

*Review*

## **Pyrrolyl Squaraines—Fifty Golden Years**

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**Abstract:** Pyrrolyl squaraines, both dyes and polymers, were first reported in 1965 and since then a fascinating body of work has been produced investigating the chemistry of these interesting molecules. A major aspect of these molecules that makes them so appealing to those researchers who have contributed to this field over the last 50 years is their chemical versatility. In this review, subjects, such as the synthetic history, an understanding of the molecular structure, an overview of the optical properties, a discussion of both the electrical conduction properties, and magnetic properties, plus use of the particles of pyrrolyl squaraines, are presented. Furthermore, previously published results are not just presented; they are in certain cases collated and used to both highlight and explain important aspects of pyrrolyl squaraine chemistry.

**Keywords:** squaraine; pyrrole; pyrrolyl squaraine; squaraine dye; polysquaraine

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### **1. Introduction**

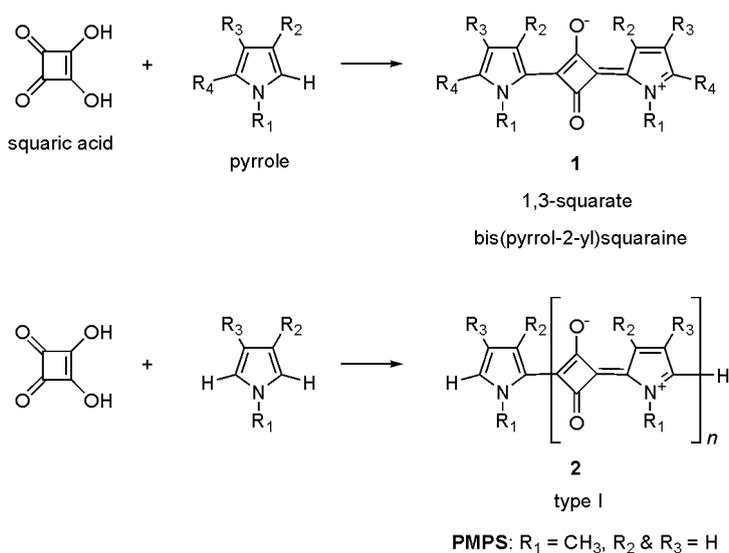
Pyrrolyl squaraines, or compounds that are the result of a condensation reaction between a pyrrole (or linked bispyrrole) derivative and squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) are fascinating and have been found to possess many metal-like properties. Research involving pyrrolyl squaraines has been disseminated in the academic press for the last 50 years [1–70] and in many ways the history of pyrrolyl squaraines is representative of the history of all squaraine compounds in that although during certain periods the focus of scientific endeavour has most certainly been on other squaraine variants, two of the first three squaraine types reported were pyrrolyl squaraines and some of the latest squaraine research involves pyrrolyl squaraines. Over this period of time a number of reviews have been written on squaraine compounds as a whole, some broad and all encompassing, some personal

research accounts, including within them, where relevant, mention of pyrrolyl squaraines [71–82], but thus far pyrrolyl squaraines, as their own unique subset of squaraine chemistry, have not been exclusively presented in a review (although a major portion of pyrrolyl squaraine chemistry can be learned by reading [74,78,82]). This article will attempt to be, as best it can, as concise and definitive as possible in terms of representing the papers that have been published on pyrrolyl squaraines and it will also attempt to collate relevant information from those publications to highlight certain important aspects of pyrrolyl squaraine chemistry. However, like previous reviews on squaraine compounds this review will undoubtedly miss something, especially papers released within this 50th year of published squaraine research.

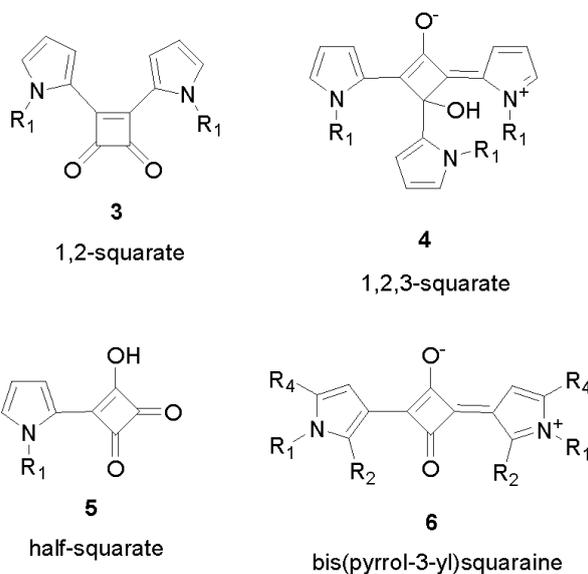
## 2. Synthesis

### 2.1. The Beginning: The First Three Years

The original Treibs and Jacob paper published in *Angewandte Chemie (Int. Ed.)* in 1965 reported the preparation of red-violet coloured 1,3-bis(pyrrol-2-yl)squaraine dyes **1** (if one of the pyrrole  $\alpha$ -positions did not contain a hydrogen atom), blue to blue-green coloured insoluble polymers of a pyrrole-derived polysquaraine **2** (if both pyrrole  $\alpha$ -positions contained hydrogen atoms), and a deep red-violet coloured squaraine dye based on phloroglucinol [1]. Treibs and Jacob defined these reactions as condensation/polycondensation reactions that did not require the removal of the produced water. The syntheses involved warming/refluxing either in ethanol for the pyrrolyl squaraines or acetic acid for the phloroglucinol squaraine. In the first three years of pyrrolyl squaraine research, either ethanol or acetic acid were the preferred solvents [1–3]. This simplicity of reaction may be the reason why pyrrolyl squaraines feature so prominently in these early years of squaraine research, although only a year after the initial Treibs and Jacob paper subsequent squaraine syntheses were reported that involved removal of the formed water by azeotropic distillation in butanol/benzene solvent mixtures [83,84]. Additionally reported in the first Treibs and Jacob paper was a note that the pyrrolyl squaraines under investigation discoloured in solutions of amines in ethanol [1]. This was the first observation that squaraine dyes are susceptible to attack by strong nucleophiles, with a solution to this problem taking almost 40 years to be reported; in 2004 with the preparation of squaraine rotaxanes [85].



