SYNTHESIS OF METAL FREE PHTHALOCYANINETETRAKIS (N-CYCLOPROPYLSULFONAMIDES)

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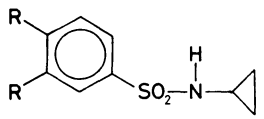
Metal free phthalocyaninetetrakis (N-cyclopropylsulfonamides) have been synthesized and their ^{1}H NMR, IR and thermogravimetric studies were reported.

Derivatives of metal and metal free phthalocyanine have attracted considerable attention in recent years, due to their great success as colouring matters[1-7]. In connection with our earlier reports about the synthesis of some metal phthalocyaninetetrakis (N-sulfonamides) and (carboxamides)[8,9], we report here the synthesis of metal free phthalocyaninetetrakis (N-cyclopropylsulfonamides) in which the cyclopropylsulfonamide groups are attached to the 3,3′,3″,3‴- and 4,4′,4″,4‴-positions respectively. Compounds *I* and *II* have been prepared, in order to compare their



I, R = H
II, R = COOH

^{1}H NMR and IR data with those of metal free phthalocyaninetetrakis (N-cyclopropylsulfonamides). The synthesis of metal free phthalocyaninetetrakis (sulfonic acids) *IIIa* and *IVa* have been carried out according to the method described in the literature by Fukada et al.[10]. Treatment of *IIIa* and *IVa* with thionylchloride, at 80–85°C for 2 h, yielded *IIIb* and *IVb*. Reactions of *IIIb* and *IVb* with aqueous cyclopropylamine at pH 8 led to precipitation of *IIIc* and *IVc*.

The ^{1}H NMR spectra for the metal free macrocycles showed that compounds substituted at 4-positions *IVb* and *IVc* exhibited absorption at higher fields than the 3-position isomers, *IIIb* and *IIIc* (Table I). Each of the compounds gave singlets ranging at δ 6·30–6·44 due to NH_b protons, attached to the isoindole units and another singlets at δ 7·00–7·21 assigned to NH_a protons connected to the quinoid part

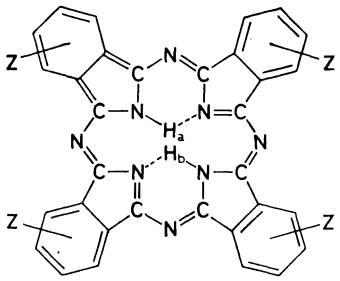
TABLE I

Characteristics of prepared compounds

Compound Yield, %	Formula M.w. (found[a]/required)	Calculated/Found % C	 % H	 % N	^{1}H NMR 4 $(CH_2)_2$ 4 CH	 NH_b NH_a	 4 NH^b 12 H arom.	IR N–H S–N	 $C–SO_2–N$	 –CH. $.(CH_2)_2$
IIIb	$C_{32}H_{14}Cl_4N_8O_8S_4$	42·30	1·54	12·33	—	6·40 s	—	3 200—3 300	1 160	—
76	911/908·6	42·84	1·81	12·35		7·03 s	7·86 m	—	1 330	
IVb	$C_{32}H_{14}Cl_4N_8O_8S_4$	42·30	1·54	12·33	—	6·30 s	—	3 250—3 400	1 165	—
70	910/908·6	42·24	1·61	12·45		7·00 s	7·84 m	—	1 340	
IIIc	$C_{44}H_{38}N_{12}O_8S_4$	53·32	3·86	16·96	0·34 m	6·44 s	4·70 m	3 150—3 300	1 160	1 035
68	995/991·1	53·90	3·97	16·53	2·11 m	7·21 s	7·89 m	890	1 335	1 440
IVc	$C_{44}H_{38}N_{12}O_8S_4$	53·32	3·86	16·96	0·31 m	6·36 s	3·69 m	3 250—3 400	1 165	1 035
63	994/991·1	52·68	3·67	17·02	2·08 m	7·03 s	7·78 m	910	1 345	1 455

[a] DMSO freezing point depression. [b] Broad signals assigned for sulfonamide-NH protons, all NH protons disappeared by deuterium exchange.

of the phthalocyanine ring. Metal free phthalocyanine showed singlet for NH_b proton at δ 6·44 and a second singlet at δ 7·03 for NH_a proton, which disappeared upon deuterium exchange. These results are in accordance with the structural assignment of metal free phthalocyanine, made by Linstead et al.[11]. On the other hand the down field shift of these signals indicates that these protons are situated out of the plane of the molecule and are not affected by the ring current. Both facts are in good agreement with the X-ray results obtained by Robertson[12]. ^{1}H NMR signals for all compounds listed in Table I are located at slightly higher field than those shown by metal phthalocyaninetetrakis (N-cyclopropylsulfonamides) (Central metals: Cu, Co, Ni, Zn and Fe) reported in previous paper[9]. In addition, all ^{1}H NMR-signals for the 3-substituted compounds *IIIb*, *IIIc* appeared at lower field than the 4-position isomers *IVb*, *IVc* (Table I).



