Cyclophane Derivatives as Functional Material: A Short Survey

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ABSTRACT

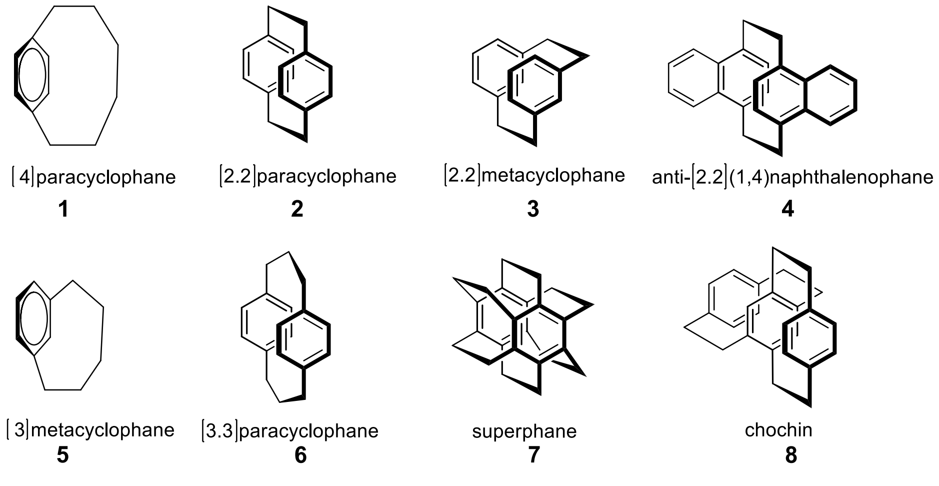
Cyclophane family is an interesting group of molecule among the many unique and fascinating structures of hydrocarbons. [2.2]Paracyclophane, [2.2]metacyclophane, [3.3]paracyclophane are of particular significance in the cyclophane family. They have two co-facial benzene rings where the interaction between the -orbitals occurs because of their close proximity, which is known as the 'phane effect.' Their derivatives have a broad range of application as important functional materials; such as, asymmetric organocatalyst, solar cell devices, photochromic molecues, OLEDs, etc. Here in this short literature survey, the derivatives of [2.2]paracyclophane are explored as different functional materials. It is anticipated that a broad scientific community will find this to be very interesting.

Key words: [2.2]Paracyclophane, Functional materials.

Introduction

The utilization of organic molecules as functional materials are of great interest in today's modern society.[1] Since the discovery cyclophanes have evolved to constitute a novel class of molecules, some of which (**1-8**) are shown in Chart 1. [2.2]Paracyclophane **2** is one of the fascinating member in the family of cyclophanes, which promises a great potential in wide range of applications as functional materials.[2-6] The two cofacially oriented benzene rings in [2.2]paracyclophane, are held rigidly at the para positions by ethylene bridges. In the two co-facial benzene rings where the interaction between the -orbitals occurs because of their close proximity, is known as the "phane effect". Due to this geometry there is a restricted rotation in the two benzene rings. This can only be likely to happen above 180 °C. The distance between the two aromatic rings is less than the sum of the van der Waals radii for carbon (3.40 A˚) and ranges from 2.78 Å (C3–C14) to a maximum of 3.09 Å for bridgehead carbons (C4–C13). Because of this rigid bridgehead structure, there occurs a strong $\square_{\text{bridge}}$– interaction, which causes lengthening of the C–C bond (1.63 Å).[7] The 'phane effect' of this novel molecule is nicely exploited in various derivatives of [2.2]paracyclophane and thus it become a very important scaffold for various functional materials, such as photochromic material,[8] sensor,[9] asymmetric organocatalyst,[10] solar cell,[11] light emitting devices,[12] chiroptical material,[13] etc. There are a large number of reports on paracyclophane based molecules used as various functional materials and describing those in a single place is quite difficult. Hope the short literature survey will be of great interest to a large science community.

Chart 1



Cyclophane Derivatives as Functional Material

The two benzene rings in [2.2]paracyclophane are distorted and give rise to a ‘boat-like’ conformation as a consequence of repulsion between π-orbitals, cf. Figure 1.

