(132), 291 (6.8), 304 (5.9), 330 (1.9)sh, 345 (3.9), 362 (7.5), 382 (11.6), 398 (6.7) sh, 404 (10.5).

1,10b-Dihydro-10b-hydroperoxyspiro[aceanthrylene-2-(6*H*),9′(10′*H*)-anthracene]-6,10′-dione (10). A solution of **3** (200 mg, 0.5 mmol) in methylene chloride (200 mL) was prepared at 0 °C under nitrogen and was kept under nitrogen at 25 °C for 3 h. The yellow solution gradually became red and subsequently yellow again. Oxygen was then bubbled through the solution for 2 h to give a colorless crystalline precipitate when part of the solvent was evaporated in vacuo. The crystals were filtered off and washed with methylene chloride: yield 120 mg (56%); mp >200 °C dec; IR 3160 cm^{-1} (OOH), 1675 and 1645 (CO); ^1H NMR δ 8.40–8.29 (m, 3 H), 8.13 ("d", 1 H, J = 8 Hz), 7.65 (d, 1 H, J = 8 Hz), 7.60–7.35 (m, 8 H), 7.20 ("d", 1 H, J = 8 Hz), 6.58 ("d", 1 H, J = 7 Hz), 3.37 and 3.14 (AB system, J = 15 Hz), the hydroperoxy H was not discernible; UV (CH_2Cl_2) λ_{max} 275 nm ($\epsilon \times 10^{-3}$, 25.3), 357 (0.5), 374 (0.5) sh. Anal. Calcd for $C_{29}H_{18}O_4$: C, 80.92; H, 4.21. Found: C, 80.29; H, 4.12.

8-Acetoxy-17*H*-3,4:6,7-dibenzocyclohept[1,2-*a*]aceanthrylen-17-one (11). A solution of **4** (50 mg, 0.13 mmol) in methylene chloride (75 mL) under argon was irradiated for 4–5 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvents after 50 min gave a red residue from which 45 mg (82%) of dark-red crystals were isolated by chromatography: mp 278–286 °C dec (recrystallized from methylene chloride/ethanol); IR 1765 cm^{-1} (OAc), 1665 (CO); ^1H NMR δ 8.16–8.05 (m, 4 H), 7.97 (d, 1 H, J = 8 Hz), 7.96–7.78 (m, 3 H), 7.71–7.36 (m, 7 H), 2.66 (s, OAc); UV (cyclohexane) λ_{max} 241 nm ($\epsilon \times 10^{-3}$, 58.4), 256 (53.7), 266 (53.6), 300 (18.4)sh, 342 (5.8), 361 (7.9), 378 (10.2), 405 (7.0), 428 (9.6), 453 (8.1), 499 (2.7); high-resolution mass spectrum, m/z calcd for $C_{31}H_{18}O_3$ 438.1257, found 438.1317 (M^+).

6(2*H*)-Aceanthrylenone (12). A solution of **1** (0.44 g, 2 mmol) in benzene (250 mL) was irradiated while acetylene was passed through the solution. The irradiation was terminated after 15 min when the color of the solution had changed from red-brown to yellow. The solvent was removed by vacuum evaporation to give a crude product, which showed three spots on TLC (SiO_2/CH_2Cl_2). The main product **12** (R_f 0.33) was isolated by chromatography and subsequent crystallization from methylene chloride/ethanol: yield 147 mg (34%) of colorless crystals; mp 180 °C dec (red melt; repeated chromatography and recrystallization from methylene chloride/*n*-hexane did not change the melting point); ^1H NMR δ 8.48 ("d", 1 H, J = 8 Hz), 8.15 (d, 1 H, J = 8 Hz), 8.02 (d, H, J = 8 Hz), 7.75 (d, 1 H, j = 7 Hz), 7.67 ("t", 1 H, J = 7 Hz), 7.56 ("t", 1 H, J = 8 Hz), 7.50 (t, 1 H, J = 8 Hz), 7.31 (t, 1 H, J = 2 Hz), 3.81 (d, 2 H, J = 2 Hz, irradiation at 3.81 leads to a singlet at 7.31); IR 1650 cm^{-1} (CO); UV (CH_2Cl_2) λ_{max} 254 nm ($\epsilon \times 10^{-3}$, 7.4), 285 (15.7), 349 (6.5), 364 (7.4); high-resolution mass spectrum, m/z calcd for $C_{16}H_{10}O$ 218.0732, found 218.0726 (M^+).