III, Z in position 3
IV, Z in position 4

In formulae *III*, *IV*: *a*, Z = SO_3H *b*, Z = SO_2Cl *c*, Z = SO_2NH—

IR-spectral data showed that metal free phthalocyaninetetrasulfonyl chloride *IIIb* and metal free phthalocyaninetetrakis (N-cyclopropylsulfonamide) *IIIc* absorb in general at lower frequencies than the 4-position isomers *IVb*, *IVc* (Table I). Higher field shift of the ^{1}H NMR signals of the latter compounds may be due to their reduced physical hindrance and higher aggregation than the former isomers[13,14]. However, molecular weight determinations by freezing point depression method using DMSO as solvent gave molecular weight consistent with the monomer form of each compound.

Pyrolytic cyclopropyl ring opening temperature (T_o) for compound *IVc* was higher (230°C) than that found for the 3-position isomer *IIIc* (220°C). Compounds containing 4-coordinated bivalent metals (Cu, Co, Ni, Zn and Fe) in the center of the molecule showed even higher T_o range (230–260)°C (ref.[9]).

EXPERIMENTAL

The IR spectra were measured on a Pye Unicam SP-300 Infrared spectrophotometer in KBr disc. ^{1}H NMR-spectra were taken on a 80 MHz NMR-spectrometer in hexadeutrated dimethyl sulfoxide using tetramethyl silane as internal reference standard. Elemental analyses were performed on Hereaus C,H,N-rapid computer H.P. 85 by Samara Laboratory, Samara, Iraq. Thermal analyses were carried out by Hereasu Thermal analyser TA-500. α-Al_2O_3 excitated at 1 300°C was used as reference material. Heating program from (25—500°C) at heating rate 10°C/min under inert nitrogen atmosphere was used.

N-Cyclopropyl Benzenesulfonamide (*I*)

Cyclopropylamine (2 ml) was added to benzene–sulfonylchloride (1 g) in 25 ml dry benzene. The solution was shaken and allowed to stand for 20 min, then evaporated, the product was recrystallized twice from ethanol (0·85 g, 71%) m.p. 55—56°C (needles). ^{1}H NMR: 0·43 m (2 CH_2): 2·04 m (CH); 3·32 d (NH); 7·5 m (5 H arom.). IR, ν_{max} (cm^{-1}): 3 200 (NH); 1 160, 1 320 (C–SO_2–N); 1 020, 1 420 (cyclopropyl); 890 (S–N). For $C_9H_{11}NO_2S$ (197·3) calculated: 54·80% C, 5·62% H, 7·10% N; found: 54·71% C, 5·42% H, 7·21% N.

4-(N-Cyclopropylsulfamoyl) Phthalic Acid (*II*)

Cyclopropylamine (3 ml) was added to a solution of 2 g of phthalic acid-4-sulfonyl chloride[15] in 30 ml dry benzene. The mixture was stirred for 1 h at room temperature and evaporated. The product was recrystallized twice from ethanol; (0·7 g, 65%) m.p. 165—170°C (needles). ^{1}H NMR: 0·71 m (2 CH_2); 2·46 m (CH); 3·32 d (NH); 8·29 m (3 H arom.). IR, ν_{max} (cm^{-1}): 3 300 (NH); 1 160, 1 330 (C–SO_2–N); 1 030, 1 450 (cyclopropyl); 900 (S–N). For $C_{11}H_{11}NO_6S$ (285·3) calculated: 46·31% C, 3·89% H, 4·91% N; found: 46·21% C, 3·80% H, 4·96% N.

Metal Free Phthalocyaninetetrakis (Sulfonyl Chlorides) (*IIIb*, *IVb*)

Thionyl chloride (7 ml) was added to 5 g (6·0 mmol) metal free phthalocyanine-3,3′,3″,3‴- and 4,4′,4″,4‴-tetrakis (sulfonic acids) (*IIIa* or *IVa*)[10]. The mixture was stirred and heated to 80 to 85°C for 2 h, then cooled to room temperature and poured onto crushed ice. The precipitate which was filtered off was washed with 1% HCl, recrystallized twice from methanol–2-propanol mixture (3 : 1) and dried under vacuum. Characteristics of the products are summarized in Table I.

Metal Free Phthalocyaninetetrakis (N-Cyclopropylsulfonamides) (*IIIc*, *IVc*)

Sulfonyl chlorides *IIIb*, *IVb* (8 g, 6·24 mmol) were added portionwise to a stirred solution of 8·5% cyclopropylamine and water (100 ml). The mixture was then heated to 45°C for 2 h. During the reaction the pH of the reaction mixture was kept constant at 8 by adding 2M-NH_4OH. The solution was then cooled to room temperature and acidified with 10% HCl. The precipitate was filtered off, washed with water and recrystallized three times from methanol–2-propanol mixture (3 : 1) and dried under vacuum. Characteristics of the products are summarized in Table I.

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