(C-O-C), 1330 cm^{-1} (C-N). UV: max, nm (log ϵ), 425 (4.43) in DMF. Fl: max, 472.2 nm in DMF.

Compound IIc. Greenish yellow needles (from methylbenzene), mp 311-312 °C. IR: 1690 and 1655 cm^{-1} (C=O), 1254 cm^{-1} (C-O-C), 1350 cm^{-1} (C-N). MS: *m/e* (TI%), 363 ($M^{\bullet+}$, 100), 319 (4.26), 270 (4.01), and 187 (3.84). UV: max (nm) (log ϵ), 423 (4.39) in DMF. Fl: max 472 nm in DMF.

Compound IId. Deep greenish yellow needles (from methylbenzene), mp 213-214 °C. IR: 3300 cm^{-1} ($-NH_2$), 1660 and 1590 cm^{-1} (C=O), 1335 cm^{-1} (C-O-C). UV: max (nm) (log ϵ), 428 (4.44) in DMF. Fl: max 474.6 nm in DMF.

Compound IIe. Greenish yellow needles (from DMF), mp 302-303 °C. IR: 1760 and 1720 cm^{-1} (C=O), 1230 cm^{-1} (C-O-C), 1295 cm^{-1} (C-N). UV: max nm (log ϵ), 425 (4.58) in DMF. Fl: max 474.6 nm in DMF.

Compound IIf. Greenish yellow needles (from methylbenzene), mp 294-296 °C. IR: 1760 and 1720 cm^{-1} (C=O), 1230 cm^{-1} (C-O-C), 1295 cm^{-1} (C-N). MS: *m/e* 377. UV: max (nm) (log ϵ), 424 (3.98) in DMF. Fl: max 473.6 nm in DMF.

Compound IIIa (IIIa-1 and IIIa-2). Orange-yellow needles (from methylbenzene), mp 235-236 °C, IR: 1660 cm^{-1} (C=O), 1620 cm^{-1} (C=N), 1450 cm^{-1} ($>CH_2$), 1240 cm^{-1} (C-O-C). UV: max (nm) (log ϵ), 426 (3.97) in DMF. Fl: max 474.7 nm in DMF.

Compound IIIb (IIIb-1 and IIIb-2). Orange-red needles (from DMF), mp 320 °C. IR: 1680 cm^{-1} (C=O), 1630 cm^{-1} (C=N), 1240 cm^{-1} (C-O-C). MS: *m/e* (TI%), 360 ($M^{\bullet+}$, 100), 180 (3.67), 44 (6.94), 32 (3.55), 28 (10.54), 18 (8.72). UV: max (nm) (log ϵ), isomer IIIb-1 479 (4.47) and isomer IIIb-2 453 (4.45) in DMF. Fl: max (nm), isomer IIIb-1 531.5 and isomer IIIb-2 499 in DMF.

The elemental analyses of the above compounds are in fair agreement with the calculated values.

The instruments used for analysis are as follows: Mp-Xh (Beijing) for the melting point determination; Shimadzu UV-365 for the recording of the visible spectra; Shimadzu IR-450 for the infrared spectra; Hitachi M-850 for the fluorescence; Hitachi M-80 for mass spectra; elemental analyses were performed by ECICT Analytic Center.

Registry No. 1, 81-84-5; 2, 4053-08-1; 3, 111669-59-1; 4, 111669-60-4; I, 36310-05-1; IIa, 35340-39-7; IIb, 111669-61-5; IIc, 111669-62-6; IId, 111669-63-7; IIe, 111669-64-8; IIf, 111669-65-9; III-1a, 111669-66-0; III-1b, 55231-31-7; III-2a, 111669-67-1; III-2b, 55231-32-8; $MeNH_2$, 74-89-5; $PhNH_2$, 62-53-3; m-$NH_2C_6H_4NH_2$, 108-45-2; p-$ClC_6H_4NH_2$, 106-47-8; p-$MeC_6H_4NH_2$, 106-49-0; $H_2N(CH_2)_2NH_2$, 107-15-3; o-$H_2NC_6H_4NH_2$, 95-54-5; o-nitrophenol, 88-75-5; cyclohexylamine, 108-91-8.

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Synthesis of Some Metal Phthalocyaninetetrakis(*N*-cyclopropylsulfonamides)

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The synthesis and characterization of 10 new metal phthalocyaninetetrakis(*N*-cyclopropylsulfonamides) are reported. Bivalent Zn, Cu, Co, Ni, and Fe were used as 4-coordinated central metals. ^1H NMR, IR, and thermogravimetric measurements studies of both series of compounds are reported.

