time t by C, the plot $1/(A_0 - C)$

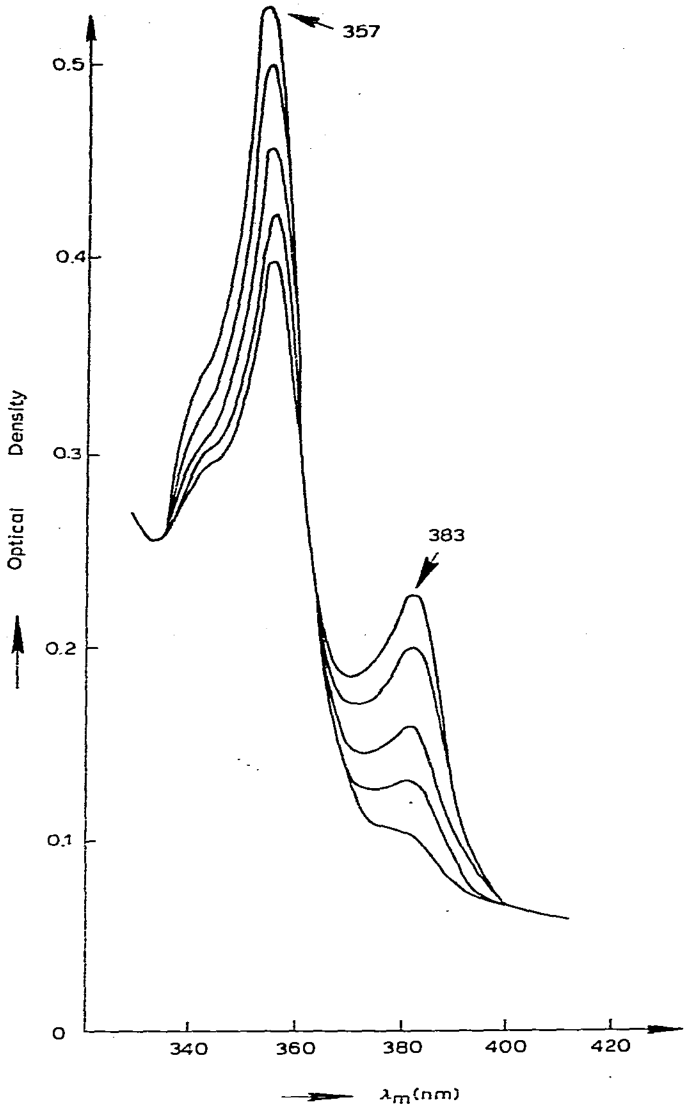


Fig. 1. Optical spectra showing the equilibrium reaction $(PFl^-, Li^+)_2$ HMTT (λ_m 357 nm) + HMTT $\rightleftharpoons$ 2 PFl^-, HMTT, Li^+ (383 nm) in cyclohexane.

versus t is linear (Figure 3). The second order rate constant was found to be 250 M^{-1} sec^{-1}, a relatively low rate constant for such an exchange reaction. Most likely, the rate is determined by the energy needed to remove the externally complexed TMEDA molecule from the tight PFl^-, Li^+ ion pair before the TMTCT ligand can attach itself to form the loose ion pair complex.

II. Complexes with magnesium salts

Preparation of compounds. An attempt to obtain di-9-(n-propyl)fluorenylmagnesium from dibutylmagnesium and propylfluorene in cyclohexane was unsuccessful. Even in the presence of 10 molar TMEDA no reaction occurred

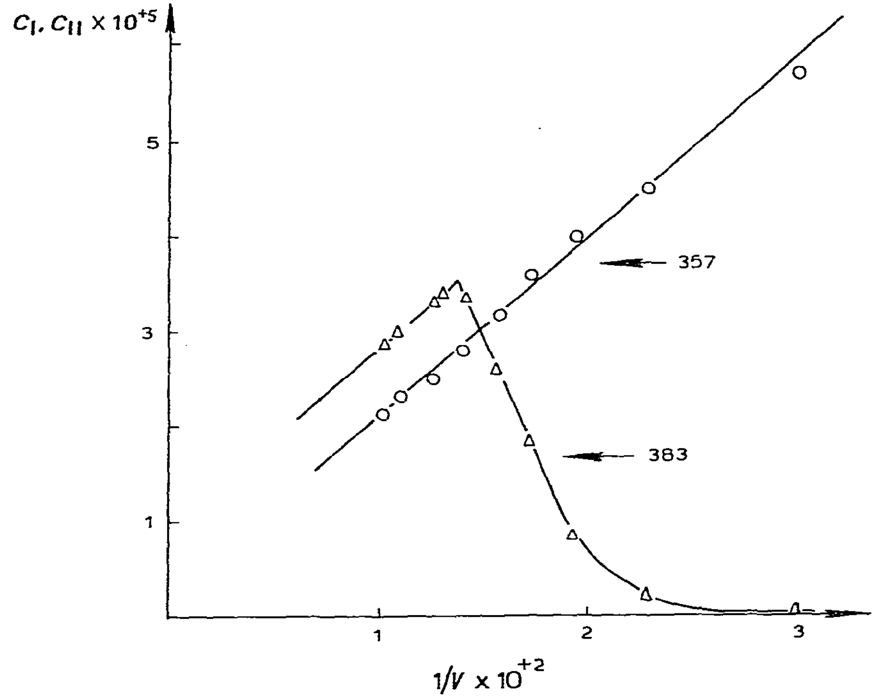


Fig. 2. The effect of total carbanion concentration on the optical densities of complex I (λ_m 383 nm) and complex II (λ_m = 357 nm). V = volume of the cyclohexane solution, containing 4.7 × 10^{-6} mol of carbanionic species (soluble or not).

