

Electrical Resistivity and Magnetoresistivity of Protonic Acid (H₂SO₄ and HCl)-Doped Polyaniline at Low Temperature

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ABSTRACT: Electrical-transport properties of protonic acid (H₂SO₄ and HCl)-doped polyaniline (PANI) in an aqueous ethanol medium were investigated in the temperature range 1.8 K ≤ *T* ≤ 300 K and in a magnetic field up to 8 T. The room-temperature resistivity of HCl-doped PANI is larger than that of H₂SO₄-doped PANI. The resistivity ratios $\rho_r = \rho(1.8 \text{ K})/\rho(300 \text{ K})$ of the samples are high. The samples in the insulating region show a crossover from a Mott to an Efros–Shklovskii variable range hopping conduction at *T* = 9.8 K for H₂SO₄-doped PANI and 8.5 K for HCl-doped PANI. The magnetoresistivity of these samples is also explained by the variable range hopping theory. The different physical parameters were calculated from the experimental data. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1480–1486, 2000

Key words: polyaniline; protonic acid; magnetoresistance; variable range hopping

INTRODUCTION

Conducting polymers have attracted considerable attention not only from a fundamental scientific interest but also from a practical point of view for growing applications in optoelectronics and microelectronics.^{1–3} The discovery of doped conjugated polymers with high conductivity has generated substantial interest in charge defects in polymers among chemists and physicists.^{1–16} The synthesis and preparation of heavily doped conducting polymers have significantly reduced the structural disorder and, thus, the effect of such a disorder on the electrical-transport properties.^{17–19} The transport properties of conducting polymers are determined mainly from the disorder-induced localization. The disorder arises dur-

ing the synthesis and processing and also due to the partial crystallinity and inhomogeneous doping. However, in the last few years, methods have been developed for producing more homogeneous and less disordered conducting polymers. Doped polyaniline (PANI) is one of the most attractive materials due to its environmental stability, solubility, and dopability by protonation. The electrical resistivity of PANI doped with H₂SO₄ and HCl prepared by the conventional synthetic route is relatively small.^{20–22} Recently, it was shown that the improved quality and conductivity can be obtained in PANI doped with HCl in aqueous ethanol.²³

The temperature dependence of the resistivity of conducting polymers follows Mott's variable range hopping (VRH) conduction mechanism in three dimensions, and, very recently, it was observed that some conducting polymers also show crossover from the Mott-to-Efros–Shklovskii (ES) VRH conduction with a small Coulomb gap.^{24–26} However, conventional HCl-doped PANI samples follow Mott's law in one dimension, in which the

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Table I Percentage Values of Carbon, Hydrogen, and Nitrogen Obtained from CHN Analysis

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
PANI-H ₂ SO ₄	52.25	4.83	10.47
PANI-HCl	54.80	5.03	10.67