6-Aceanthrylenol Acetate (13). A solution of **12** (50 mg, 0.23 mmol), acetyl chloride (0.18 g, 2.3 mmol), and pyridine (0.1 g, 1.26 mmol) in methylene chloride (10 mL) was stirred under argon at room temperature for 3 days. The dark-red solution was diluted with methylene chloride, then washed with water, and dried over $MgSO_4$. Vacuum evaporation of solvents gave a red residue from which **13** was isolated by chromatography (R_f 0.60): yield 17 mg (28%) of red crystals from methylene chloride/ethanol; mp >130 °C dec; IR 1770 cm^{-1} (OAc); ^1H NMR δ 8.23 ("d", 1 H, J = 9 Hz), 8.01 ("d", 1 H, J = 8 Hz), 7.87 (d, 1 H, J = 9 Hz), 7.75 (d, 1 H, J = 7 Hz), 7.62–7.42 (m, 4 H), 7.08 (d, 1 H, J = 5 Hz, a singlet is discernible at 7.52 (1 H) on irradiation at 7.08), 2.62 (s, OAc); UV (cyclohexane) λ_{max} 240 nm ($\epsilon \times 10^{-3}$, 37.9), 256 (52.3), 348 (3.8), 365 (6.8), 383 (4.4), 402 (5.2), 418 (3.7), 425 (3.9); high-resolution mass spectrum, m/z calcd for $C_{18}H_{12}O_2$ 260.0837, found 260.0891 (M^+).

Phenanthro[9,10-*a*]aceanthrylen-8-ol Acetate (16). Spiro[aceanthrylene-2(6*H*),9′-[9*H*]fluorene]-6-one (**15**) (50 mg, 0.14 mmol) in methylene chloride (75 mL) under argon was irradiated for 4 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvent after 30 min gave a mixture of unchanged starting material and the acetylated photoproduct **16**, which was isolated by chromatography. Yield 33 mg (59%) of brown crystals from methylene chloride/ethanol: mp dec >237 °C; IR 1760 cm^{-1} (OAc); ^1H NMR δ 8.81–8.67 (m, 5 H), 8.50 (d, 1 H, J = 7 Hz), 8.07 ("d", 1 H, J = 9 Hz), 7.91 ("d", 1 H, J = 9 Hz), 7.72–7.46 (m, 7), 2.65 (s, OAc); UV (cyclohexane) λ_{max} 259 nm ($\epsilon \times 10^{-3}$, 97.9), 322 (14.3), 336 (14.8), 361 (6.7), 380 (8.6), 392 (5.8), 411 (7.1), 434 (12.3), 461 (12.6), 518 (3.0); high-resolution mass spectrum, m/z calcd for $C_{30}H_{18}O_2$ 410.1306, found 410.1313 (M^+).