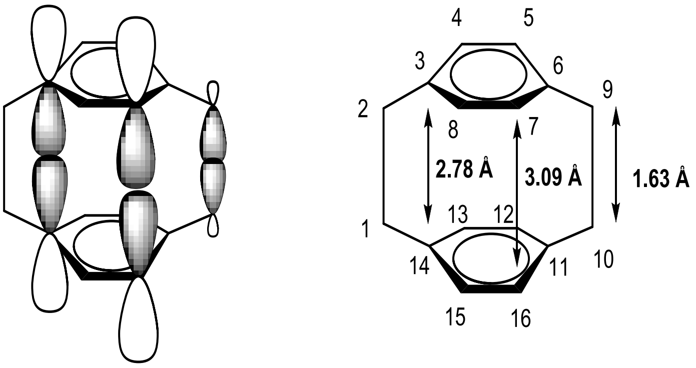


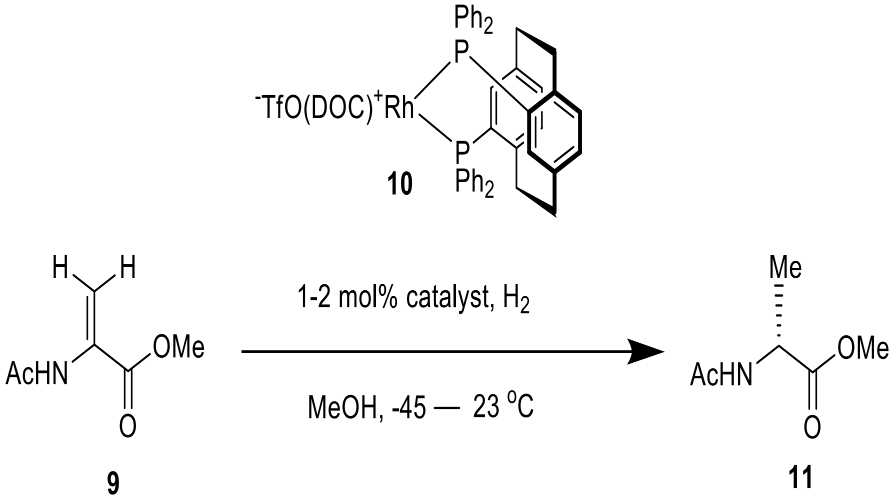
Figure 1. The orbital interactions and distances between the carbon atoms in [2.2]paracyclophane.

Cyclophanes also manifest in a strong π interaction between the two rings, which leads to a unique extended π-system. This structural feature renders [2.2]paracyclophane to undergo electrophilic substitution more rapidly than simple aryl systems and imparts enhanced ability to form π-complexes.[7]

Since its first synthesis, [2.2]paracyclophane has been at the focus of attention of organic chemists. The chemistry of [2.2]paracyclophane is very exciting as that of its structure. Its reactivity is akin to that of the normal aromatic compounds, although the substituents on one ring have a significant influence on the reactivity of the other ring; this, however, need not always be the case because of its deformed structure. In general, the novel [2.2]paracyclophane scaffold has largely been exploited to i) to develop chiral [2.2]paracyclophane derivatives as catalysts for stereoselective synthesis and ii) design a variety of molecular electronic materials such as linear and non-linear optoelectronics and conductive polymers by capitalizing on its unique electronic properties.

