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Synthesis and Phase Transitions of 4-(Dodecyloxy)benzamide Derivatives of Azacrowns [14]-N_4 and [18]-N_6

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The hexakis(4-dodecyloxy)benzamide and hexakis(4-hexyloxy)benzamide derivatives of [18]-N_6 (**2** and **3**) and the tetrakis(4-dodecyloxy)benzamide derivative of [14]-N_4 (**5**) were prepared, and their phase transition temperatures were determined by differential scanning calorimetry and polarizing microscopy. The melting and isotropic transition temperatures of the mesophase of **2** differed substantially from those reported earlier, apparently due to the presence of water.

Introduction

The optical properties of liquid-crystalline materials are both intriguing and useful. Liquid crystals are used in the most common electrooptic displays in calculators and watches, and their nonlinear optical properties may be put to use in the future in new electrooptic devices. Many polymers have liquid crystalline states, and they can be produced as films, glasses, and fibers. Polymeric liquid crystals are of two major types: those with mesogens in the main chain, and those with mesogens in side chains.[1-5] Because the mesogenic units are rigid, the main-chain liquid-crystalline polymers usually have mesogenic states at high temperature and tend to be fiber forming.[1-8] Side-chain liquid-crystalline polymers with flexible backbones and flexible spacer chains connecting the mesogens to the main chain are a subset of branched, comblike polymers that often are anisotropic glasses at low temperature and liquid crystalline at convenient temperatures in the 0–200 °C range.[1-5,9-13] We have started a program to incorporate unusual mesogenic structures into side chains of flexible main-chain polymers. The advantages of side-chain macromolecular liquid crystals over low molar mass liquid crystals for optical studies are that they may be obtained as transparent, glassy films and they can be processed as thermoplastics.

Acyl derivatives of azacrowns such as the hexakis(4-dodecyloxy)benzamide derivative **2** of [18]-N_6 (**1**) have been reported by Lehn et al.[14] to form "tubular" mesophases. The mesophase of **2** has a hexagonal columnar structure.[14] With the long-range goal of producing polymer liquid crystals with side-chain macrocycles, we have prepared **2** and some close relatives of **2** to determine if they also have mesophases. In a similar investigation Mertesdorf and Ringsdorf[15] found that compounds with an aromatic ring in the side chains of [18]-N_6 had mesophases, and those lacking the aromatic ring did not.

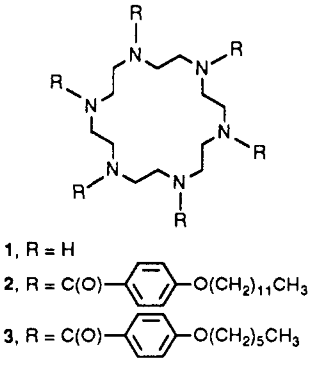


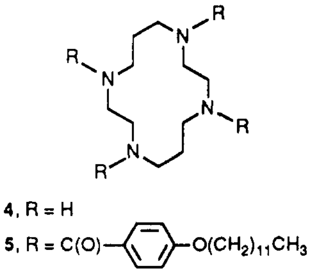
Table I. Phase Transitions of Macrocyclic Amides

compd	expt	transitions,[a] °C (Δ*H*, kcal mol^{-1})
2[b]	PM	C 105 M 134 I
2[b]	DSC	C 102 (30.4) M 131 (0.65) I
2[c]	DSC	C 121.5 (37.5) M 141.5 (0.7) I
2[d]	DSC	C 108 (25.4) M 140 (0.6) I
3	DSC	C 109 I
5	DSC	C_1 133 (6.6) C_2 209 (15.2) I

[a] C = crystal, M = mesophase, I = isotropic. [b] This work. [c] Data from Lehn et al.[14] [d] Data from Mertesdorf and Ringsdorf.[15]

Results

All compounds were characterized by ^1H and ^{13}C NMR spectra and IR spectra, and their purities were tested by thin-layer and high-performance liquid chromatography. The hexakis(4-dodecyloxy)benzamide and hexakis(4-hexyloxy)benzamide derivatives **2**, **3**, and **5** were synthesized from the parent azacrowns and the 4-alkoxybenzoyl chlorides.