2,2-Diphenyl-6(2*H*)-aceanthrylenone (17). 2′,2′-Diphenylspiro[anthracene-9(10*H*)-1′-cyclopropan]-10-one (0.72 g, 1.9 mmol; cf. Starting Materials paragraph) under argon was dissolved in refluxing xylene (50 mL) to give a colorless solution. Refluxing was continued for 3 h, as the color of the solution eventually became light-yellow. The solvent was removed by vacuum distillation, and the residue was dissolved in benzene (50 mL) under argon. Silver oxide (2 g) was suspended in the solution and the suspension was stirred vigorously for 16 h under argon. Workup by filtration through Celite, followed by vacuum evaporation of solvent, gave a residue from which **17** was isolated by chromatography (R_f 0.37): yield 0.51 g (71%) of colorless crystals which, according to ^1H NMR analysis, contained a trace of an impurity believed to be 1,10b-dihydro-2,2-diphenyl-6(2*H*)-aceanthrylenone. An analytically pure sample was prepared as follows. A solution of impure **17** (200 mg) in acetic anhydride (5 mL) and pyridine (5 drops) under argon was refluxed for 5 min. Vacuum evaporation of solvents gave a residue from which 170 mg (85%) of colorless crystals were isolated by chromatography and subsequent crystallization from methylene chloride/ethanol: mp 204–206 °C (depending on the intensity of the the inspection light of the hot-stage microscope; lit.[8] yellow micro crystals, mp 224–225 °C); IR 1660 cm^{-1} (CO); ^1H NMR δ 8.48 ("d", 1 H, J = 8 Hz), 8.14 ("d", 1 H, J = 8 Hz), 8.02 ("d", 1 H, J = 8 Hz), 7.73–7.47 (m, 5 H; a singlet is discernible at 7.50, 1 H), 7.34–7.24 (m, 10 H); UV (CH_2Cl_2) λ_{max} 284 nm ($\epsilon \times 10^{-3}$, 14.6), 296 (14.0), 308 (11.1) sh, 360 (8.0) sh, 372 (9.0); high-resolution mass spectrum, m/z calcd for $C_{28}H_{18}O$ 370.1358, found 370.1363 (M^+).

1,2-Diphenyl-6-aceanthrylenol Acetate (18). A solution of **17** (50 mg, 0.14 mmol) in methylene chloride (75 mL) was irradiated for 5 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvents after 30 min gave a red residue from which 51 mg (92%) of dark-red crystals were isolated by chromatography; mp 210–214 °C (recrystallized from methylene chloride/ethanol); IR 1765 cm^{-1}; ^1H NMR δ 8.01 ("d", 1 H, J = 8 Hz), 7.93 ("d", 1 H, J = 9 Hz), 7.80 ("d", 1 H, J = 7 Hz), 7.73 ("d", 1 H, J = 9 Hz), 7.64–7.58 (m, 1 H), 7.52–7.21 (m, 12 H), 2.64 (s, OAc); UV (cyclohexane) λ_{max} 238 nm ($\epsilon \times 10^{-3}$, 37.2), 261 (66.9), 357 (5.3), 374 (7.8), 396 (6.2), 414 (7.7), 436 (5.9), 498 (2.6); high-resolution mass spectrum, m/z calcd for $C_{30}H_{20}O_2$ 412.1464, found 412.1457 (M^+).

Lanthanide Tetrakis(β-diketonates) as Effective NMR Shift Reagents for Organic Salts

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Introduction

Lanthanide-induced shifts have been reported for organic salts in the presence of lanthanide tris(β-diketonates).[1-5] Substrates include ammonium,[1-5] phosphonium,[5] sulfonium,[5] and oxonium[4] cations. This is a rather unexpected occurrence, and the most likely explanation is that the anion of the organic salt complexes with the lanthanide tris chelate. An ion pair then forms between the organic cation and the anionic lanthanide

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Table I. Lanthanide-Induced Shifts in the NMR Spectrum of Diethylamine Hydrochloride (0.1 M) and Diethylamine Hydrobromide (0.1 M) in $CDCl_3$ with Various Shift Reagents (0.05 M)

shift reagent	$-CH_2-$	$-CH_3$
Diethylamine Hydrochloride		
$Eu(fod)_3$	2.87	2.20
$Eu(fod)_3/K(fod)$	4.35	2.47
$Eu(fod)_3/Ag(fod)$	4.77	2.73
Diethylamine Hydrobromide		
$Eu(fod)_3$	0.60	0.52
$Eu(fod)_3/K(fod)$	4.54	2.60
$Eu(fod)_3/Ag(fod)$	4.91	2.78

species.[1] The equilibria representative of the interaction of a lanthanide tris(chelate) with an organic salt is shown in eq 1.

$$Ln(\beta\text{-dik})_3 + R^+X^- = R[Ln(\beta\text{-dik})_3X] \quad (1)$$

The lanthanide-induced shifts in the NMR spectrum of organic salts are dependent on the nature of the anion. The induced shifts for organic salts decrease as the counterion is changed from Cl^- to Br^- to I^-.[1,5] It has been postulated that the harder chloride ion may associate more strongly than bromide or iodide with the lanthanide tris(chelate).[1] The larger association constant would therefore result in larger shifts. The chloride complex may also have the smallest distance between the lanthanide and the cation.[5]

