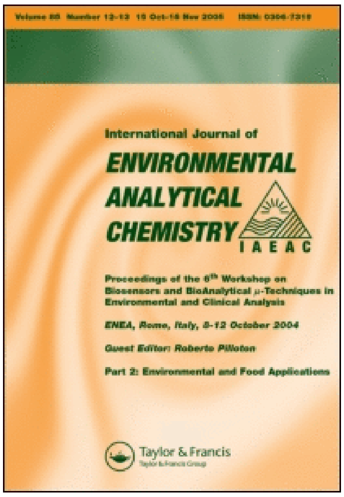

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Identification of Polyaromatic Carbonyl Compounds in a Neutral Coal Oil Fraction†

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An aromatic carbonyl compound-enriched fraction constituting 0.14 wt.% of a crude coal liquid was isolated by acid-base extraction, followed by Sephadex LH-20, silicic acid and normal phase HPLC separations. Analysis of this fraction by GC/MS showed six major peaks which were identified as benz(de)anthracenone, C_1-benz(de)anthracenone, C_2-benz(de)anthracenone, benzo(cd)pyrenone, and C_1-benzo(cd)pyrenone. High resolution mass spectrometric and infrared spectroscopic analyses of this fraction exclude the presence of isobaric compounds, such as dibenzocinnoline. Benz(de)anthracenone, the most prevalent carbonyl species was confirmed by comparison of GC retention time and high resolution mass spectrum with that of an authentic standard. It was estimated to be present at 150 ppm in the crude coal oil sample. The other five components were tentatively identified by high resolution mass spectrometry and determined at 7-38 ppm each.

KEY WORDS: Polyaromatic carbonyl compounds, benz(de)anthracenone, benzo(cd)pyrenone, neutral coal oil fraction, high resolution mass spectra, gas and liquid chromatography.

INTRODUCTION

Studies in this laboratory of the toxicological properties of petroleum substitutes have demonstrated[1,2] that in several crude coal

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liquids and shale oils, the neutral aromatic polar subfraction contributes substantially to the bacterial mutagenicity contained in the neutral chemical fraction. Forty-three percent of the neutral fraction mutagenicity of a coal-derived crude oil, and 80% of the neutral fraction mutagenicity of a crude shale oil were contributed[1] by the neutral aromatic polar subfraction. This exceeded the contribution of the polycyclic aromatic hydrocarbon (PAH) subfraction and often that of the neutral nitrogen-substituted aromatic (N-PAH) subfraction.[2]

Chemical characterization of the neutral aromatic polar subfraction has shown[3],[4] the presence of primary polycyclic aromatic amines, azaarenes, hydroxyl substituted PAH, and in one case, polyaromatic carbonyl compounds.[4] In the gas chromatographic profile of a highly mutagenic aromatic polar subfraction of a crude coal liquid, 51 area percent of the profile was contributed by polyaromatic carbonyl compounds.[4] Polyaromatic carbonyl compounds have been identified in various environmental samples[5,6] and several polyaromatic ketones have been shown to be mutagenic[7] or potentially carcinogenic.[8] Because their presence in a coal liquid derived by catalytic hydrogenation is unexpected, a detailed study of this class of compounds was conducted.

This paper reports a detailed identification of the major polyaromatic carbonyl compounds in a heavy coal oil sample derived from a more recent pilot plant scale coal liquefaction operation. Chromatographic and spectral evidence are presented for the unambiguous identification of benz(de)anthracenone, and the tentative assignment of C_1-, C_2-benz(de)anthracenone and C_0-, C_1-benzo(cd)pyrenone structure to five other prominent compounds in a highly purified subdivision of the neutral aromatic polar subfraction.

EXPERIMENTAL

Sample and reagents A sample of heavy oil (sample no. 591) from the H-coal pilot plant was supplied through the DOE Synthetic Fuels Repository.[9] The sample number serves to underscore the fact that this was a discrete sample not necessarily representative of the technology as a whole or of a product from a future commercial operation.