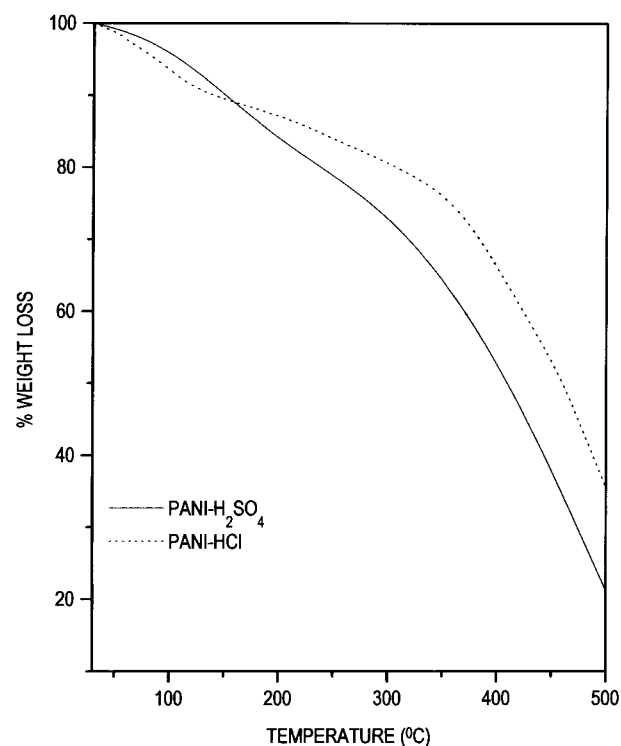
conducting chains are essentially isolated. Wang et al.^{27,28} suggested that interbundle hopping due to strong interchain coupling results in quasi-one-dimensional behavior for the macroscopic conductivity. Experimental studies²⁷⁻²⁹ using, for example, thermopower, the microwave dielectric constant, and electron paramagnetic resonance (EPR) indicated that the electrons are three-dimensionally delocalized. However, the quasi-one-dimensional VRH is not valid if all the bundles are coupled. Thus, considerable controversy exists concerning the applications of quasi-one- and three-dimensional VRH models for PANI samples. To remove such controversy, a transport-property study of PANI is essential. The electronic properties of conducting polymers are strongly influenced by the polymerization condition. Hence, the transport properties of PANI protonated with H₂SO₄ and HCl in alcohol medium will be more interesting. In this article, we report the temperature dependence of the resistivity and magnetoresistivity of H₂SO₄-doped PANI and HCl-doped PANI samples prepared in an ethanol medium.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Aniline (Merck, Worli, Bombay, India) and ethyl alcohol (Bengal Chemical and Pharmaceutical Works, Calcutta, India) were distilled as described earlier.³⁰ The dispersion polymerization was carried out with aniline in an acidified 50% (by volume) aqueous ethanol medium. The temperature of the medium was maintained at -5°C. The ratio of the aniline-to-ammonium persulfate (E. Merck, Darmstadt, Germany) concentration was 1.25. For PANI-H₂SO₄, the concentration of the sulfuric acid was 1.5M, and for the PANI-HCl sample, the hydrochloric acid concentration was 1.5M. The whole mixture was stirred magnetically for 4 h. The green precipitate of PANI salt

was filtered from the reaction vessel and then washed with distilled water. The sample was dried at room temperature for 24 h in a dynamic vacuum. The dried samples were ground and pelletized in a hydraulic press with a pressure of up to 5 tones/cm². The weight percentage of PANI was determined by elemental analysis using a CHN (2400 Series-II, Perkin-Elmer, USA) and the results are shown in Table I. Thermal degradation studies were performed under nitrogen using a Shimadzu DT-30 at a linear heating rate of 10°C/min from room temperature to 500°C. The thermogravimetric analysis (TGA) of the samples is shown in Figure 1. From the figure, it is shown that the mass loss is greater in PANI-HCl than in PANI-H₂SO₄ up to 150°C. This may be due to the moisture effect. However, for the temperature $T > 150^\circ\text{C}$, the mass loss occurs more rapidly for PANI-H₂SO₄ than for PANI-HCl. This may be due to the oxidation degradation of a polymer in air.

The electrical conductivity of PANI was measured by a standard four-probe method. For electrical contact, a highly conducting graphite adhesive (Electrodag 5513, Acheson) was used. The ohmic contact down to the lowest temperature

**Figure 1** TGA curves of PANI-H₂SO₄ and PANI-HCl samples.

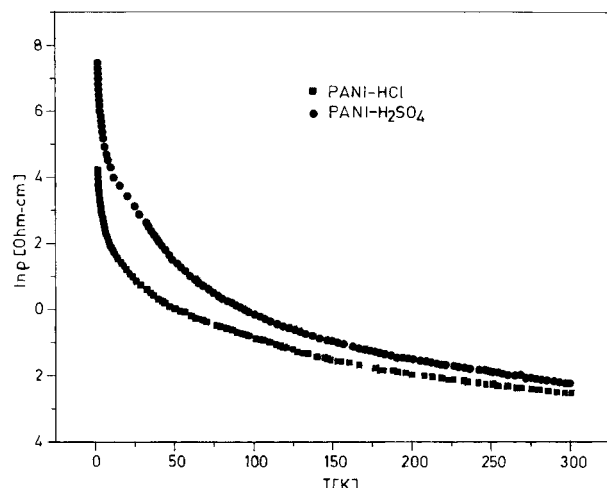


Figure 2 Variation of resistivity of PANI–H₂SO₄ and PANI–HCl samples with temperature.