We wish to report that an organic-soluble lanthanide species of the form $[Ln(\beta\text{-dik})_4]^-$ can be employed as a shift reagent for organic ammonium halides. The shifts in the NMR spectrum of ammonium cations in the presence of $[Ln(\beta\text{-dik})_4]^-$ are larger than those observed with $[Ln(\beta\text{-dik})_3X]^-$. The tetrakis($\beta$-diketonate) anion is formed by the addition of a lanthanide tris(β-diketonate) and silver(I) β-diketonate. Binuclear silver–lanthanide complexes have been reported as shift reagents for olefins, aromatics, halogenated compounds, and phosphines.[6] When an ammonium halide is added to the binuclear lanthanide–silver complex in a solvent such as chloroform, the silver halide precipitates from solution. An ion pair forms between the ammonium ion and the lanthanide tetrakis(chelate) ion, resulting in shifts in the NMR spectrum of the cation. A set of equilibria representative of this process is shown in eq 2 and 3.

$$Ln(\beta\text{-dik})_3 + Ag(\beta\text{-dik}) = Ag[Ln(\beta\text{-dik})_4] \quad (2)$$

$$Ag[Ln(\beta\text{-dik})_4] + R^+X^- = R[Ln(\beta\text{-dik})_4] + AgX(s) \quad (3)$$

We have recorded the lanthanide-induced shifts in the NMR spectra of *N*-methylnicotinium iodide, *N*-ethylquinolinium iodide, tetrabutylammonium iodide, diethylamine hydrochloride, diethylamine hydrobromide, dimethylamine hydrochloride, diphenylamine hydrochloride, and [3-(dimethylamino)propyl]trimethylammonium iodide in the presence of $Eu(fod)_3$, $Eu(fod)_3/K(fod)$, and $Eu(fod)_3/Ag(fod)$. For all substrates except diphenylamine hydrochloride, which exhibited essentially no induced shifts in the presence of any of the reagents, the induced shifts were significantly larger with $Eu(fod)_3/Ag(fod)$.

Results and Discussion

Induced shift data for the compounds diethylamine hydrochloride and diethylamine hydrobromide are listed in Table I. The shifts for the chloride are larger than for the bromide when $Eu(fod)_3$ is employed as the shift reagent. This observation correlates with previous reports.[1,5] In contrast to the observations with $Eu(fod)_3$, the induced shifts with the anion species formed in situ from either the potassium or silver reagent are virtually the same for the bromide and chloride. Similar shifts are expected since the halide counterion plays no role in the interaction between the cation and $Eu(fod)_4^-$.

Table II. Lanthanide-Induced Shifts in the NMR Spectrum of [3-(Dimethylamino)propyl]trimethylammonium Iodide (0.1 M) in $CDCl_3$ with Various Shift Reagents (0.05 M)

$$\overset{E}{(CH_3)_2}N\text{-}\overset{D}{CH_2}\text{-}\overset{C}{CH_2}\text{-}\overset{B}{CH_2}\text{-}\overset{A}{N(CH_3)_3}^+\ I^-$$

shift reagent	A	B	C	D	E
$Eu(fod)_3$	9.63	4.07	3.02	1.68	1.30
$Eu(fod)_3/K(fod)$	2.80	1.13	0.95	0.48	0.25
$Eu(fod)_3/Ag(fod)$	12.68	5.25	3.80	1.83	1.11
	1.32[a]	1.29	1.26	1.09	0.85

[a] Ratio of the lanthanide-induced shifts with $Eu(fod)_3/Ag(fod)$ to those with $Eu(fod)_3$.