Solvents used in gravity flow column chromatography were reagent grade and freshly redistilled. Hexane and isopropanol used in high pressure liquid chromatography were ultraviolet (UV) grade (Burdick and Jackson, Muskegon, MI) and freshly redistilled. Standard 7-H-benz(de)anthracene-7-one (benz[de]anthracenone) was purchased from Pfaltz and Bauer, Inc. (Flushing, NY) and purified by vacuum sublimation.[10]

Separation procedure Figure 1 shows the separation approach used in this study. Part of this procedure has been described in detail elsewhere.[3,11] Briefly, the approach is as follows: (1) after solvent extraction[12] of acidic and basic components from the crude oil sample, the neutral fraction was separated on a Sephadex LH-20 gel column[13] into saturates, aromatics, polyaromatics, and a residue; (2) the polyaromatic fraction was subdivided into four subfractions (polycyclic aromatic hydrocarbons plus nitrogen-containing aromatics, moderately polar I, moderately polar II, and highly polar) on a silicic acid column;[2,14] and (3) the moderately polar II subfraction was finally resolved into subfractions HP-1 and HP-2 by normal phase semipreparative scale high performance liquid chromatography (HPLC).

High performance liquid chromatography (HPLC) The HPLC system consists of a simplex reciprocating pump (Laboratory Data Control Division, Milton Roy Co., Riviera Beach, FL), a syringe loading sample injector (Model 7125, Rheodyne Corp., Cotati, CA) with a 100 μl sampling loop, and a pressure gauge (Ashcroft Gauge, Dresser, Inc., Stratford, CT).

An MPLC® guard column with a "Silica Spheri-5" MPLC® cartridge (Brownlee Labs, Santa Clara, CA) was connected to a semipreparative scale (10 mm ID × 25 cm) silica column packed with 5 μm Lichrosphere Si-100 (Altex Associates, Berkeley, CA). The mobile phase was 1.5% (v/v) isopropanol in hexane and was pumped at 2 ml/min (300 psi). The effluent was monitored with a fixed wavelength (254 nm) UV detector (Model 1285, Laboratory Data Division, Milton Roy Co., Riviera Beach, FL). The elution volume of benz(de)anthracenone was used to define the approximate collection volume of fraction HP-1.

Gas chromatography A Perkin-Elmer Model 3920 gas chromato-

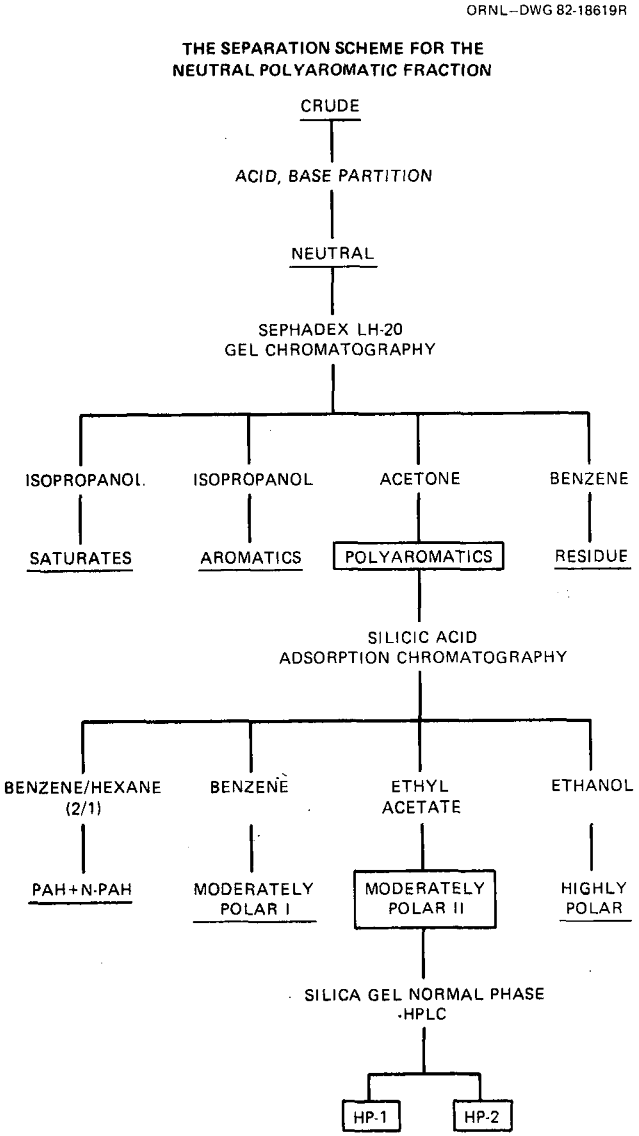


Figure 1 Separation scheme for the neutral polyaromatic fraction.