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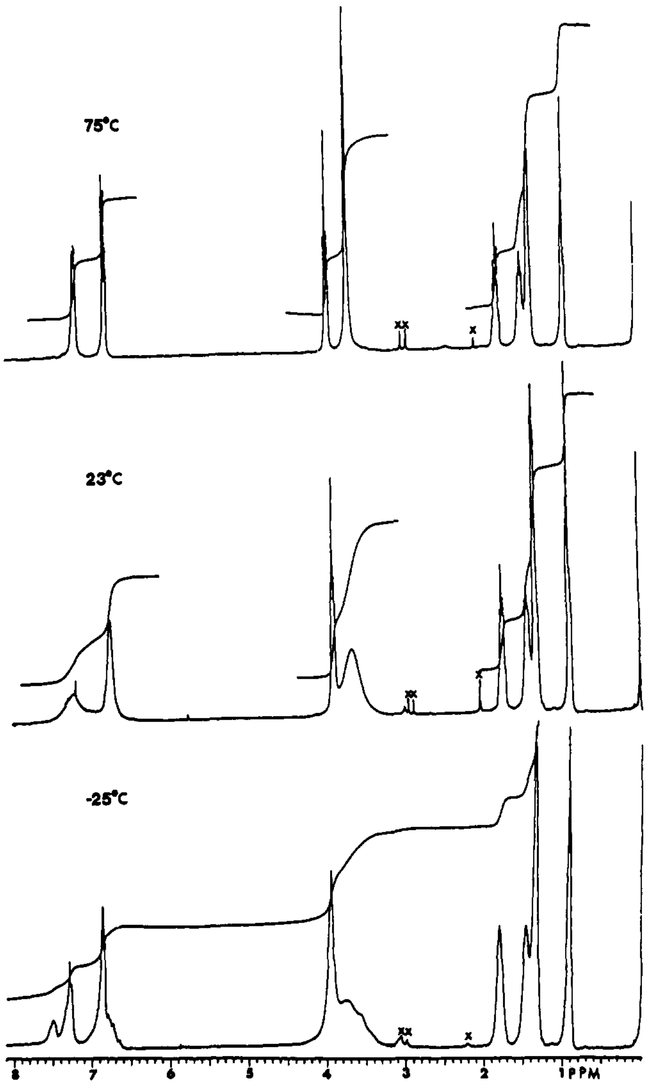

Figure 1. ^{1}H NMR spectra of hexakis(4-(hexyloxy)benzamide) (3). Peaks marked × are due to a trace of *N,N*-dimethylacetamide.

The macrocyclic amides **2**, **3**, and **5** all had temperature-dependent ^{1}H and ^{13}C NMR spectra. Figures 1 and 2 show spectra of **3**. The aromatic protons at 7.2 ppm and carbons at 129 ppm ortho to the amide function and the protons and carbons of the macrocycle at 3.7 ppm and 46–50 ppm, respectively, give broad signals at room temperature. Those signals are sharper when spectra are recorded at 75 °C, and more peaks are seen at −25 °C. Thus **2**, **3**, and **5** undergo conformational changes on the NMR time scale at room temperature, which may be attributed to hindered rotaion about the amide C(O)–N bonds and may also involve conformational changes of the macrocycles. At 75 °C the C–N bond rotations and macrocycle conformational interconversions are fast on the NMR time scale.

Our hexakis(4-dodecyloxy)benzamide of [18]-N_6 (**2**) has a mesophase with a texture like that shown by Lehn,[14] but the phase transition temperatures agree more closely with those of Mertesdorf[15] than with those of Lehn. Our results in Table I are from a purified sample that shows one peak in HPLC and has ^{1}H and ^{13}C NMR spectra with no detectable impurity peaks. The elemental analyses of four different samples of **2** fit the composition of a tetrahydrate. The same analytical results within experimental error were obtained with samples that were isolated directly from column chromatography, isolated from preparative HPLC, and recrystallized and from samples that were dried at either 25 or 80 °C under vacuum. There was a water peak in the infrared spectrum of **2**. Typical differential scanning calorimetry (DSC) thermograms are in Figure 3. The melting transitions of **2**, **3** and **5** appeared only during the first heating cycle. A glass transition appeared in its place during subsequent heating cycles. The mesophase to isotropic transition appeared in second and third heating cycles and in cooling cycles with high precision of ΔH (±0.02 kcal mol^{-1}).