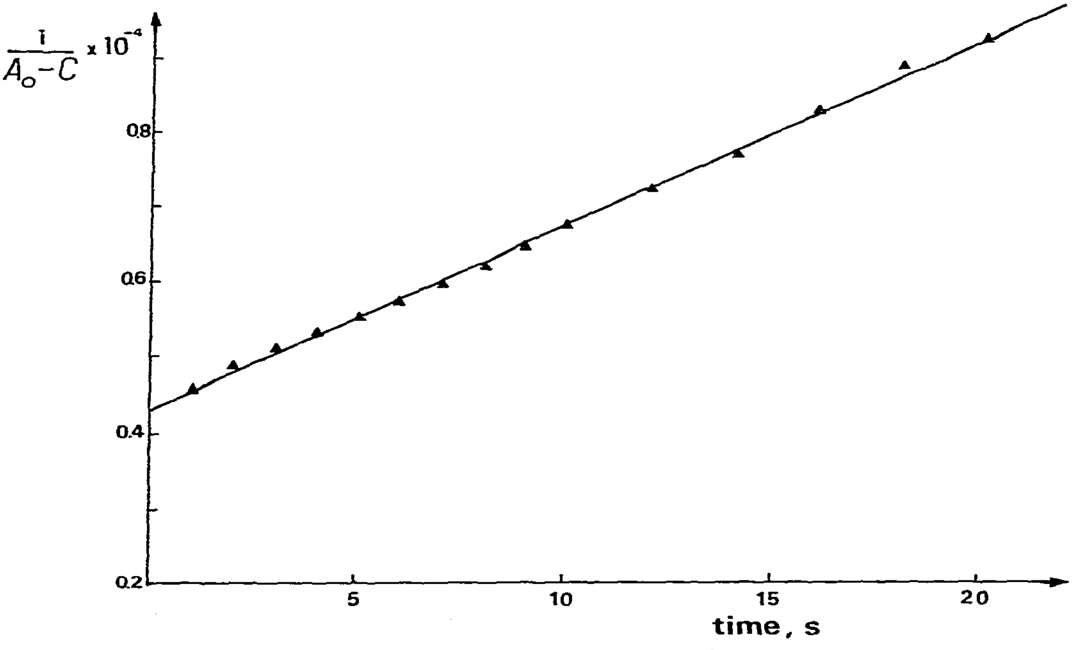


Fig. 3. Plot of $1/(A_0 - C)$ versus time (sec) for the reaction PFl$^-$, Li$^+$, TMEDA + TMTCT → PFl$^-$, TMTCT, Li$^+$ in cyclohexane at 25°C. A_0 denotes the initial concentration of PFl$^-$, Li$^+$, TMEDA and C is the concentration of PFl$^-$, TMTCT, Li$^+$ at time t.

during several weeks. However, in pure TMEDA a red colored compound (λ_m 382 nm) is rapidly formed. In the presence of HMTT (HMTT/dibutylmagnesium between 0.5 and 2.0) the red colored compound in cyclohexane is only formed slowly. No precipitation occurs below 10^{-2} *M* of the organometallic compound. With TMTCT the red colored species, λ_m 382 nm, is formed rapidly, but precipitates after about one hour. The ^{1}H NMR of this precipitate, dissolved in toluene-d_8 shows that the compound is a 1 : 1 complex of TMTCT and of n-butyl-9-(n-propyl)fluorenylmagnesium. That only one butyl group is replaced by fluorenyl is corroborated by a study of the hydrolysis products, i.e., determination of propylfluorene by UV spectroscopy and of magnesium by EDTA.

Complexes of n-butyl-9-(n-propyl)fluorenylmagnesium (III) with tertiary polyamines. Interaction of III with TMEDA produces a species whose optical spectrum resembles that of a loose ion pair, λ_m = 382 nm. Since the complex did not precipitate out, we could not determine its stoichiometry. The presence of the n-butyl group prevents formation of an externally complexed TMEDA ion pair such as in propylfluorenyllithium. Hence, complexation of one TMEDA molecule with the divalent cation probably requires that the interionic Mg^+ ... fluorenyl ion pair distance be sufficiently enlarged to accommodate a TMEDA molecule, i.e., $C_4H_9Mg^+$, TMEDA, PFl^-. With HMTT and TMTCT the complexes slowly precipitate from cyclohexane but solubilize in benzene or toluene. Absorption maxima in cyclohexane and toluene are at 382 nm and 386 nm, respectively, indicative of loose ion pair complexes. At all ratios of amine/Mg, the NMR analysis of the precipitate gives one amine molecule per Mg ion. Contrary to what is found for PFl^-, Li^+, the amine HMTT at $r = 0.5$ does not give a spectrum with I at λ_m 355 nm but only at 382 nm, suggesting that no externally solvated tight ion pair exists. Again, because of the presence of the alkyl group, coordination of HMTT or TMTCT requires separation of PFl^- and Mg^+ before the polyamine can complex with the cation.

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