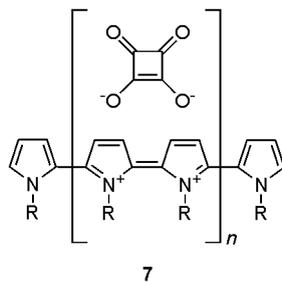
More extensive chemistry on pyrrolyl squaraines was reported in 1966 by Treibs and Jacob [2], and included (among other things) a proposal for the reaction pathway to produce a pyrrolyl squaraine, infrared analysis of the squarate  $C=O$  resonance, synthesis of 1,2-bis(pyrrolyl)squaraine dyes **3**, and a note that a third pyrrole could be reacted with a 1,3-bis(pyrrolyl)squaraine to create a 1,2,3-tris(pyrrolyl)squaraine dye **4**. A detailed description of all of the precise squaraine variants can be found in [82]. The first published review of squaraine chemistry was reported later that same year by Maahs and Hegenberg [71], which included a section on pyrrolyl squaraines. The final Treibs and Jacob article on pyrrolyl squaraines was published in 1968 and reported syntheses of (what is now commonly known as) the half-squaraine **5** and also 1,3-bis(pyrrol-3-yl)squaraines where the pyrrole was attached to the squarate group at the pyrrole 3-position **6** [3] (when the  $R_2$  and  $R_4$  positions are substituted). The papers on pyrrolyl squaraines published during the three years from 1965 to 1968 created a foundation of synthetic information upon which all subsequent papers on the subject would build and by this stage the squaraine condensation reaction was known to be acid catalyzed with the squaric acid itself, in most cases, strong enough to self-catalyze its own reaction.



## 2.2. The Next Twenty Years: 1970–1990

The first major review article (or what is considered by many as the first major review article, discounting the Maahs and Hegenberg review) on squaraine chemistry came in 1980, written by Arthur H. Schmidt [72]. This review has often been referenced in squaraine papers because it is very thorough and details all of the early work previously mentioned. In 1984, a patent from BASF reported an electrochemical synthetic procedure producing (what at the time was claimed to be) a copolymer of pyrrole and squarate groups [86], although later knowledge of polypyrrole chemistry suggests that the product would actually be polypyrrole charge-balanced with squarate ions **7** [87]. Up to this point in time all papers on pyrrolyl squaraines came from researchers based in German institutions and three (of the five) of these early papers were written in German. Moving forward, apart from a mention in the introduction section of a paper in 1990 [4], the only paper from 1970–1990 to report any new research on pyrrolyl squaraines was for the polysquaraine derived from 1-methylpyrrole [poly(1-methylpyrrolylsquaraine) or **PMPS**] in 1990. In this paper, **PMPS** was prepared by refluxing

in butanol and was studied as a dark blue insoluble precipitate with one water molecule per squarate unit [5].



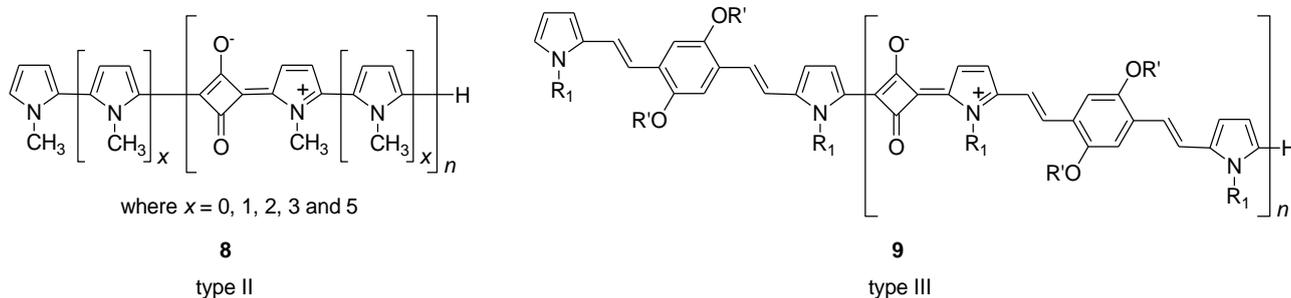
### 2.3. Picking Up Pace: 1991–2000

New spectroscopic work proceeded from 1992 to 1996 in three papers on previously reported bis(pyrrolyl)squaraines, with no new synthesis methodologies reported [6–8]. The first use of a butanol:benzene solvent mixture with the azeotropic removal of water to prepare any type of pyrrolyl squaraine came in 1997 with the synthesis of two *N*-alkyl ( $C_{12}H_{25}$  and  $C_{12}H_{22}OH$ ) pyrrole-derived polysquaraines [10]. These polysquaraines were prepared with longer *N*-alkyl chains to aid solubility because shorter *N*-alkyl variants were insoluble. From this point onwards, the use of butanol:benzene (1:1, 2:1, 3:1 or 1:3) or (to a lesser extent) butanol:toluene (1:1, 2:1 or 1:2) mixtures with the azeotropic removal of water became the preferred synthetic methodology with few reports since 1997 utilizing either just ethanol or butanol as the reaction solvent. The first pyrrolyl squaraine reactions to be undertaken in an inert atmosphere (nitrogen) in a 2:1 mixture of butanol:benzene with azeotropic removal of water was in 1998 [15]. Since 1998, the majority of pyrrolyl squaraine reactions have been undertaken using this solvent mixture (with removal of water) under nitrogen, with very few reactions undertaken in an argon atmosphere. Interesting unsymmetrical pyrrolyl squaraines are given as examples in two patents during this period [88,89].