In continuation of our efforts directed toward further preparations and applications of metal and metal-free phthalocyaninetetrakis(carboxamides) and -(sulfonamides) (*1-4*), we have undertaken the synthesis of 10 novel metal phthalocyaninetetrakis(cyclopropylsulfonamides) (**3a-e**) and (**4a-e**) which were obtained by the reactions of metal phthalocyaninetetrakis(sulfonyl chlorides), (**1a-e**) and (**2a-e**), with cyclopropylamine. Zn, Cu, Co, Ni, and Fe were used as bivalent 4-coordinated central metals. The thermal stabilities of cyclopropane in compounds **3a-e** and **4a-e** was examined.

Experimental Section

The IR spectra were obtained on a Pye Unicam SP-300 infrared spectrophotometer using KBr disk.

† Ph.D. Thesis, University of Baghdad, 1986.

^1H NMR spectra were obtained on a 80-MHz NMR spectrometer in hexadeuteriated dimethyl sulfoxide using tetramethylsilane as internal reference standard.

Satisfactory elemental analysis, molecular weight measurements, and TLC were obtained for all new compounds.

Elemental analyses were performed on Hereaus C,H,N-rapid computer HP 85 by Samara Laboratory, Samara, Iraq, and submitted for review.

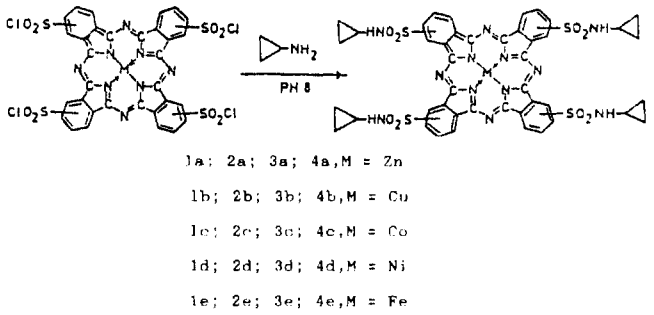
Differential thermal analyses (DTA) of all new compounds were carried out by Hereaus thermal analyzer TA 500; α-Al_2O_3 at 1300 °C was used as reference material. Heating in the range 25-500 °C was programmed at a rate of 10 °C/min under inert nitrogen atmosphere.

Metal phthalocyanine-3,3′,3″,3‴-tetrakis(sulfonyl chlorides) (**1a-e**) were prepared as follows: **1a** was synthesized according to Clark's method (*5*); compounds **1b-d** were prepared by the method given in the literature (*6*); **1e** was obtained according to the procedure of Mayhew (*7*). Metal phthalocyanine-4,4′,4″,4‴-tetrakis(sulfonyl chlorides) (**2a-e**) were prepared as reported (*5*) (Scheme I).

Metal Phthalocyanine-3,3′,3″,3‴-tetrakis(N-cyclopropylsulfonamides) (3a-e). In each treatment (30 g, 29 mmol) of the corresponding compounds (**1a-e**) were added over a period of 30 min at 0 °C to a stirred solution of 8.5% cyclopropylamine and water (100 mL). The mixture was then

0021-9568/88/1733-0529$01.50/0

Scheme I



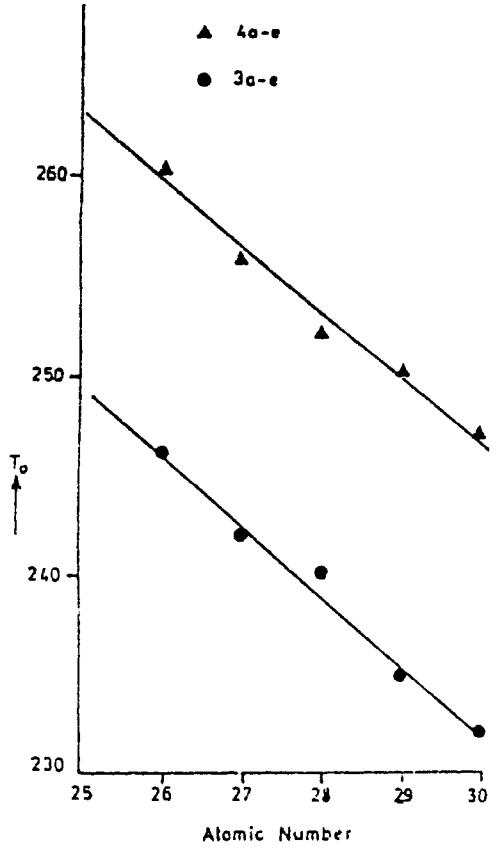


Figure 1. Relationship between pyrolytic cyclopropyl ring opening temperatures and metal atomic numbers for compounds **3a–e** and **4a–e**.