graph equipped with a flame ionization detector was used. The column was a 25 m × 0.2 mm ID fused silica capillary column (Scientific Glass Engineering, Inc., Austin, TX) coated with OV-101 (0.25 μm film thickness). The column oven initial temperature was held at 90°C for 4 min then raised to 275°C at 4°C/min. Helium carrier gas was maintained at a head pressure of 25 psig. The concentrations of aromatic carbonyl compounds were estimated by comparison of peak heights with that of a known standard, and correcting for the percentage weight of the fraction analyzed. The response factors of all aromatic carbonyl compounds were assumed to be the same as that of benz(de)anthracenone.

Gaschromatography/mass spectrometry (*GC/MS*) GC/MS analyses were performed on a Hewlet-Packard 5985B gas chromatograph/mass spectrometer. Electron impact spectra were generated with the ion source at 70 eV. Gas chromatographic separation was performed on a 25 m × 0.25 m ID fused silica capillary column (J&W Scientific, Inc., Orangeval, CA) coated with SE-52 (0.25 μm film thickness). The column oven temperature was maintained at 80°C for 5 min and then programmed to 250°C at 3°C/min. Helium carrier gas was maintained at a head pressure of 28 psig. A splitless injector was used to introduce the sample.

High resolution mass spectrometry (*HRMS*) HRMS analysis was performed on a Kratos MS50/DS50 mass spectrometer/data system operating at a resolution of 11,000 with 10% valley definition, in the electron impact (70-eV) mode. Samples of fraction HP-1 were introduced into the mass spectrometer using a direct insertion probe inlet system. The ion source was maintained at 180°C, and the probe temperature adjusted from 50°C to 200°C in 20°C increments. Data were acquired via computer controlled dynamic scanning at 10 s/decade, with a bandwidth of 10,000 Hz.

Infrared spectrometry The infrared spectrum was obtained on a Digilab FTS-20/C Fourier Transform Infrared Spectrometer equipped with a diffuse reflectance attachment JASCO Model DRA-100 (Digilab, Division of Bio-Rad Laboratories, Cambridge, MA). Details of sample preparation for diffuse reflectance Fourier transform infrared spectra of fossil fuel derived liquids have been reported elsewhere.[15]

RESULTS AND DISCUSSIONS

Neutral fractions derived from the diethylether/aqueous partitioning are known to constitute more than 90% of the total mass of H-Coal heavy oils[11] and to contain a wide variety of components varying in aromaticity and polarity.[3,4] Isolation of a minor fraction enriched in aromatic carbonyl compounds from this complex mixture requires an extensive and lengthy separation procedure. The separation scheme reported here is a combination of acid/base extraction scheme,[12] Sephadex LH-20 gel filtration chromatography,[13] and silicic acid adsorption chromatography.[2,14] An additional elution step was added to the silicic acid chromatography to separate moderately polar from highly polar constituents. Two moderately polar subfractions were separated from the polyaromatic fraction of the sample by sequential elution of the silicic acid column with benzene and ethyl acetate after the collection of PAH and N-PAH subfractions.[2] The highly polar subfraction was obtained by cleaning the column with ethanol.

A preliminary analysis of these polyaromatic subfractions by GC/MS revealed that the carbonyl-containing polyaromatics were concentrated in the moderately polar II subfraction, which constitutes only 1 wt.% of the crude oil sample (Table I). However, the complexity of this subfraction made the unequivocal identification

Table I Weight distribution of the neutral fraction from a crude coal-derived heavy oil

Fraction		Weight (%)[a]	
Saturates		32.31	
Aromatics		46.60	
Polyaromatics		14.49	
PAH + N-PAH		11.59	
Moderately polar I		0.75	
Moderately polar II	HP-1	1.02	0.14
	HP-2		0.64
Polar		0.44	
Residue		0.052	

[a] Weight percentage of the crude sample.

of carbonyl-substituted aromatics by complementary spectral techniques rather difficult. Therefore, further separation of the moderately polar II subfraction was carried out on a semipreparative scale normal phase HPLC system using 1.5% isopropanol in hexane as eluent. The elution volume of benz(de)anthracenone, a polyaromatic carbonyl compound, was used to define the approximate collection volume of fraction HP-1 (Figure 2).