was confirmed by checking the linear relationship of voltage and current. The resistivity was measured using a Keithley 220 programmable current source and a 181 nanovoltmeter. The temperature dependence of the resistivity and magnetoresistance were studied using a He⁴ cryostat equipped with a 8 T Nb–Ti superconducting magnet. For the controlling and measurement of the temperature, we used a carbon glass resistance sensor and a DRC91CA, Lake Shore temperature controller. For measurements below 4.2 K, the samples were immersed directly in liquid helium, and for measurements above 4.2 K, the samples were kept in a helium exchange gas atmosphere to ensure excellent thermal contact. Details of the experimental technique were given in a previous work.³¹ Magnetoresistance measurements were performed up to a magnetic field of 8 T. Both the resistivity and magnetoresistivity measurements were carried out from 300 K down to 1.8 K using a computer-controlled measuring system.

RESULTS AND DISCUSSION

The d.c. resistivity of H₂SO₄-doped PANI (PANI–H₂SO₄) and HCl-doped PANI (PANI–HCl) was measured at different temperatures (1.8 K ≤ *T* ≤ 300 K) without and with a magnetic field up to 8 T. The variation of resistivity with temperature in the absence of a magnetic field is shown in Figure 2 for the samples PANI–H₂SO₄ and PANI–HCl, respectively. The resistivity of PANI–

H₂SO₄ is higher in comparison to the resistivity of PANI–HCl. This may be due to the low mobility of the heavy mass SO₄²⁺ ion than to the Cl[−] ion. For both samples, the resistivity increases with decrease in the temperature, showing semiconducting behavior in the whole range of temperature, and the resistivity ratio $\rho_r = \rho(1.8 \text{ K})/\rho(300 \text{ K})$ is 2.05×10^4 for the PANI–H₂SO₄ and 2.33×10^4 for the PANI–HCl samples. Menon et al.³² described the metal–insulator (*M–I*) transition behavior in PANI depending on the value of the resistivity ratio (ρ_r). They identified three types of behavior of PANI: (i) metallic region ($\rho_r < 2$); (ii) critical region ($2 < \rho_r < 6$); and (iii) insulating region ($\rho_r > 6$). Since the resistivity ratios of our investigated samples are very large, we may treat them to be in the insulating region. To understand the conductivity mechanism in PANI–H₂SO₄ and PANI–HCl, we calculated the reduced activation energy as the logarithmic derivative of $\rho(T)$ ³³:

$$W = -T[\Delta \ln \rho(T)/\Delta T] = \Delta(\ln \rho(T))/\Delta(\ln T) \quad (1)$$

and

$$\rho(T) = \rho_0 \exp(T_0/T)^x \quad (2)$$

where $x = 1/(1 + d)$ is the fractional variable range hopping exponent which depends on the system dimension “*d*” and *T*₀ is the characterization temperature.

From the experimental data, we calculated the activation energy and plotted it with temperature as shown in Figure 3. The points are the experimentally calculated values, whereas the solid lines represent theoretical values which are given by eq. (3) as obtained from eqs. (1) and (2):

$$\log_{10} W(T) = A - x \log_{10} T \quad (3)$$

where,

$$A = x \log_{10} T_0 + \log_{10} x$$

where $A = x \log_{10} T_0 + \log_{10} x$. The values of *x* are determined from the slopes of the *W* versus *T* plot as shown in Figure 3 and these values are listed in Table II. It is shown in the figure that the values of the exponent *x* are different in two different regions. The crossover temperature (*T*_{cross}) was determined from the intersection of the two straight lines of different slopes as shown in Fig-

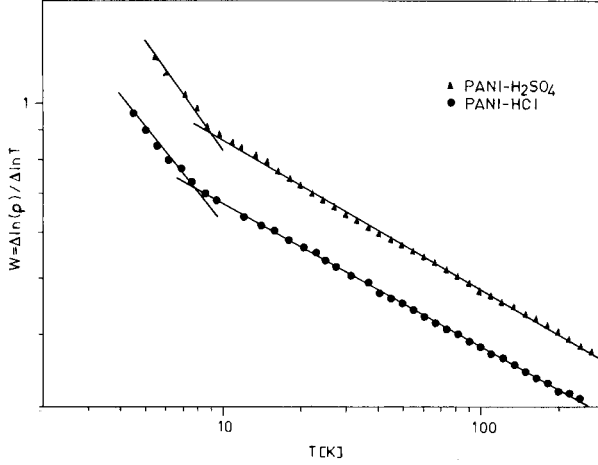


Figure 3 Log-log plot of W versus T for PANI-H₂SO₄ and PANI-HCl samples. Solid lines represent different ranges in which $x = 1/2$ (higher slopes) or $x = 1/4$ (lower slopes).