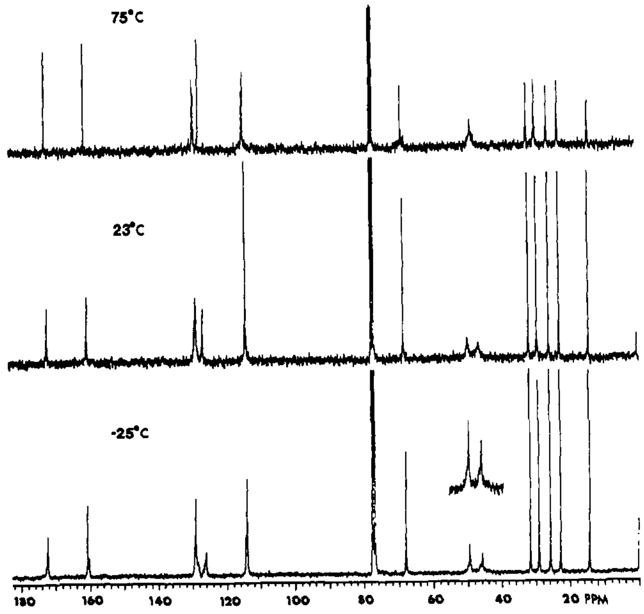

Figure 2. ^{13}C NMR spectra of 3.

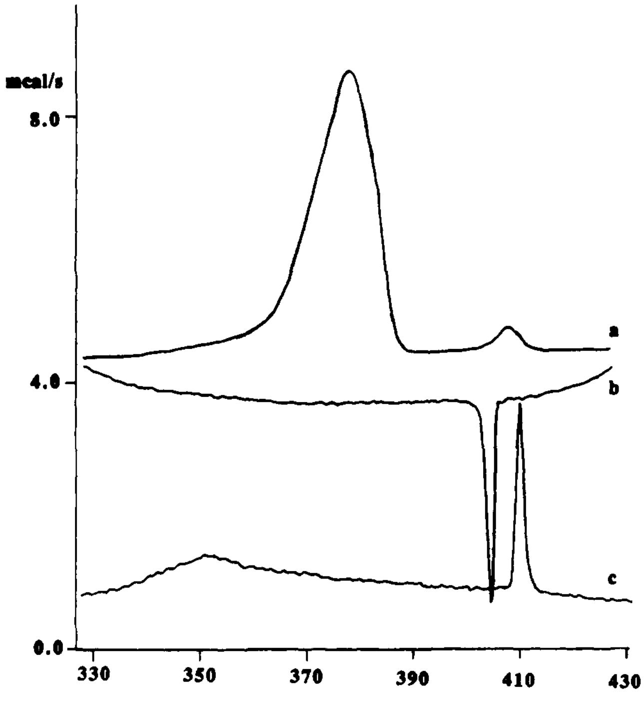

Figure 3. DSC thermograms of 2: (a) first heating; (b) first cooling; (c) third heating, showing T_g at 342 K. The vertical scales of b and c are expanded 4 times relative to that of a.

The hexakis(4-hexyloxy)benzamide of [18]-N_6 (**3**) and the tetrakis(4-dodecyloxy)benzamide of [14]-N_4 (**5**) had no detectable mesophases. By DSC **5** had two transitions, but no change occurred in the birefingence of the sample at the first transition at 133 °C, and the sample did not form droplets of liquid until the melting transition at 209 °C.