The major components found in the gas chromatographic profile (Figure 3) of fraction HP-1 are of relatively low volatility. The adsorption band at 1655 cm^{-1} in the FTIR spectrum of this fraction strongly suggests the presence of compounds with aromatic carbonyl or conjugated carbonyl functional groups.[10,16] The nominal molecular ions at mass/charge ratios (m/z) of 230, 244, 258, 254 and 268 revealed in low resolution GC/MS were examined by HRMS to establish their exact mass and chemical compositions (Table II). The measured molecular weights of these six components compared very well with the calculated molecular weights of the postulated compounds. Their deviations ranged from 0.1 to 0.8 millimass units. Thus, the major components in this fraction were almost certainly oxygen-containing compounds with molecular weights of 230 and 254, and their alkylated homologs (m/z of 244 and 258; and 268, respectively).

The most abundant constituent in the HP-1 fraction (peak 1, Figure 3) was identified as benz(de)anthracenone (I). The electron

Table II High resolution mass spectrometric analysis of fraction HP-1

GC/MS nominal mass	Elemental composition	HRMS measured mass	Exact mass based on C-12 = 12.000000	Deviation mmu[a]
230	$C_{17}H_{10}O_1$	230.0733	230.0731	+0.2
244	$C_{18}H_{12}O_1$	244.0893	244.0888	+0.5
258	$C_{19}H_{14}O_1$	258.1049	258.1044	+0.5
254	$C_{19}H_{10}O_1$	254.0734	254.0731	+0.3
268	$C_{20}H_{12}O_1$	268.0896	268.0888	+0.8
230	standard benz(de)anthracenone ($C_{17}H_{10}O_1$)	230.0732	230.0731	+0.1

[a] mmu = millimass unit.

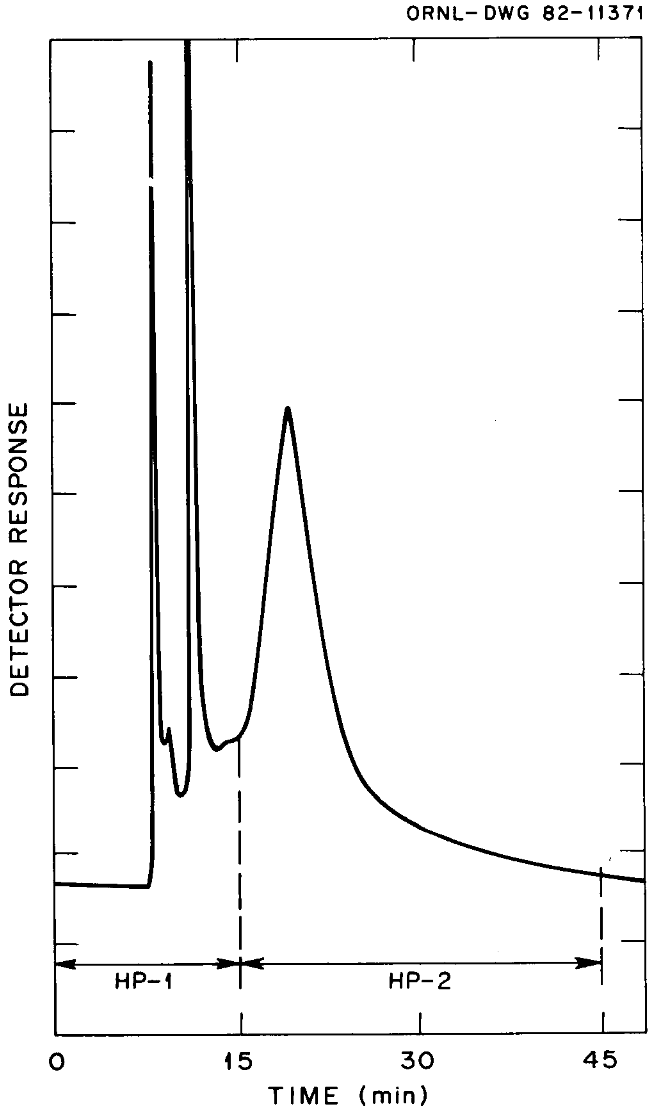


Figure 2 Chromatogram for the separation of the moderately polar II fraction on Lichrosphere S-100 column.