### 2.4. The Pyrrolyl Squaraine Explosion: 2001–Current

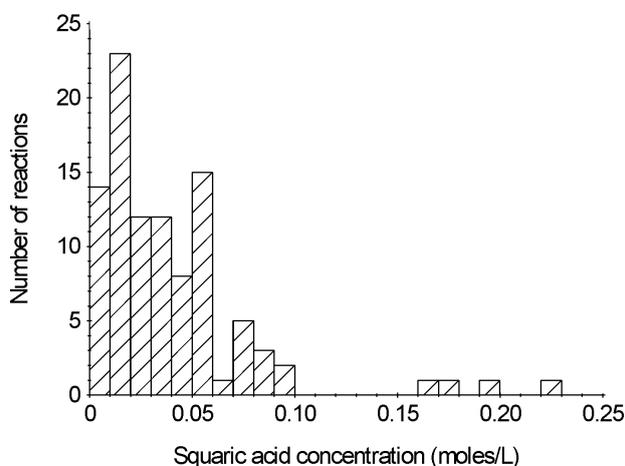
In terms of synthetic procedures the key change that occurred in two papers, both published within a few months of each other in 2001, was the use of linked pyrroles, **8** and **9**. Thus, far type I pyrrole-derived polysquaraines had utilized the two available  $\alpha$ -H atoms on the same pyrrole to propagate the polymer. Lynch *et al.* reported type II polysquaraines made from oligo(1-methylpyrroles) (*i.e.*, where the inner pyrrole groups, between the two outer pyrroles, were directly linked) [20], and Ajayaghosh and Eldo reported type III polysquaraines made from divinylbenzene bridged bispyrroles [21]. Ajayaghosh and Eldo also altered their synthetic procedure for the production of type III polysquaraines by first producing the bis(pyrrolyl)squaraine (2:1 molar ratios of pyrrole derivative and squaric acid) and then polymerizing that with a second reaction involving another molar equivalence of squaric acid. Although this two-step polysquaraine synthetic procedure has not been widely adopted, the majority of polysquaraines derived from pyrrole from this paper onwards were of the Ajayaghosh and Eldo type III in their molecular structure (*i.e.*, divinylbenzene bridged bispyrroles). Additionally increasing throughout this period of time was the synthesis of unsymmetrical pyrrole squaraine dyes [19,39,48,53,57,69,70]. Although a synthetic route to the pyrrole half-squaraine, semisquaraine,

or emisquaraine (the necessary precursor to an unsymmetrical pyrrole squaraine dye), was first proposed in 1968 [3], more efficient (and safer) routes have been developed in recent times (refer to [82] for a good description and schematics). Mention should also be added on the increase in recent years in the synthesis of (what in [82] is referred to as) core substituted squaraines, although only one example of this type of squaraine is known in a pyrrole squaraine [53].



### 2.5. Reaction Concentration and Time

The use of solvent/solvent mixtures for the synthesis of pyrrolyl squaraines has already been mentioned but what is worth noting is the distribution of reactant concentration within that solvent/solvent mixture. This is a noteworthy point because if pyrrolyl squaraines are ever to become commercial and manufactured in significant quantities then optimizing both reaction concentrations and yields become important. Figure 1 is a plot of squaric acid concentration in each of the published reactions where information was available and it can be seen that most reactions are undertaken using concentrations of squaric acid that are  $<0.06$  moles per  $\text{dm}^3$  of solvent. These are very inefficient concentration ranges for commercial production and would result in significant solvent waste/recycling issues. It should be noted that the squaric acid concentration is calculated using total solvent volume and not just the volume of the alcohol constituent.



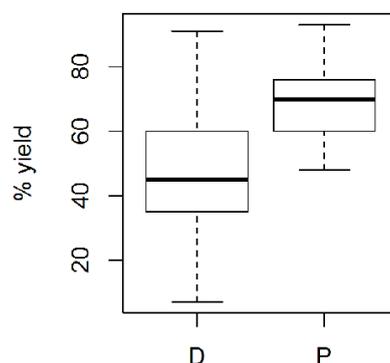
**Figure 1.** Bar graph showing the number of reactions undertaken covering each range of concentration of squaric acid used (+0.01 moles/L); calculated from total solvent volume.

The most common reaction times stated indicate overnight runs (*i.e.*, 16 h or more) with many being 24 h. If any pyrrolyl squaraine were to be prepared commercially in significant quantities then the reaction time may need to be investigated and ideally reduced down to be contained within an 8 h

shift pattern. Any squaraine reaction time should be recorded from the beginning of solvent reflux and not from “switch on”.

### 2.6. Reaction Yields and Polymer Size

Further investigation of the available synthetic data revealed that reaction yields (across all types of pyrrolyl squaraines) vary widely, although if the yields are split into bis(pyrrolyl)squaraine dyes and pyrrole-derived polysquaraines then it is the polymers that, on average, are produced in higher yields; the medians are 45 and 70, respectively, while the means are 47.5 (standard deviation 21.2) and 69.0 (standard deviation 10.6). That is, not only are the polymer yields higher, but they are also markedly less variable. Figure 2 is a boxplot illustrating this. There appears to be no obvious explanation for this although the answer may lie in a detailed investigation of the reaction intermediates of each pyrrole type and the increased reactivity of the polymer intermediates, as opposed to the dye intermediates, because in the polymer intermediate half-squaraines, the pyrrole ring still contains a reactive  $\alpha$ -H atom.



**Figure 2.** Boxplot of percentage yield for bis(pyrrolyl)squaraine dyes (D) and pyrrole-derived polysquaraines (P).

In terms of the polymer molecular weights, a number of measurements, primarily using gel permeation chromatography (GPC) in THF against polystyrene standards and quoting either or both number-average molecular weights ( $M_n$ ) or weight-average molecular weights ( $M_w$ ), along with the associated polydispersity index ( $M_w/M_n$ ), have been reported.  $M_n$  values range from 3000–30,000 g/mol and  $M_w$  values range from 1800–307,260 g/mol. However, as noted by Eldo and Ajayaghosh [22], molecular weight analysis of rigid polymers using flexible polystyrene standards may not provide the exact molecular weights of polymers. Eldo and Ajayaghosh noted that the observed molecular weights of rigid polymers in several cases are much higher, typically by a factor of 2–3, than the absolute value.