Discussion

The phase transition data in Table I for compound **2**, which has a "tubular" mesophase,[14] show how supposedly the same material prepared in three different laboratories can have different properties. Both the transition temperatures and the heats of melting differ. Although some of the differences may be due to different DSC heating and cooling rates, we believe those effects are not large enough to explain the discrepancies. The elemental analyses of our sample fit the composition of a tetrahydrate of **2**, and the IR spectrum but not the ^{1}H NMR spectrum showed a water peak. The sample reported by Lehn had elemental analyses that agreed with calculated values,[16] whereas that of Mertesdorf was 0.76 and 0.94% low on carbon in duplicate analyses and agreed with calculated values for H and N.[17] If our sample is a tetrahydrate, that of Mertesdorf could be a monohydrate. Since the details of sample preparation and purification in the other laboratories are not available, we can identify only those differences between the samples reported here. We did not detect the melting transition in the second and later DSC scans, as the mesophase supercooled to room temperature. Kinetic control of the melting transition is common in DSC of polymer liquid crystals but is not usually reported for low molar mass materials.[18] However, **2** has a molecular weight of 1988.7. Although the transition temperatures differ, our sample had the same microscopic texture as that of Lehn.[14]

The tubular mesophase of **2** is a structural class of discotic mesophases.[14,16] Although the work "tubular" suggests void spaces in the centers of the macrocycles, there is not likely much free volume. The NMR spectra at 23 and −25 °C in Figures 1 and 2 indicate that in solution at low temperature compound **3** has more than one conformation, or there is one conformation of low symmetry.

Mertesdorf and Ringsdorf[15] reported that several acyl derivatives of [14]-N_4, including **5**, and the hexakis(4-dodecanoyl) and hexakis(tetradecanoyl) derivatives of [18]-N_6 had no mesophases, whereas the hexakis(4-dodecyloxy)benzamide **2** and its hexakis(4-tetradecyloxy)benzamide analogue each had one mesophase. Our results confirm theirs.

In conclusion, our results show problems of reproducibility of the preparation of materials such as **2** in different laboratories, most likely due to the difficulty of purification and the retention of water.

Experimental Section

N,*N*-Dimethylacetamide (DMA) was freshly distilled from calcium oxide. All other reagents and solvents were used as received unless noted otherwise.

HPLC analyses were performed with a Waters Model 590 pump, a Rheodyne injector with either a 200- or a 20-μL sample loop, a normal-phase 5-μm silica column (Whatman Partisil 5 for analytical use or Whatman Magnum 9 for semipreparative use), and a Beckman Model 153 analytical 254-nm UV detector fitted with a 10-mm path length flow cell for analytical use or a 2-mm path length cell for semipreparative use. The eluting solvent was 90/10 v/v chloroform/methanol unless noted otherwise.

^{1}H and ^{13}C NMR spectra were recorded at 300.0 and 75.43 MHz with a Varian XL-300 instrument in $CDCl_3$ with internal Me_4Si reference at 22 °C except when noted otherwise. IR spectra were recorded with a Perkin-Elmer 681 instrument. Polarizing microscopy was performed with a Nikon Optiphot-Pol microscope equipped with an Instec hot stage and mkl temperature controller operated with an Apple IIe computer (Instec. Inc., PO Box 7246, Boulder, CO 80306). Photographs were taken with a Nikon N-2000 35-mm single-lens reflex camera. Differential scanning calorimetry was performed with a Perkin-Elmer DSC-2C instrument equipped with a Model 3600 data station. All data were obtained during heating at 20 °C min^{-1} under a nitrogen atmosphere. No transitions were detected at <50 °C because the DSC was calibrated only for experiments starting at or above room temperature.

1,4,8,11-Tetrakis(4-(dodecyloxy)benzoyl)-1,4,8,11-tetraazacyclotetradecane (5). 4-(Dodecyloxy)benzoyl chloride (DBCl) was prepared by stirring a suspension of 4-(dodecyloxy)benzoic acid (Aldrich) in benzene with 2 mol equiv of oxalyl chloride at room temperature for 4 h. Evaporation of the liquid left a solid (mp 35–36 °C) that was used without purification; ^{1}H NMR δ 0.88 (t, 3 H), 1.27 (m, 16 H), 1.46 (m, 2 H), 1.78 (m, 2 H) 3.96 (t, 2 H), 6.86 (d, 2 H), 7.27 (br, 2 H); ^{13}C NMR δ 14.1, 22.7, 25.9, 29.0, 29.3, 29.5, 29.6, 31.9, 68.6, 114.6, 125.1, 134.0, 165.0, 166.9.