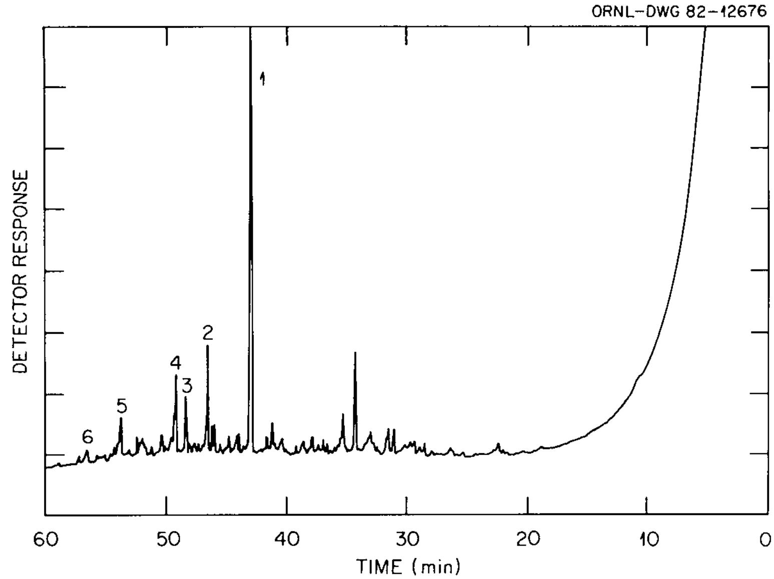
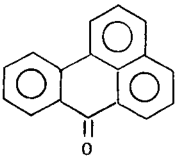


Figure 3 Capillary column gas chromatogram of fraction HP-1.

impact (EI) mass spectrum of this component was found to be in excellent agreement with the observed spectrum of the authentic compound, as determined under the same conditions, and with spectra reported in the literature.[17] The base peak was observed at an m/z of 230, with the major fragment at an m/z 202 (relative abundance = 45%), corresponding to loss of CO (Figure 4). Furthermore, the GC retention time was the same for peak 1 and for standard benz(de)anthracenone, thus indicating that peak 1 was benz(de)anthracenone.



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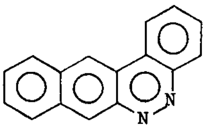

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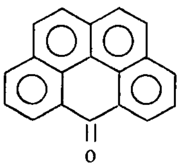

III

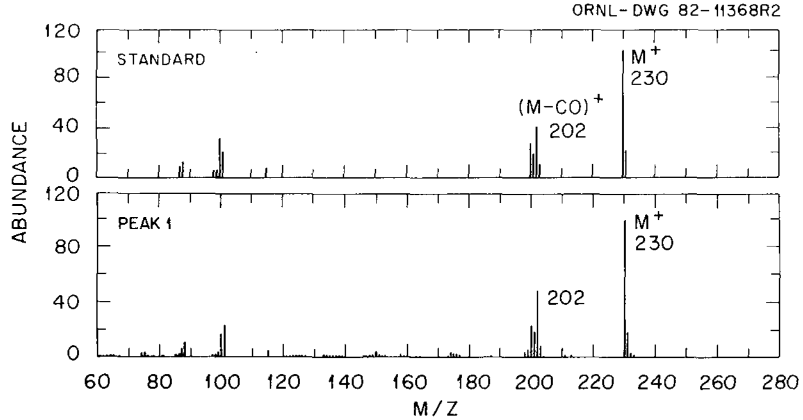

Figure 4 Electron impact mass spectra of standard benz(de)anthracenone and peak 1 from fraction HP-1.