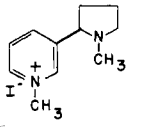
The induced shifts in the NMR spectrum of [3-(dimethylamino)propyl]trimethylammonium iodide (I) with

$$(CH_3)_2NCH_2CH_2CH_2N(CH_3)_3^+I^-$$
$$\text{I}$$

$Eu(fod)_3$ have been reported in the literature.[3] Our observations are similar to the literature results and the induced shifts are listed in Table II. Compound I is a bifunctional substrate. The $Eu(fod)_3$ can coordinate either at the quaternary nitrogen atom by forming an ion pair or by interacting with the lone pair of electrons of the tertiary amine. The induced shifts indicate that $Eu(fod)_3$ preferentially interacts with the ionic group of I. The shifts recorded in the spectrum of I with $Eu(fod)_3/K(fod)$ and $Eu(fod)_3/Ag(fod)$ are listed in Table II for comparison. Also included in the table is the ratio of the shifts with $Eu(fod)_3/Ag(fod)$ to $Eu(fod)_3$.

The shift ratios exhibit a systematic decrease as the proton becomes further removed from the quaternary nitrogen. With $Eu(fod)_3$ the induced shifts are actually larger for the 3-methyl group than with $Eu(fod)_3/Ag(fod)$. Apparently the $Eu(fod)_3$ is less specific than $Eu(fod)_3/Ag(fod)$ and interacts with both the tertiary nitrogen lone pair and the quaternary nitrogen atom. The $Eu(fod)_3/Ag(fod)$ species appears selective enough to serve as a probe for ammonium functionalities in the presence of electron pair donor groups.

One other bifunctional substrate, *N*-methylnicotinium iodide (II), was investigated. The induced shifts of all



(II)

resolved resonances were larger with $Eu(fod)_3/Ag(fod)$. The improvement varied from 20 to 80% depending on the particular proton. There was no systematic pattern to the ratios that would imply $Eu(fod)_3$ complexation with the pyrrolidine nitrogen. The variation of the ratios probably reflects a change in the geometry of the two shift reagent–substrate complexes.

The data in Table II also points out the relative ineffectiveness of the $Eu(fod)_3/K(fod)$ combination. For all substrates except diethylamine hydrochloride and hydrobromide and *N*-ethylquinolinium iodide, the induced shifts with $Eu(fod)_3/K(fod)$ were less than those with $Eu(fod)_3$. Since the anion should be the same with $Eu(fod)_3/K(fod)$ and $Eu(fod)_3/Ag(fod)$, the cation initially employed in the

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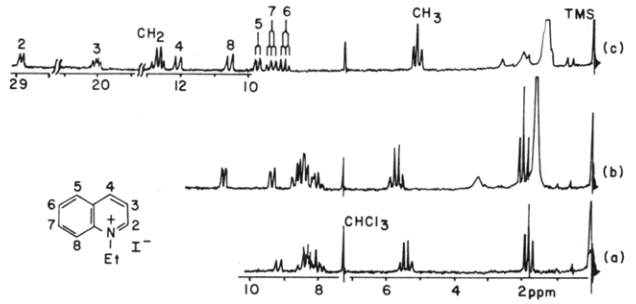

Figure 1. Proton NMR spectrum of *N*-ethylquinolinium iodide (0.1 M) in $CDCl_3$ with (a) no shift reagent, (b) 0.05 M $Eu(fod)_3$, and (c) 0.05 M $Eu(fod)_3$ and 0.05 M Ag(fod).

formation of the shift reagent influences the magnitude of the induced shifts.

The spectra reproduced in Figure 1 for *N*-ethylquinolinium iodide demonstrate the shifting ability of $Eu(fod)_4^-$ formed in situ from $Eu(fod)_3$/Ag(fod). The spectrum for the substrate without any shift reagent is shown in Figure 1a. In the unshifted spectrum only one aromatic proton is resolved. Figure 1b is the spectrum obtained for the substrate (0.1 M) with $Eu(fod)_3$ (0.05 M). In this example three of the aromatic protons are resolved. In the presence of $Eu(fod)_4^-$ at a similar concentration, however, the spectrum is completely first order. This spectrum is shown in Figure 1c. The shifts were large enough to perform decoupling experiments and confirm the assignments.