A solution of 1.0 mmol of [14]-N_4 (**4**, Aldrich) and 4.0 mmol of 4-(dimethylamino)pyridine (DMAP, Aldrich) in 5 mL of *N*,*N*-dimethylacetamide (DMA) was stirred under argon. A solution of 4.2 mmol of DBCl in 25 mL of DMA was added, and the mixture was kept at 95 °C for 48 h. To the cool solution 200 mL of chloroform was added. The solution was extracted once with 5% aqueous HCl and twice with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and evaporated to give 2.8 g of crude product. Chromatography through 50 g of silica gel gave impurities with 1/1 chloroform/ethyl acetate as eluant, and then with only chloroform as eluant gave 1.36 g of **5**, mp 198–200 °C; ^{1}H NMR δ 0.88 (t, 12 H), 1.27 (m, 64 H), 1.46 (m, 8 H), 1.78 (t, 8 H), 2.09 (br, 4 H), 3.49 (br, 8 H), 3.75 (br, 8 H), 3.96 (t, 8 H), 6.86 (m, 8 H), 7.27 (m, 8 H); ^{13}C NMR δ 14.1, 22.7, 26.1, 29.2, 29.4, 29.5, 29.7, 31.9, ca. 46 (br), 68.1, 114.4, 127.5, 128.7, 160.5, 172.3.

1,4,7,10,13,16-Hexakis[(4-dodecyloxy)benzoyl]-1,4,7,10,13,16-hexaazacyclooctadecane (2). A solution of 100 mg of [18]-N_6 (**1**), the acid chloride from 715 mg of 4-(dodecyloxy)benzoic acid, 0.15 mL of pyridine, and 15 mL of DMA was stirred for 72 h at 95 °C. A white solid precipitated upon cooling, and 400 mg was isolated by filtration. It was purified by silica gel chromatography using 90/10 v/v chloroform/methanol as eluant. The component of highest R_f was isolated and crystallized from 50/50 methanol/diethyl ether to provide a solid that showed only one peak by HPLC analysis; ^{1}H NMR (50 °C) δ 0.88 (t, rel A 14, 18 H), 1.20–1.55 (m, rel A 93, 90 H), 1.77 (m, rel A 14, 12 H), 3.70 (br s, rel A 23, 24 H), 3.96 (t, 12 H), 6.82 (d, 12 H) 7.21 (br s, 12 H) (relative peak areas are given for signals that did not integrate exactly to the expected number of protons); ^{13}C NMR (50 °C) δ 13.9, 22.6, 26.0, 29.2, 29.4, 29.5, 31.9, 48.0, 68.2, 114.4, 127.1, 128.9, 160.7, 172.2; IR (KBr) 3440 (br, H_2O), 2960, 2920, 2850, 1630, 1605, 1500, 1465, 1425, 1300, 1250, 1170, 835, 760 cm^{-1} (all strong and medium absorbance peaks are listed). See Table I for DSC and microscopy data.

Anal. Calcd for $C_{126}H_{198}N_6O_{12}$: C, 76.09; H, 10.03; N, 4.22. Calcd for $C_{126}H_{198}N_6O_{12}\cdot 4H_2O$: C, 73.47; H, 10.01; N, 4.08. Found: C, 73.46, 73.77, 73.65, 73.85; H, 9.93, 10.09, 9.92, 10.01; N, 4.20, 4.01, 4.12, 4.29 (four independent samples).

1,4,7,10,13,16-Hexakis[(4-hexyloxy)benzoyl]-1,4,7,10,13,16-hexaazacyclooctadecane (3). 4-(Hexyloxy)benzoyl chloride (HBCl) was prepared by the method used for DBCl; ^{1}H NMR δ 0.9 (t, 3 H), 1.4 (m, 4 H), 1.5 (m, 2 H), 1.8 (m, 2 H), 4.05 (t, 2 H), 7.0 (d, 2 H), 8.1 (d, 2 H); ^{13}C NMR δ 14.0, 22.6, 25.6, 28.9, 31.5, 68.6, 114.6, 125.2, 134.0, 165.0, 167.1; IR (neat) 3440 br (H_2O), 2930, 2860, 1635, 1610, 1510, 1465, 1425, 1250, 1175, 835, 760 cm^{-1} (all strong and medium absorbance peaks are reported).