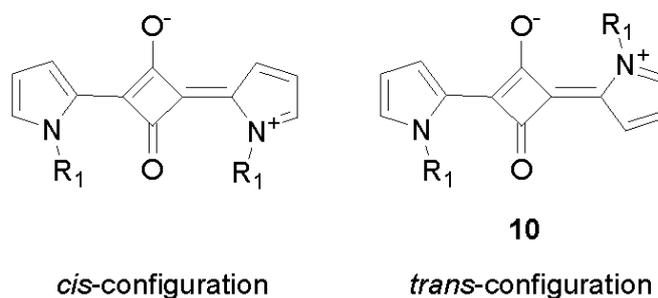
### 2.7. Check Your $^1\text{H}$ NMR

Pyrrolyl squaraine dyes and polymers, like all squaraine dyes, are very intensely coloured and one of the first indications that a squaraine reaction is proceeding (after dissolution of the reactants) is an increase in the intensity of the reaction colour, which for simple pyrrolyl squaraines is an increasing red-purple colouration. However, the intensity of colouration can be deceiving, particularly if upon cooling of the reaction an intensely coloured precipitate is collected because what could be easily thought of as being a successful reaction might not be. It should at this stage be highlighted that

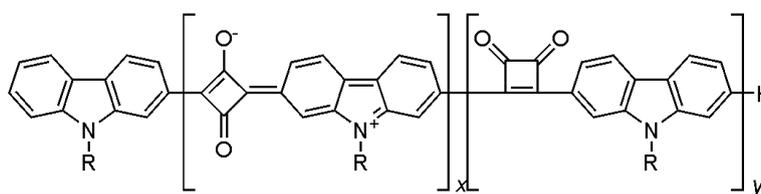
the author (of this review) has only ever observed the following when preparing type I pyrrolyl squaraines with *N*-attached long alkyl chains, although as a general principle  $^1\text{H}$  NMR is an ideal analysis technique for the comparison of the pyrrole starting material against the squaraine product. In many cases, where the author has attempted to prepare the types of pyrrolyl squaraines mentioned the  $^1\text{H}$  NMR has shown that the intensely coloured product is mostly the pyrrole starting material, mixed with a low percentage of dye. When an electron-accepting group is attached to an aromatic or heterocyclic ring system then there is a resultant downfield shift in the positions of the remaining pyrrole H atoms (as well as the N-CH<sub>2</sub> atoms) in the  $^1\text{H}$  NMR spectrum of the product. Ashwell *et al.* in their re-preparation of 2,4-bis(*N*-octadecylpyrrol-2-yl)squaraine (which would currently be referred to as a 1,3-squaraine, not a 2,4-squaraine) gave the H positions in the  $^1\text{H}$  NMR at (in reverse order)  $\delta = 0.88, 1.25, 1.7\text{--}1.8, 3.86, 6.13, 6.65$  and  $7.42$  ppm [13]. These positions (except for  $\delta = 7.42$  ppm) are identical to those reported for the starting material *N*-octadecylpyrrole ( $\delta = 0.90, 1.25, 1.75, 3.86, 6.13$  and  $6.65$  ppm) [11], indicating that Ashwell *et al.* did little more than study the starting material, which is corroborated by their differential scanning calorimetry results showing a melting point of  $32\text{--}36$  °C. Thankfully, as far as the author (of this review) is aware, this mistake has not been made elsewhere by any other pyrrolyl squaraine researcher.

### 3. Molecular Structure

The structure and resonance of 1,3-bis(pyrrolyl)squaraines has been accepted since its first proposal in the original Treibs and Jacob paper [1], which, although inferred in the numerous X-ray crystal structures of squaraine dyes of other aromatic/heterocyclic compounds since 1974, has been recently verified by at least four crystal structures specifically of 1,3-bis(pyrrolyl)squaraines [45,64,90]. All four structures, like the majority of symmetrical squaraine dyes, adopt the *trans* configuration **10** in the solid-state. Within the central squarate group, investigation of every known squaraine structure shows that the average C—C distance is  $1.465$  Å with a standard deviation of  $0.013$  Å, indicating just how square that the central ring is in a squaraine. Interestingly, the C—O bonds are also very narrow in their variability with an average distance of  $1.239$  Å and a standard deviation of  $0.012$  Å, although if the C—O distances are split into those that, in the solid-state, are involved in hydrogen-bonding associations, then the average C—O distance becomes  $1.237$  Å (standard deviation of  $0.014$  Å) for non-hydrogen bonded O-atoms and  $1.242$  Å (standard deviation of  $0.008$  Å) for hydrogen bonded O-atoms (irrespective of whether the hydrogen-bonding associations are intra or inter the squaraine molecule). Although the difference between these two latter values is  $0.005$  Å, this is still a statistically significant difference given the sample sizes of fifty-four and forty respectively (P value = 0.006 for a one-tail test).