Figure 3 and the values are 9.8 K for PANI-H₂SO₄ and 8.5 K for PANI-HCl. For the temperature $T > T_{\text{cross}}$, the values of x are 0.25 ± 0.01 for PANI-H₂SO₄ and 0.24 ± 0.02 for PANI-HCl. The values of x reveal that the temperature dependence of the resistivity can be described by the three-dimensional ($d = 3$) Mott VRH model. Therefore, we analyzed the resistivity data for the temperature $T > T_{\text{cross}}$ by the three-dimensional VRH theory among localized states as described by Mott and Davis³⁴.

$$\rho(T) = \rho_0 \exp(T_{\text{Mott}}/T)^{1/4} \quad (4)$$

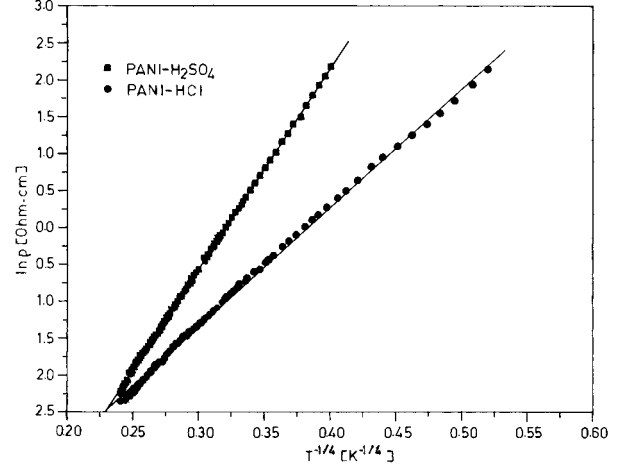


Figure 4 Variation of resistivity of PANI-H₂SO₄ and PANI-HCl samples with $T^{-1/4}$. Resistivity is plotted in logarithmic scale.

$$T_{\text{mott}} = 16/[K_B N(E_F) L_{\text{loc}}^3] \quad (5)$$

where K_B is the Boltzmann constant; $N(E_F)$, the density of states at the Fermi level; and L_{loc} , the localization length. We plotted $\ln \rho$ as a function of $T^{-1/4}$. This plot exhibits a straight-line behavior for all the samples as shown in Figure 4. From the slope of the straight line, the values of the parameter T_{mott} can be evaluated and are listed in Table II. The localization length L_{loc} can be calculated from the magnetoresistivity data as shown in Figure 5. From the VRH theory, resistivity in the presence of a magnetic field can be written as³⁵

Table II Experimental Values and VRH Parameters

Sample Parameters	PANI-H ₂ SO ₄	PANI-HCl
$\sigma(300 \text{ K})$ (S cm ⁻¹)	9.5	12.47
$\rho_r = \rho(1.8 \text{ K})/\rho(300 \text{ K})$	20,533.96	23,315.58
$x = 1/4$ (Mott)	0.25 ± 0.01	0.24 ± 0.02
$x = 1/2$ (ES)	0.51 ± 0.02	0.52 ± 0.01
T_{Mott} (K)	538,562.39	66,047.03
T_{ES} (K)	78.73	29.82
T_{cross} (K)	9.8	8.5
L_{loc} (Å)	56	60.5
$N(E_F)$ (no. states/eV/cm ³)	1.69×10^{18}	1.09×10^{19}
ϵ	106.1	259.3
Δ_c (meV)	0.065	0.043
$R_{\text{hop,Mott}}$ (Å) at 50 K	213.9	136.8
$R_{\text{hop,ES}}$ (Å) at 4.2 K	60.6	40.3
$\Delta_{\text{hop,Mott}}$ (meV) at 50 K	10.98	6.50
$\Delta_{\text{hop,ES}}$ (meV) at 4.2 K	0.784	0.483