In general, the ketone derivative of benzanthracene cannot be distinguished from their isobaric compounds such as dibenzo(c, g)cinnoline (II) by low resolution mass spectrometry since both have the same molecular ion at a nominal mass of 230 and their fragmentation patterns may be very similar.[17-19] However, the absence of dibenzocinnoline ($C_{16}H_{10}N_2$, m/z 230.0844) in the HP-1 fraction was demonstrated by HRMS. The only ion found at a nominal mass of 230 in the high resolution mass spectrum had an exact mass of 230.0733 which was in excellent agreement with the exact mass of compound I, as shown in Table II. The loss of 28 mass units, corresponding to a probable loss of CO, is ascribed to the peak at m/z 202.0783 ($C_{16}H_{10}$). The probability of $C_{15}H_6O$ (m/z = 202.0419), corresponding to a loss of C_2H_4, is virtually excluded by the HRMS measurement.

The mass spectrum of peak 2 in Figure 3 has a molecular ion at m/z of 244 (relative abundance = 100%) and a fragment at m/z of 215 (relative abundance = 40%) corresponding to the loss of COH. The mass (m/z of 244.0893) determined by HRMS confirms the elemental composition as $C_{18}H_{12}O$ (Table II) which corresponds to a methyl derivative of benz(de)anthracenone.

Peaks 3 and 4, with molecular ions at m/z of 258 (relative abundance = 100%), were assigned as C_2-alkyl derivatives of benz(de)anthracenone. Their EI mass spectra were virtually identical; the parent ions in both cases lose 15 mass units (loss of CH_3) to give a fragment at m/z of 243 (relative abundance = 20%). High resolution mass spectrometry indicated the elemental composition to be $C_{19}H_{14}O$ (m/z of 258.1049) which readily showed that these peaks are not benz(a)anthracenedione ($C_{18}H_{10}O_2$, m/z of 258.0681) or ethylene-bridged derivatives of dibenzocinnoline ($C_{18}H_{14}N_2$, m/z of 258.1157).

Peaks 5 and 6 produced molecular ions at m/z of 254 and 268 (relative abundance = 100%) and were identified as isomers of benzo(cd)pyrenone (III) and its methyl derivative, respectively. The fragmentation pattern in the EI mass spectrum of peak 5 was consistent with the mass spectrum of benzo(cd)pyrenone reported elsewhere.[16-18] Results from HRMS analysis (Table II) supported this assignment. Identification of peaks 2 to 6 was based on both low and high resolution mass spectra alone. It was not possible to match their GC retention times with that of authentic standards because of the unavailability of such standards. None of the other peaks in the chromatogram of the fraction exhibited mass spectra suggesting their identification as aromatic carbonyl compounds.

Estimations of the concentrations of these aromatic carbonyl compounds in the coal-derived heavy oil are given in Table III. The concentration of benz(de)anthracenone was 150 μg/g while its C_1- and C_2-alkylated homologs were present at 20–38 μg/g each. Benzo(cd)pyrenone and its methyl derivative were found at lower

Table III Estimated concentrations of aromatic carbonyl compounds identified in a crude coal-derived heavy oil

Peak no.[a]	Identification	Concentration[b] (μg/g)
1	Benz(de)anthracenone	150
2	C_1-Benz(de)anthracenone	38
3	C_2-Benz(de)anthracenone	20
4	C_2-Benz(de)anthracenone	30
5	Benzo(cd)pyrenone	20
6	C_1-Benzo(cd)pyrenone	7

[a] Figure 3.
[b] Concentration in crude oil, corrected for recovery of HP-1 subfraction.

levels than were the benz(de)anthracenones. The two unsubstituted polyaromatic carbonyl compounds were present in substantially higher concentrations than were their C_1- and C_2-substituted homologs. These concentration levels also are somewhat lower than those of typical four- and five-ring polycyclic aromatic hydrocarbons also found in crude coal-derived heavy oils.

CONCLUSIONS

Extensive fractionation is necessary to obtain a subfraction sufficiently pure to allow the identification and measurement of aromatic carbonyl compounds in a highly complex crude mixture. Benz(de)anthracenone was unambiguously determined at 150 μg/g in crude coal-derived liquid. Three C_1- and C_2-benz(de)anthracenones, benzo(cd)pyrenone, and a C_1-derivative also were tentatively identified and determined at 7–38 μg/g each. It is not clear if these compounds were created during liquefaction or, more likely, were formed subsequently in degradation reactions.

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