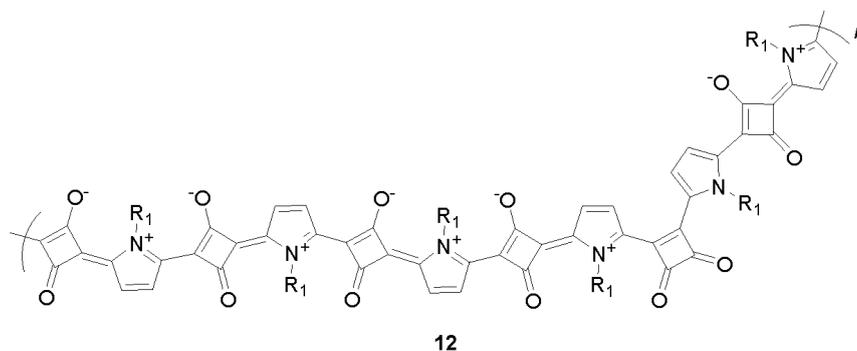


In contrast to the pyrrolyl squaraine dyes, the exact structure of pyrrole-derived polysquaraines is less defined. In the simplest sense, the structure of these types of polysquaraines can be split into two groups, those that include measurable levels of 1,2-squarates **3** in their polysquaraine backbone and those that do not. The structural marker that appears to separate the two can be defined as those with short *N*-alkyl chains and those with long *N*-alkyl chains, although the exact length of *N*-alkyl chain has not yet been specifically determined. The occurrence of 1,2-squarates in the backbone of a polysquaraine was first reported by Chen and Hall in 1986 through their examination of a polysquaraine derived from *N*-alkylcarbazole **11** [91]. An indication of the presence of the 1,2-squarate was noted by the presence of a strong peak  $\sim 1750\text{ cm}^{-1}$  (can appear from  $\sim 1730\text{ cm}^{-1}$  or above, to  $1790\text{ cm}^{-1}$ , but is commonly  $1750\text{ cm}^{-1}$ ) in the infrared spectrum, assigned as a C=O stretching frequency. Normally, the C—O<sup>−</sup> stretching frequency is observed lower, usually  $1620\text{--}1600\text{ cm}^{-1}$ . Chen and Hall determined, by means other than just comparing the heights of the two peaks (which would be inaccurate), the 1,2-squarate content ( $y$ ) as being between 36%–43%. In a latter paper, on a type I polysquaraine derived from *N*-alkylated pyrrole, Lynch *et al.* determined the 1,2-squarate content to be  $\sim 44\%$  [12], although the specific nature of this system within polymethylmethacrylate means that the pyrrole should be treated as being highly hindered during the squaraine synthesis.

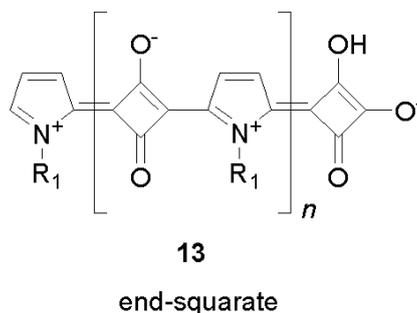


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The occurrence of measurable levels of 1,2-squarate groups in pyrrole-derived polysquaraines appears to happen when the pyrroles contain bulky *N*-attached groups, or are otherwise hindered, as in the case just mentioned. Examination of the available infrared analysis data suggests that there is a general trend for the observance of a C=O peak if the pyrrole has an octyl chain (or longer) attached at either the 1-(*N*-) or 3-position (although this should be compared to [43]). It should be stressed that this remains a general observation given the available data and no specific detailed study has thus far been undertaken to investigate this. However, no pyrrole-derived polysquaraine, where the pyrrole group(s) contains a *N*-CH<sub>3</sub> attachment (and no other 3-position attachment), has reported the observance of a C=O peak in the infrared spectrum (unless the cause is due to another known source in the chemical structure). An indication of why bulky side chains may promote 1,2-squarate groups in the polysquaraine backbone comes when a pyrrole-derived polysquaraine is drawn with appropriate bond angles **12**. Assuming *trans*-configuration, the 1,3-squarates produce a linear zig-zag polymer but the introduction of a 1,2-squarate group introduces a perturbation that significantly changes the direction of the polymer chain. These perturbations may be necessary to accommodate the attached side chains, which would invariably be out of the plane of the squaraine (as noted in all squaraine crystal structures with attached alkyl chains longer than propyl groups). A polysquaraine chain of pure 1,3-squarates would bend and twist over molecularly long distances but may not create enough disturbance within the packing structure to accommodate for bulky side chains, as would 1,2-squarates.



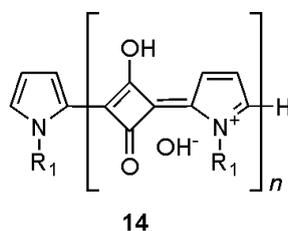
It should be noted that Ajayaghosh *et al.* interpreted infrared C=O stretching frequency peaks at  $1730\text{ cm}^{-1}$  and  $1790\text{ cm}^{-1}$  as possibly being due to the presence of end-squarate groups **13**, as an alternative explanation to the presence of 1,2-squarates in the polymer backbone [10]. If present then these half-squaraine end groups would be available to react with any adjacent end pyrrole groups containing free  $\alpha$ -H atoms so the existence of 1,2-squarates to explain the presence of C=O peaks appears, certainly to the author (of this review), as being an explanation that better fits all of the available data on the issue. Furthermore, any prepared pyrrole-derived polysquaraine should also undergo some form of purification, whether by column chromatography if the polymer is soluble or by solvent extraction if the polymer is insoluble, because the existence of soluble short-chain material, which gets absorbed into the precipitated polymer and invariably includes half-squaraine material, can give a “false positive” with respect to the observance of a C=O peak in the infrared [92]. Discussion over the existence of either 1,2-squarates or half-squaraine end groups in pyrrole-derived polysquaraines is important because many of the physical effects discussed throughout this review may be affected by the presence of 1,2-squarates in the polysquaraine backbone. Although conjugation along the backbone is maintained through 1,2-squarates, their dimer counterparts (*i.e.*, 1,2-bis(pyrrolyl)squaraines **3**) do not mirror the electronic or spectroscopic properties of the 1,3-squarates thus experimental observation suggests that 1,2-squarates are not beneficial to pyrrole-derived polysquaraines. However, this has not always been the case [17] so their existence and cause of appearance still requires better understanding.



The presence of 1,2,3-squarate groups **4** in a pyrrole-derived polysquaraine has had little research because unlike the observance of a C=O peak in an infrared spectrum, the only indication of the presence of 1,2,3-squarate groups is the C—OH stretching frequency, which can be almost impossible to detect because pyrrolyl squaraines have been reported, from the very beginning, to crystallize from reaction with the equivalence of one water molecule per squarate group [1,5]. However, the four known X-ray crystal structures of 1,3-bis(pyrrolyl)squaraines are non-hydrates [90], although this may be due to their purification and recrystallisation processes. In pyrrole-derived

polysquaraines, each chain will end with a free pyrrole  $\alpha$ -H atom, or (possibly) an end-squarate group, and any free pyrrole  $\alpha$ -H atom is then capable of forming a 1,2,3-squarate with an adjacent 1,3-squarate group so their existence along such a polysquaraine backbone should be assumed, although not yet quantified.

A final comment on the molecular structure of the polymers comes from the results of one particular study on the structure of two separate polysquaraines, one **PMPS** and the other made from 1-dodecylpyrrole [28]. The spectroscopic results of this study suggest that the incorporation of the known “one water molecule per squarate unit” (as mentioned previously) is actually part of the polysquaraine molecular structure **14**. However, it should be noted that in this study, although both polymers were washed, after collection of the precipitated mass, they were not purified, by either solvent extraction or column chromatography. The reason why this is important, particularly in this case, is because **PMPS** particles are very porous and can be collected, washed and dried while still containing significant amounts of reaction byproduct [92]. In terms of the micromolecular structure of pyrrole-derived polysquaraines, studies on type I polysquaraines have reported a switchable structure induced by both metal ions [42] and metal surfaces [47,65].