$$\ln[\rho(H)/\rho(0)] = t(L_{10c}/L_H)^4(T_{\text{Mott}}/T)^{3/4} \quad (6)$$

where $t = 5/2016$, $L_H = (\hbar/eH)^{1/2}$ is the magnetic length, $h (= 2\pi\hbar)$ is Planck's constant, c is the velocity of light, e is the electronic charge, and H is the magnetic field. The plot of $\ln \rho(H, T)$ against $T^{-3/4}$ is a straight line as shown in Figure 5 for the different samples. From the slope of these straight lines, we can determine the values of L_{10c} for the PANI-H₂SO₄ and PANI-HCl samples, which are listed in Table II. Using the values of T_{mott} and L_{10c} for different samples in eq. (5), the values of the density of states $N(E_F)$ were calculated for different samples and are listed in Table II.

At low temperature $T < T_{\text{cross}}$, the values of x are 0.51 ± 0.02 for PANI-H₂SO₄ and 0.52 ± 0.01 for PANI-HCl. Therefore, the low-temperature resistivity can be analyzed also by VRH conduction as predicted by Shklovskii and Efros³⁵:

$$\rho(T) = \rho_0 \exp(T_{\text{ES}}/T)^{1/2} \quad (7)$$

where T_{ES} is the characteristic Efros-Shklovskii temperature which is related to the dielectric constant (ε) by the relation

$$\varepsilon = \beta_1 e^2 / (K_B T_{\text{ES}} L_{10c}) \quad (8)$$

where β_1 is a numerical constant and its value is 2.8. The linear dependence of $\ln \rho(T)$ on $T^{-1/2}$ as shown in Figure 6 indicates that the ES VRH conduction is valid at low temperature. Thus, the

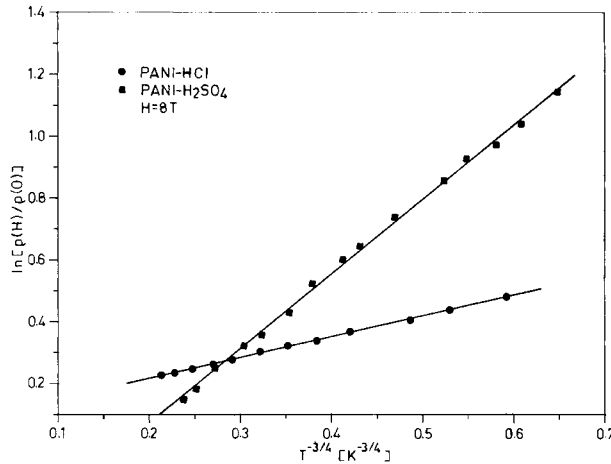


Figure 5 Variation of magnetoresistivity of PANI-H₂SO₄ and PANI-HCl samples with $T^{-3/4}$. Magnetoresistivity is plotted in logarithmic scale.

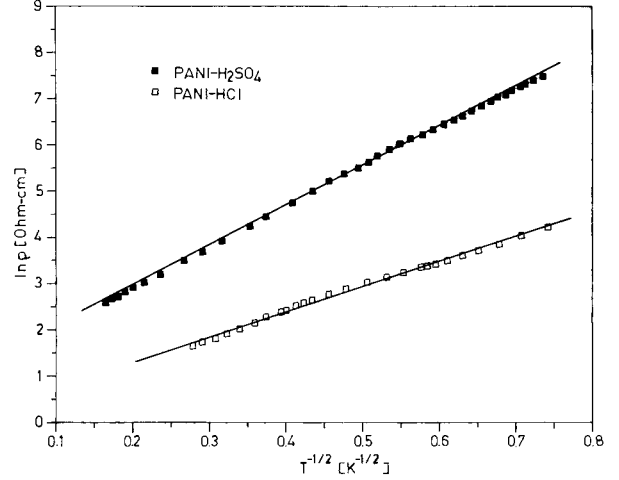


Figure 6 Variation of resistivity of PANI-H₂SO₄ and PANI-HCl samples with $T^{-1/2}$. Resistivity is plotted in logarithmic scale.

