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LETTERS TO THE EDITOR

Triarenotetraazachlorins: A New Class of Dyes of the Near-IR Range

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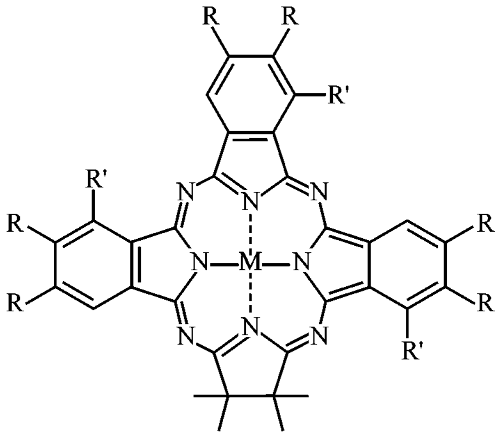
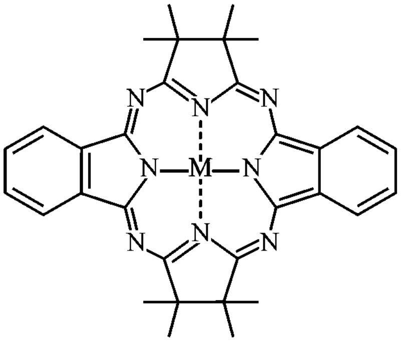
Previously we described the routes to the tetraazachlorin system involving reaction of succinimide with lithim alcoholates [1] or the Diels–Alder reaction of unsubstituted tetraazaporphine with some dienes of the anthracene series [2]. Here we report on mixed condensation of phthalogens (primarily dinitriles of aromatic *ortho*-dicarboxylic acids) with substituted succinonitriles as a route to annelated analogs of tetraazachlorin, triarenotetraazachlorins. It is known [3, 4] that reaction of succinimide or succinonitrile with phthalonitrile yields a mixture of tribenzotetraazaporphine and phthalocyanine. Indeed, instead of the expected tribenzotetraazachlorin, from the reaction of succinonitrile with phthalonitrile in the presence of lithium dimethylaminoethylate we isolated a mixture of di- and tribenzotetraazaporphine and phthalocyanine. Benzo-substituted tetraazachlorin and tetraazabacteriochlorin forming in the course of the synthesis proved to be less resistant to oxidation than the unsubstituted tetraazachlorin, which is apparently due to extension of the π system of the macroring. To prepare tribenzotetraazachlorins that would be resistant to oxidation, we took in the reaction instead of unsubstituted succinonitrile its derivatives with the stabilized C–C bond: tetramethylsuccinonitrile, which is readily available as the product of thermal decomposition of azobis(isobutyronitrile), and 2,2'-dimethylbutanodinitrile. The tribenzotetraazachlorins formed from these nitriles can undergo dehydrogenation only with migration of methyl groups.

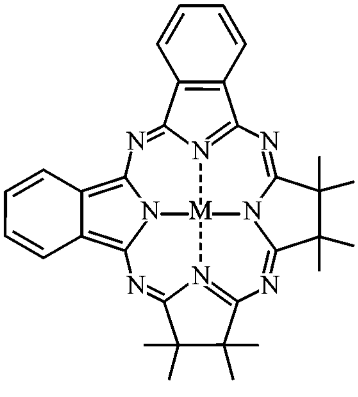
On refluxing of phthalonitrile with tetramethylsuccinonitrile (1 : 1 ratio) in dimethylaminoethanol in the presence of lithium dimethylaminoethylate for 20 h, tetramethyltribenzotetraazachlorin **Ia** is formed in a small yield (~2%) along with phthalocyanine which is the major product. Better results were obtained when the condensation of these nitriles was performed in refluxing quinoline with metal salts (VCl_3, CuCl, $NiCl_2$, etc.) in the presence of catalytic amounts of ammonium molybdate. For example, the 2-h reaction of equimolar amounts of tetramethylsuccinonitrile and phthalonitrile with VCl_3 in refluxing quinoline gave a mixture of vanadyl phthalocyanine and three new vanadyl compounds: tetramethyltribenzotetraazachlorin (**Id**, yield 15%, long-wave maximum λ_{max} 763 nm), octamethyldibenzotetraazabacteriochlorin (**IId**, yield



Ia–Id, **IVc**, **Vc**, **Vd**



IIc, **IIc**



IIIc, **IIIc**

M = HH (**a**), Cu (**b**), Ni (**c**), VO (**d**). R = R' = H (**Ia–Id**); R = CH=CH–CH=CH, R' = H (**IVa**), Ph (**Vc, Vd**).

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~1%, λ_{max} 898 nm), and, presumably, octamethyldibenzotetraazaisobacteriochlorin (**IIId**, yield ~1%, λ_{max} 721 nm), which were separated by chromatography on silica gel. Variation of the reaction conditions (reactant ratio, temperature, heating time) led only to a certain increase in the yield of tetramethyltribenzotetraazachlorin (to 21%) or to its drastic decrease; we failed to increase the yield of bacteriochlorins.

Metal complexes of tetramethyltribenzotetraazachlorin are also formed with the use of other *o*-phthalic acid derivatives as phthalogens, such as anhydride or imide in the presence of urea and 1,3-diiminoisoindoline; as solvents were used sulfolane, dimethylaminoethanol, and nitrobenzene.

Reactions of tetramethylsuccinonitrile with derivatives of 2,3-naphthalenedicarboxylic acid (anhydride, imide, or their 1-phenyl-substituted analogs; 2,3-dicyanonaphthalene) in refluxing quinoline or sulfolane in the presence of metal salts (VCl_3, $NiCl_2$) and catalytic amounts of ammonium molybdate give a mixture of the corresponding metal complexes of 2,3-naphthalocyanine and β,β,β'β'-tetramethyltri-2,3-naphthotetraazachlorin (**IVc**) or β,β,β',β'-tetramethyltri-2,3-(1-phenylnaphtho)tetraazachlorin (**Vc**, **Vd**), whose yield is 6–8%. The long-wave absorption maximum of the 1-phenyl-substituted vanadyl complex **Vd** lies at 871 nm, and that of the 1-phenyl-substituted nickel complex **Vc**, at 819 nm. It should be noted that in the case of $NiCl_2$ the electronic absorption spectrum of the reaction mixture also contains a band with λ_{max} 900 nm, apparently belonging to the nickel complex of octamethyldi-2,3-(1-phenylnaphtho)tetraazabacteriochlorin, which, however, was not isolated pure.

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