#### 4. Optical Properties

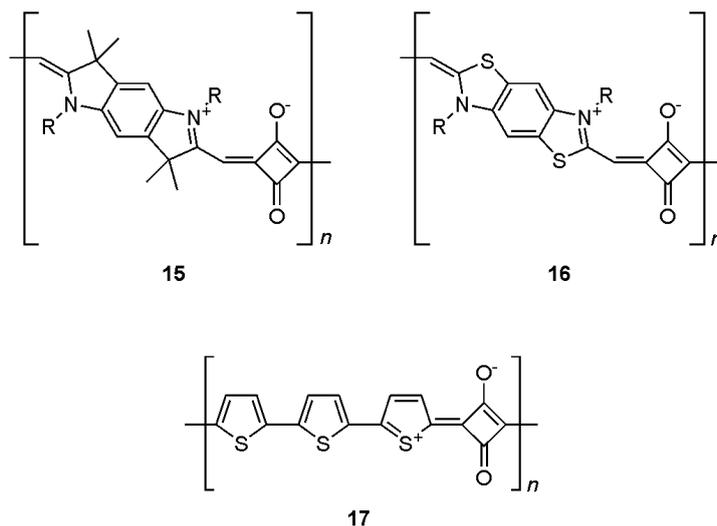
As previously mentioned, pyrrolyl squaraines (both dyes and polymers) like all squaraine dyes, are intensely coloured, because of the unique resonant nature of the 1,3-squarate **1** formation. Colour intensity is not as prevalent in 1,2-squarates **3**, even though conjugation is maintained. All of the early syntheses for the dyes reported absorption maximum ( $\lambda_{\max}$ ) values, usually recorded in chloroform, of  $>550$  nm with molecular absorptivities ( $\epsilon$ ) of  $>1 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>. The simplest dye, 1,3-bis(1-alkylpyrrolyl)squaraine **1** (where  $R_2, R_3, R_4 = \text{H}$ ), had  $\lambda_{\max}(\text{CHCl}_3) = 548.5$  nm with  $\lambda_{\max}$  increasing with additional substitution around the pyrrole [14]. The early studies also found that the dyes were solvatochromic [3,6] (with the polymers also subsequently being found to be solvatochromic [10]) and that the dyes fluoresced ( $\lambda_{\text{em}} > 580$  nm) with varying efficiency in different solvents [6,7,11,14] and within a substituted methacrylate polymer [12] (with subsequent reports of the soluble polymers fluorescing [16]). Generally, pyrrolyl squaraine dyes are reported as being red-purple in colour whereas pyrrole-derived polysquaraines are dark blue-black, although in both cases surface plasmon optical effects can give the impression that the powders are metallic green, metallic yellow-brown or metallic red-purple [59]. Fluorescence in the soluble pyrrole-derived polysquaraines has been useful in the investigation of these materials as molecular sensors [16,18,34,70]. Their optical properties have also lead to recommendations that they are suitable candidates for photodynamic therapy (PDT) [25,32].

The observance that pyrrolyl squaraines absorbed at high visible wavelengths, towards the near-infrared, lead to studies that were aimed at increasing not only the  $\lambda_{\max}$  but also their overall absorption from 200–900 nm. One reason for doing this was the inclusion of pyrrolyl squaraines in the development of organic solar cells [30,31,41,48,51,53,54,57,63,69], or similarly for organic photovoltaics [35,38,45,50,64,67]. It has also been possible that the some pyrrole-derived polysquaraines, such as that derived from pyrrole itself, can be used as black colour materials in toners and inks just because they are produced as black intractable powders [40]. One interesting study improved the holographic data storage characteristics of a known photopolymer by adding the polysquaraine derived from 3-octylpyrrole [46]; there is one reported example of near-infrared thermochromism in a pyrrole-derived polysquaraine [62], and one reporting improved photocatalytic activity with the inclusion of a pyrrolyl squaraine dye [68].

An early study on **PMPS** recorded third-order nonlinear optical behaviour [5] with a follow up study on a pyrrolyl squaraine dye [8]. Reports of large third-order susceptibilities, based on the observance of large two-photon absorption cross-sections, have continued [29]. Other studies have been undertaken that just concentrate on the large two-photon absorption cross-sections that pyrrolyl squaraine dyes exhibit [32,33,52,55,66]. Following the discovery that symmetrical bis(anilino)squaraine dyes exhibit second-order nonlinear optical effects as Langmuir-Blodgett deposited monolayers on hydrophilic glass slides [93], results for a range of pyrrolyl squaraines were similarly reported [11,13,14]. Latter second-order non-linear optical studies on pyrrolyl squaraines have employed electric-field induced second harmonic generation (EFISH) measurements, although these measurements can only be taken on unsymmetrical pyrrolyl squaraine dyes [39].

## 5. Electrical Properties

In 1992, Havinga and Wynberg (working for Philips Electronics n.v.), and ten Hoeve (working for Syncom b.v.) proved that polysquaraines, derived from either a bis-indolenine type molecule **15** or bis-benzothiazoline type molecule **16**, exhibited electrical conduction values of  $10^{-7}$  S/cm (undoped) as pressed bars, measured using the four-point probe method [94]. Furthermore, the optically measured band gaps for these two polymers were 1.15 and 0.8 eV, respectively. That same year Philips Electronics also submitted a patent application covering the polysquaraine derived from terthiophene **17** as a N-type conductive polymer [95]. Havinga, ten Hoeve and Wynberg further presented their idea in 1993 [96] of creating small band-gap polymers through the use of alternating donor and acceptor moieties along a conjugated polymer, hence the development of polysquaraines, which experimentally displayed band-gaps of  $\sim 1$  eV and (undoped) electrical conductivities of  $10^{-7}$ – $10^{-5}$  S/cm. Havinga, ten Hoeve and Wynberg were also concerned about how their initially intractable polymers could be processed so they developed solvent soluble variants [97], which allowed for optical band gap measurements on thin films of soluble polysquaraines that had been spun coated on glass slides [98]. As a follow-up to this early experimental work, four theoretical papers, one each by Tol [99] and Brocks [100], and the latter two by both researchers [101,102], showed that theoretical bands gaps in polysquaraines could reach as low as 0.2 eV, thus promising very high electrical conductivity in the right polysquaraine system.