crossover from Mott to ES hopping is observed in these samples at $T = T_{\text{cross}}$. From the straight-line fits, we calculated the values of T_{ES} for different samples and they are listed in Table II. Taking the values of the Mott and ES temperatures, the density of states, and the localization length, we calculated the mean hopping distance R_{hop} and the energy difference between the sites Δ_{hop} in the Mott and ES limits by using the following relations^{34,35}:

$$R_{\text{hop,Mott}} = (3/8)(T_{\text{mott}}/T)^{1/4}L_{10c} \quad (9)$$

$$\Delta_{\text{hop,Mott}} = (1/4)K_B T (T_{\text{Mott}}/T)^{1/4} \quad (10)$$

$$R_{\text{hop,ES}} = (1/4)(T_{\text{ES}}/T)^{1/2}L_{10c} \quad (11)$$

$$\Delta_{\text{hop,ES}} = (1/2)K_B T (T_{\text{ES}}/T)^{1/2} \quad (12)$$

The calculated values of $R_{\text{hop,Mott}}$ at 50 K and the corresponding values of $\Delta_{\text{hop,Mott}}$ and $R_{\text{hop,ES}}$ at 4.2 K and the corresponding values of $\Delta_{\text{hop,ES}}$ are listed in Table II. The values of $R_{\text{hop,ES}}$ in the ES region are small compared to those for Mott, and this may be due to the small values of T_{ES} .

The values of the dielectric constant were calculated from the known values of T_{ES} and L_{10c} using eq. (8) and are shown in Table II. The static dielectric constant can be expressed as³⁶

$$\varepsilon = \varepsilon_x + 4\pi e^2 N(E_F) L_{10c}^2 \quad (13)$$

where ϵ_x is the core dielectric constant. Castner³⁶ showed that, near the $M-I$ transition, the dielectric constant can be approximated by $\epsilon = 4\pi e^2 N(E_F) L_{loc}^2$. However, for our samples, ϵ is much greater than $4\pi e^2 N(E_F) L_{loc}^2$. Yoon et al.²⁴ showed that the samples having $\rho_r < 10^2$ are in the region very close to the $M-I$ transition. Since the resistivity ratio of the investigated samples are far away from the region of the $M-I$ transition ($\rho_r > 10^2$), the above approximation is not valid for these samples.

The Coulomb gap energy according to ES theory³⁵ was calculated from the following relation:

$$\Delta_C = e^3 N(E_F)^{1/2} / \epsilon^{3/2} \quad (14)$$

where $N(E_F)$ is the unperturbed density of states at the Fermi level and ϵ is the dielectric constant. From the calculated values of the density of states and dielectric constant, the Coulomb gap was estimated as shown in Table II. The Coulomb gap is small (0.065 for PANI-H₂SO₄ and 0.043 for PANI-HCl) due to the large value of the dielectric constant. The crossover from the Mott to the ES VRH conduction with a small Coulomb gap was also observed for other conducting polymers such as hexafluorophosphate-doped polypyrrole and iodine-doped polyalkylthiophenes.²⁴ The small Coulomb gap was also observed theoretically by numerical simulations, taking into account multielectron hopping.^{37,38}

CONCLUSIONS

The resistivity and magnetoresistivity of H₂SO₄-doped PANI and HCl-doped PANI samples prepared in aqueous ethanol were performed at temperatures between 1.8 and 300 K and in the presence of a magnetic field of up to 8 T. The resistivity of all the samples decreases with increasing temperature, that is, the temperature coefficient of resistivity is negative. The resistivity ratio ρ_r is very high, that is, the samples are in the insulating region. The controversy about the applications of quasi-one- and three-dimensional VRH models in the PANI samples are explained by the accurate measurement of the VRH exponent x from the temperature dependence of the activation energy. The resistivity of these samples follows the three-dimensional Mott VRH conduction at high temperature and the ES VRH conduction at low temperature, that is, it shows a

Mott-to-ES transition at 9.8 K for PANI-H₂SO₄ and at 8.5 K for PANI-HCl with a small Coulomb gap. The magnetoresistivity of these samples follows the VRH theory. The different physical parameters $N(E_F)$, L_{loc} , ϵ , Δ_C , R_{hop} , Δ_{hop} , and D , etc., can be determined from the experimental data using the VRH theory.

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