The species $Eu(fod)_4^-$ formed in situ from $Eu(fod)_3$ and Ag(fod) is a powerful organic-soluble NMR shift reagent for organic salts. One reason for the effectiveness is that precipitation of the silver halide enhances the degree of ion pair formation. It is also possible that the geometric term for a cation paired with $Eu(fod)_4^-$ is more favorable than with $Eu(fod)_3X^-$. The geometric term refers to the distance and angle values of the pseudocontact shift equation.[7,8] In addition to ammonium salts, we expect $Eu(fod)_4^-$ to function as an effective NMR shift reagent for sulfonium, oxonium, and phosphonium salts provided the silver complex with the associated anion is insoluble in solvents such as chloroform.

Experimental Section

The $Eu(fod)_3$[9] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) and Ag(fod)[9] were prepared according to procedures reported in the literature. The K(fod) was prepared by a procedure analogous to that used to prepare other potassium β-diketonate complexes.[10] $Eu(fod)_3$ and Ag(fod) are also available from commercial sources. The substrates were purchased and used as received or prepared by literature methods.[3,11] When recording the NMR spectrum of a substrate in the presence of $Eu(fod)_4^-$, the appropriate amount of $Eu(fod)_3$, Ag(fod), and substrate were weighed into a test tube. The correct amount of chloroform-*d* was added via pipet. The test tube was stoppered, and the mixture was vigorously shaken for 1 min. The silver halide was removed by centrifugation and decantation of the supernatant. Prior to recording the spectrum, the test tube and NMR tube were covered with aluminum foil to exclude light.

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Azaindolizines. 6. The Synthesis of 7-Azaindolizines from Methylpyrazines

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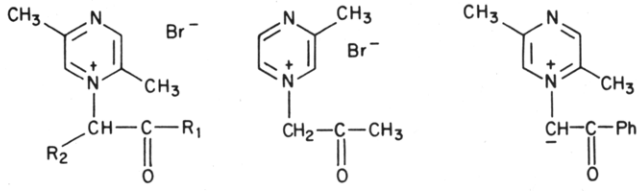
One of the simplest methods of synthesis for 5-, 6-, and 8-azaindolizines has been by the Chichibabin quaternization–cyclization reactions of 3-methylpyridazines and 4-(6)-methyl- and 2-methylpyrimidines with an α-halo ketone.[1-4] In contrast the synthesis of 7-azaindolizines has commonly involved a pyrrole precursor onto which a six-membered ring has been grafted.[5-7] There has been no report of the direct successful application of the Chichibabin procedure to the synthesis of 7-azaindolizines from 2-methylpyrazines.

Boekelheide et al.[8] attempted to synthesize 6-methyl-2-phenyl-7-azaindolizine (**1**) (Table I) by reacting 2,5-dimethylpyrazine with phenacyl bromide, the resulting quaternary salt **2**, however, did not cyclize when treated



2, R_1 = Ph; R_2 = H
4, R_1 = CH_3; R_2 = H
5, R_1 = CH_3; R_2 = CH_3

6 **3**

with bicarbonate but was interpreted to give the zwitterion **3**. We repeated this reaction between 2,5-dimethylpyrazine and phenacyl bromide and found that the resulting salt on treatment with bicarbonate gave 2,5-dimethylpyrazine but none of the 7-azaindolizine **1**. It is suggested that the salt **2** on reaction with base besides giving the zwitterion **3** undergoes nucleophilic displacement with loss of the 2,5-dimethylpyrazine as the leaving group. The expected abstraction of a proton from the 2-methyl group of **2** followed by cyclization is evidently not favored. Similarly 2,5-dimethylpyrazine was obtained when the salt **4** formed between 2,5-dimethylpyrazine and bromoacetone was treated with base. However, on using 3-bromobutan-2-one as the quaternizing α-halo ketone the resulting salt **5** on reaction with base gave the 2,3,6-trimethyl-7-azaindolizine (**7**) in low yield. In this case it would appear that the methyl branching reduces the acidity of the methine hydrogen and also suppresses substitution sufficiently to allow some cyclization to occur.

Reaction of 2-methylpyrazine with bromoacetone gave a single quaternary salt which when treated with base regenerated the 2-methylpyrazine. It is likely that 2-methylpyrazine preferentially quaternizes at the more accessible nitrogen N-4 to give **6** from which 2-methyl-

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