Polysquaraines derived from bis-indolenine type molecules continue to provide a wealth of chemical possibilities as low band-gap materials [103] but the first two type I pyrrole-derived polysquaraines measured for electrical conduction were reported in 1997 by Ajayaghosh *et al.* with (undoped) four point probe conductivities of  $2.4 \times 10^{-6}$  and  $2 \times 10^{-7}$  S/cm [10]. Since then the (undoped) electrical conductivities of pyrrole-derived squaraines have been reported thirteen times [15,17,20–22,28,43,47,49,56,58,59,61], with the best conduction being no greater than  $5 \times 10^{-4}$  S/cm [21]. The reported band gap for this type III polysquaraine **9** was 0.79 eV, the lowest recorded for any pyrrole-derived polysquaraine. Some papers have reported band gaps but not actual electrical conductivities [30,31,41,50,51,54,62], although apart from **9**, all reported band gaps exceed 1 eV. This in many respects is disappointing because pyrrole-derived polysquaraines approximate some of the theoretical chemicals models of Brocks and Tol and theoretically, the performance of pyrrole-derived squaraines should be better. This would then suggest that there are other factors that hinder electrical conductivity performance.

The theoretical calculations made by Brocks and Tol are based upon the existence of pure 1,3-squarates along the polymer backbone. The existence of 1,2-squarate groups in polysquaraines has been previously discussed and it is interesting that for the type I polysquaraine made from 3-dodecylpyrrole the purposeful introduction of 1,2-squarate units improved the (undoped) electrical conduction from  $8 \times 10^{-6}$  S/cm to  $2.3 \times 10^{-5}$  S/cm, although the electrical conductivity of the comparative 1-dodecylpyrrole variant remained unchanged [17]. Examination of the current (undoped) electrical conductivity data reveals that pyrrole-derived polysquaraines prepared under a nitrogen or argon atmosphere, with the associated azeotropic removal of water, are more likely to electrically conduct in comparison to those that were not, unless there is definite evidence of a peak at  $d = 3.4$  Å in the powder X-ray diffraction of the polymer. Electrical conductivities have only ever been reported on pyrrole-derived polysquaraines without the  $d = 3.4$  Å peak if they have been prepared under an inert atmosphere, otherwise all of the other reported conductivities come from polymers that display close  $\pi$ -stacking interactions (as indicated by a peak at  $d = 3.4$  Å in the powder diffraction pattern). The possibility of a chain-hopping mechanism contributing to the electrical conduction in pyrrole-derived polysquaraines was first discussed by Lynch *et al.* in 2001 [20] and was further developed in 2013 [59]. The reasons why this mechanism is not required in pyrrole-derived polysquaraines prepared under an

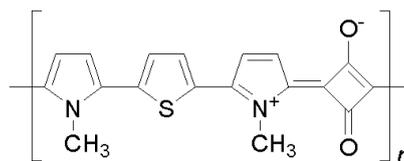
inert atmosphere to allow electrical conduction is currently unknown. There is simply too little data on the structure of these particular polymers for the author (of this review) to postulate any answer. It is possible that the production methodology has nothing to do with why these pyrrole-derived polysquaraines electrically conduct without the aid of a chain-hopping mechanism.

To confuse matters even more, some mention should be made of two opposing electrical conduction results for **PMPS**. This polymer, made from squaric acid and 1-methylpyrrole, was reported by Lynch *et al.* to be an electrical insulator with a dielectric breakdown of 0.025–0.9 MV/cm [20], whereas Sant’Ana *et al.* reported an electrical conductivity of  $\sim 10^{-6}$  S/cm [28]. The difference between these two papers was the preparation of the polymer. Lynch *et al.* refluxed the two component chemicals in butanol and then cleaned the collected product with overnight solvent extraction in ethyl acetate; Sant’Ana *et al.* refluxed the two component chemicals in a 2:1 mixture of 1-butanol and benzene, under nitrogen, with the azeotropic removal of water, with the collected powder being washed with benzene and methanol. The discrepancy between these two electrical conduction results may be explained by the difference in synthesis methodologies discussed in the last paragraph although, as previously mentioned, **PMPS** particles are porous and require thorough cleaning to extract all of the residual low molecular weight material, and that this residual material may also be the cause of the electrical conductivity in the Sant’Ana *et al.* sample, as commented upon in [9]. Evidence of interference from this residual material is seen in the paper by Yu *et al.* [5] with notation that the polymer is partially soluble in DMF and *m*-cresol (in which it forms blue solutions). If the residual material that is left behind in **PMPS** is appropriately extracted then no such ‘partial solubility’ is observed [92].

Electrical conductivity measurements have exclusively been undertaken on pyrrole-derived polysquaraines. However, pyrrolyl squaraine dyes have undergone cyclic voltammograms to measure their redox chemistry [23,33,39,49,51,53,57,63,68] as have pyrrole-derived polysquaraines [30,41,49,50,54]. It is also worth noting that current density versus voltage (or *J-V*) curves have been measured, particularly on organic photovoltaics containing pyrrolyl squaraines [35,45,48,51,67]. Whang *et al.* have recently focused on the preparation of free-standing flexible films of type III pyrrole-derived polysquaraines with electrical conductivities down to  $\sim 10^{-5}$  S/cm [56,61]. In many cases where electrical conductivity has been measured the pyrrole-derived polysquaraine has also been doped with iodine, to improve upon the undoped measurement, but these values have not been discussed here. Thus far, there have been no reports of ferroelectricity in pyrrole-derived polysquaraines, as in [104].