heated to 45–47 °C for 3 h. During this reaction the pH was kept constant at 8 by adding 2 N NH_4OH. The solution was then acidified with 10% HCl (60 ml) and left to stand for 1 h at room temperature. The precipitate was filtered off, washed with water, and then dried under vacuum to yield **3a–e**. IR (KBr) 3200–3300 (NH); 1030–1040, 1440–1460 (cyclopropyl); 1155–1160, 1320–1330 (C–SO_2–N); 890–930 (S–N) and 385–400 (M–N) cm^{-1}. Yields, ^1H NMR data, and DTA results are given in Table I. Figure 1 shows the relationship between cyclopropyl ring opening temperature (T_0) and the atomic number of the corresponding metal.

Table I. Yields and Physical Properties of the Compounds Prepared

compd	yield, %	^1H NMR (DMSO-d_6) δ 4 $(CH_2)_2$	4 CH	4 NH[a]	12 H_{arom}	cyclopropyl ring opening temp, T_0, °C
3a	70	0.668 (m)	2.43 (m)	4.46	8.12 (m)	232
3b	80	0.70 (m)	2.48 (m)	4.40	8.11 (m)	235
3c	65	0.54 (m)	2.51 (m)	4.36	8.18 (m)	240
3d	60	0.70 (m)	2.52 (m)	4.20	8.07 (m)	242
3e	75	0.51 (m)	2.48 (m)	3.54	8.06 (m)	246
4a	80	0.42 (m)	2.35 (m)	4.32	7.58 (m)	247
4b	66	0.54 (m)	2.42 (m)	3.97	7.39 (m)	250
4c	78	0.47 (m)	2.43 (m)	3.58	8.05 (m)	252
4d	64	0.55 (m)	2.35 (m)	3.99	7.90 (m)	256
4e	70	0.43 (m)	2.42 (m)	3.36	7.99 (m)	260

[a] Broad signals assigned for NH protons.

Compounds **4a–e** was prepared starting with **2a–e** in a similar manner as described above for compounds **3a–e**.

Metal Phthalocyanine-4,4′,4″,4‴-tetrakis(N-cyclopropylsulfonamides) (4a–e). IR (KBr) 3250–3400 (NH); 1035–1040, 1450–1480 (cyclopropyl); 1160–1165, 1330–1335 (C–SO_2–N); 910–950 (S–N) and 400–420 (M–N) cm^{-1}. Yields and ^1H NMR data are reported in Table I. DTA data are given in Table I and Figure 1.

Registry No. **1a**, 114251-83-1; **1b**, 14518-21-9; **1c**, 114251-84-2; **1d**, 14325-19-0; **1e**, 114251-85-3; **2a**, 114251-86-4; **2b**, 28802-09-7; **2c**, 107011-09-6; **2d**, 105766-71-0; **2e**, 114251-87-5; **3a**, 114251-88-6; **3b**, 114251-89-7; **3c**, 114251-90-0; **3d**, 114251-91-1; **3e**, 114251-92-2; **4a**, 114251-93-3; **4b**, 114251-94-4; **4c**, 114251-95-5; **4d**, 114251-96-6; **4e**, 114251-97-7; cyclopropylamine, 765-30-0; phthalocyanine-3,3′,3″,3‴-tetrakis(sulfonyl chloride), 114273-29-9; phthalocyanine-4,4′,4″,4‴-tetrakis(sulfonyl chloride), 75922-27-9.

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Synthesis of 4-Aminopyrimido[4′,5′:4,5]thieno[2,3-*b*]quinolines

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Compounds containing 4-aminothieno[3,2-*d*]pyrimidine in a novel tetracyclic condensed quinoline system are synthesized for evaluating their blood platelet aggregation inhibition activity.

A number of 4-aminothieno[3,2-*d*]pyrimidines have been found to exhibit blood platelet aggregation inhibition activity (*1–3*). We report herein the synthesis of 4-aminopyrimido-[4′,5′:4,5]thieno[2,3-*b*]quinoline (IV) and its derivatives (V, VII–X) which contain the thieno[3,2-*d*]pyrimidine structure in

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