A solution of 130 mg (0.50 mmol) of **1**, 725 mg (3.0 mmol) of HBCl, 370 mg (3.0 mmol) of DMAP, and 20 mL of DMA was stirred for 42 h 90 °C. A white precipitate of DMAP–HCl was filtered out. The filtrate was mixed with chloroform, extracted twice with 25 mL of 10% HCl, washed with saturated NaCl, dried over anhydrous $MgSO_4$, and evaporated to 700 mg of a viscous oil which solidified upon standing. The product (500 mg) was chromatographed through 75 g of neutral alumina with di-

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chloromethane to remove less polar impurities and with 2% ethanol in dichloromethane to elute **3**, 450 mg (62%) of white solid, mp 109 °C (DSC), which showed one peak by HPLC analysis; ^1H NMR ($CDCl_3$, 75 °C) δ 0.91 (t, 18 H), 1.34 (m, 12 H), 1.46 (t, 12 H), 1.77 (t, 12 H), 3.70 (br s, 24 H), 3.96 (t, 12 H), 6.82 (d, 12 H), 7.21 (d, 12 H); ^{13}C NMR ($CDCl_3$, 80 °C) 13.7, 22.5, 25.7, 29.2, 31.5, 48.0 (br), 68.4, 114.7, 127.5, 128.9, 160.8, 172.2. NMR spectra at three temperatures are shown in Figure 1.

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Preparation, Purification, and Densification of Zinc Sulfide Powder from Organometallics

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Zinc sulfide powders were prepared from diethylzinc and hydrogen sulfide in toluene solution at −20 °C. The powder consisted of agglomerates of 0.1-μm-sized particles. The residual zinc ethyl group content was determined by acid hydrolysis followed by gas chromatography and varied from 10^{-4} to 3 mol % depending on reaction conditions. Reactivity varies with alkyl group as di-*tert*-butylzinc > diethylzinc > dimethylzinc. Toluene and 2-propanethiol were identified as organic impurities with 2-propanethiol originating in the H_2S reagent. Adventitious tetrahydrofuran impurity was converted to tetrahydrothiophene upon heating at 137–159 °C. Organic impurities were oxidized by treatment of the powder with O_2 at 400 °C or 1 mol % O_3 in O_2 at 25 °C. Particle growth was evident in the O_2-treated sample but not in the O_3-treated sample. The oxidized samples contained about 2 mol % $ZnSO_4$, and EPR spectra provided evidence for SO_2^- radicals. The $ZnSO_4$ impurity was converted to ZnO by heating at 800 °C. Hot isostatic pressing of the treated powders at 775 °C produced fragmented opaque compacts with grain sizes varying from 0.1 to 0.5 μm. The densified samples exhibited about twice the hardness of commercial Raytran ZnS but only half the fracture toughness.

Introduction

Zinc sulfide is an important infrared optical material.[1,2] Synthetic routes to ZnS vary from room-temperature precipitation in aqueous solutions to high-temperature solid-state reactions. High-temperature methods tend to give highly crystalline products with large grain sizes, while low-temperature syntheses can yield powders of uniform submicron particles.[3-6] The latter are desirable for producing high-quality fine-grained ceramics.[7] Aqueous preparations can suffer from oxide impurities due to hydration and also from anionic impurities.

We are interested in organometallic routes to ZnS powders. Organometallic reagents have potential advantages of high purity, high reactivity, and use in nonaqueous environments. Dimethylzinc and diethylzinc have been used to make ZnS thin films by reaction with H_2S, in the temperature range 350–750 °C.[8-10] Ethyl(*tert*-butylthio)zinc pentamer forms submicron particles and single-crystal whiskers of ZnS when subjected to a two-step treatment with H_2S at 22 and 500 °C.[11] Oligomeric bis(methylthio)zinc forms ZnS when heated at 260–280 °C.[12] We have examined the utility of the reaction of homoleptic metal alkyl complexes with H_2S in toluene solution for the preparation of metal sulfide powders.[13] In this paper we describe our efforts to synthesize submicron ZnS powder, purify it of organic impurities, and convert it into a fine-grained ZnS ceramic with potentially improved mechanical properties. Preliminary reports have appeared[14-16] as well as an independent report on the preparation of ZnS pow-

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