## 6. Magnetic Properties

In 1995, Tanaka *et al.* proposed a model for polaronic ferromagnetic polymers based on alternating spin supplier blocks and spacer units [105]. This model was used as a guide for a series of type II polysquaraines that were examined for both magnetic and magneto-optic properties with the subsequent discovery that one particular type II polysquaraine **18** exhibited strong a magnet-optic effect and the particular characteristic of the effect suggested that **18** was either a one-dimensional or two-dimensional ferromagnet [58]. Magneto-optic behaviour has also been observed in thin films of polyalkylthiophenes [106].



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## 7. Structural Properties

The purpose of this section is not to repeat discussions about the molecular structure of pyrrolyl squaraines but to discuss the use of these materials as macromolecular structural entities. This is best demonstrated by **PMPS** whose particles are collected as spheres with diameters of 1.3–4  $\mu\text{m}$  [26,44]. These particles can be used as sacrificial templates to produce hollow silica shells [26,44] and hollow silica shells containing metal oxides [44]. This is possible because **PMPS** particles not only adsorb the silica precursor, tetraethoxysilane, into their outer layers but they also adsorb metal ions deep inside their internal porous network [92]. **PMPS** particles have also been utilized as a carrier particle for ammonium phosphate into polypropylene fibres [27], as well as an odour adsorbent in polylactide/cellulose fibre composites [60]. In fact **PMPS** particles are easily compounded into a whole range of commercial polymers and resins [92]. Electron microscopy images of several other pyrrolyl squaraines have been reported and they indicate a wide variety of sizes and shapes [58,59,61], but thus far only **PMPS** particles have their size and shape been exploited, although other type II polysquaraines are clearly adsorbent in the solid-state [59].

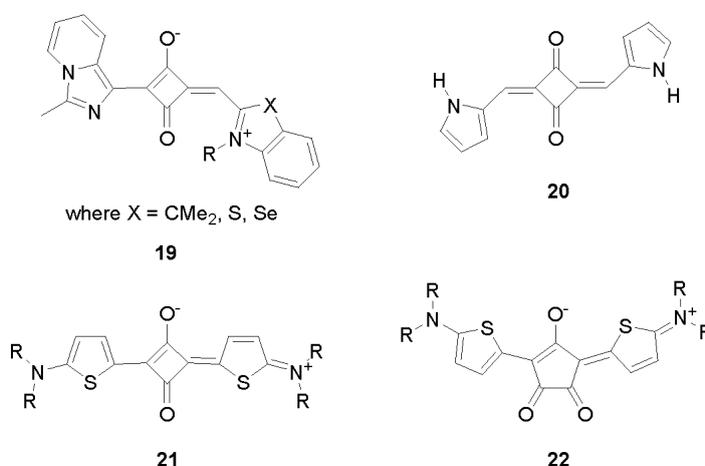
## 8. Toxicity

It is important at this stage to also add a comment on the toxicity of pyrrolyl squaraines because if any are to be produced in commercial quantities then this information is important. In addition to this some pyrrolyl squaraines have been identified as having biomedical applications where proof of their toxicity, or more accurately their non-toxicity, is essential. When discussing the toxicity of any group of chemicals it should be noted that toxicity variation between individual molecules can be large, some times simply because of a shift in substituent groups, and each molecule within that group should be considered separately. This should certainly be the case for pyrrolyl squaraines where there is a large variation in molecular structure across the series although each is still bound to the general toxicity of squaraine molecules. In the pyrrolyl squaraine literature there appear to be no extensive studies measuring toxicity although some evidence can be inferred from the studies where the molecules have been studied with biological entities. In the second of the two studies aimed at PDT [25,32] there is mention of a simple cellular toxicity assay where no effect was reported and cellular uptake studies proceeded. Preliminary bacterial culture experiments, which preceded model porous pavement studies [27], showed that **PMPS** particles were non-inhibiting to bacterial growth. A pyrrolyl squaraine dye was also used to measure levels of aminothiols in human blood plasma without reporting any detrimental effects on the blood plasma [34] (also linked to [70]). Cytotoxicity assays were performed on two pyrrolyl squaraine dyes using two commonly employed cell lines (HCT 116, one of the human colorectal cancer cells and COS 7, a kidney cell line from African green monkeys) and concentrations of 20 and 30  $\mu\text{M}$  left 80% of viable cells after 20 hours incubation [55]. The author (of this review) has

had **PMPS** particles tested for blood haemolysis as a preliminary study into their biocompatibility. Compounds which cause haemolysis are not suitable for in vivo use and can lead to medical complications. According to the obtained data, none of the samples were haemolytic in the concentration range tested (0.5–5 mg/mL) [90]. Although not extensive, none of the results obtained thus far have suggested that pyrrolyl squaraines are toxic in the concentration ranges studied.

## 9. And Finally

Squaraine dyes derived from imidazo[1,5-a]pyridine **19** [107] have not been considered for this review, and neither was **20**, which was examined in a theoretical study calculating the third-order nonlinear optical properties of a range of similar compounds including the 2-thienyl variant [108]. 2-Thienyl squaraines **21** have also been reported in conjunction with their associated croconaines **22** [109–112] but have certainly not generated as much research interest in comparison to the pyrrolyl squaraines. The author (of this review) is not aware of any reports of pyrrolyl croconaines, neither is the author aware of any pyrrolyl bis-squaraines (*i.e.*, compounds that contain two squarate units, either side by side [113] or linked by a suitable linkage group [114]).



## 10. Conclusions

In covering the 50-year history of pyrrolyl squaraine chemistry in this review the author has endeavoured to highlight the variety of metal-like behaviour thus far revealed in these highly conjugated alternating donor-acceptor dyes and polymers. Their properties, which include a range of spectroscopic characteristics, electrical conduction, and magnetism indicate possible applications in biotechnology and pharmacology as well as sensors, energy conversion, optoelectronics and plastics. The research undertaken has been inventive, astonishing and fundamentally driven by the almost limitless chemical possibilities of what can be attached either to pyrrole molecules or between two pyrrole groups. However, the unfulfilled potential of low band gaps below 0.5 eV remains a major challenge. Hopefully future generations of researchers will ensure that the next 50 years of pyrrolyl squaraine chemistry will be many times even more fruitful than these first 50 years.

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## Conflicts of Interest

The authors declare no conflict of interest.

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