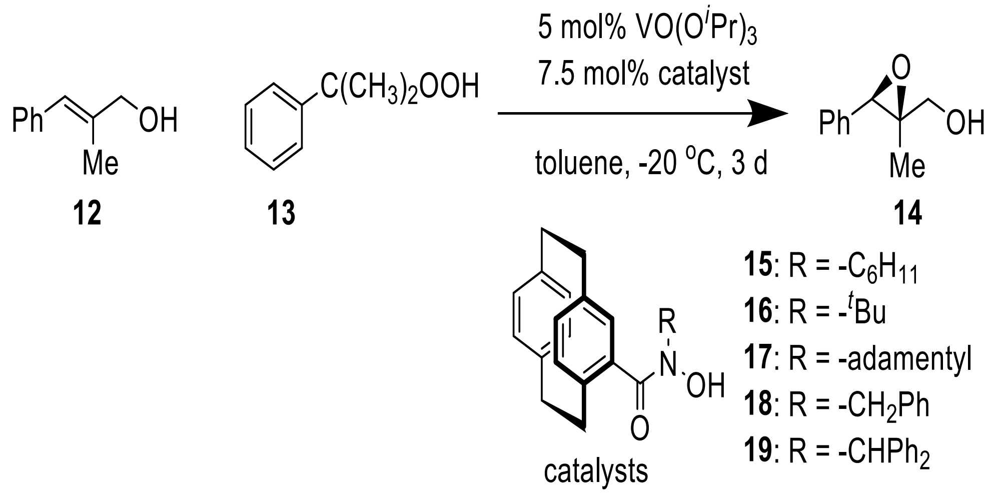
Pye and co-workers reported rhodium(I) (R)-[2.2]PHANEPHOS, **10** for enantioselectieve hydrogenation under very mild conditions leading to enantioselectivity up to 99.6%, cf. Scheme 1.[2a] In this catalyst, the chirality is imparted by the [2.2]paracyclophane scaffold.

Scheme 1



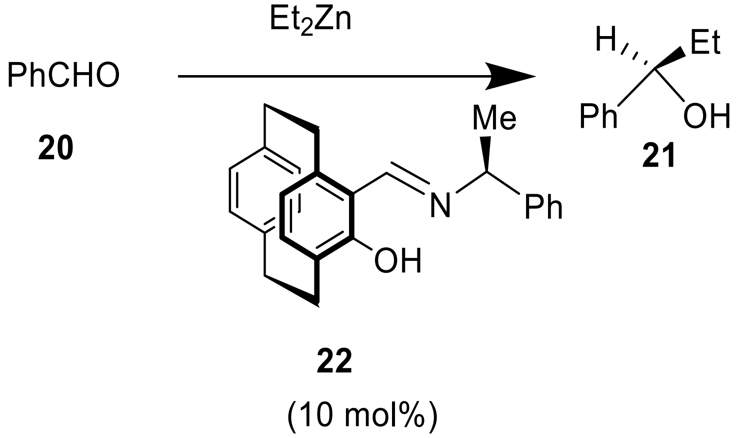
Fringuelli et al.[2b] utilized the 1,3-oxazol-2(3H)-one derived from (R)-(+)-4-hydroxy-[2.2]paracyclophane as a chiral auxiliary in asymmetric Diels-Alder, Michael and aldol reactions. The endo-exo and facial-diastereoselectivity is good and is solely dependent on the spatial orientation of the C9-C10 ethylene bridge of the [2.2]paracyclophane moiety. The chiral auxiliary was shown to be recovered once the reaction is over. Bolm and Kühn have developed an interesting class of vanadium complexes based on N-hydroxy[2.2]paracyclophane-4-carboxylic amides and used them as catalysts for the asymmetric epoxidation of allylic alcohols.[2e] Ligands **15-19** were screened to identify the optimum ligand system for catalysis at room temperature, cf. Scheme 2. Cyclophane **17**, where R = adamentyl, was shown to yield epoxide **14** with an ee of 52% and overall yield of 88%.

Scheme 2



Hopf and Rozenberg synthesized the chiral iminophenol ligand based on the [2.2]paracyclophane scaffold (**22**, Scheme 3), and employed in the enantioselective addition of diethylzinc to benzaldehyde to afford alcohols in good to excellent ee and yields.[2d]

Scheme 3

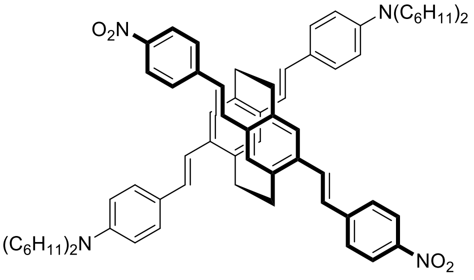


Insofar the application of cyclophanes for optoelectronic materials is concerned, there is lot of interest in exploring the absorption properties that are very different from benzene; the parent [2.2]paracyclophane shows absorption bands at 225, 244, 286 and 302 nm. The band at 302 nm is known as ‘cyclophane band’. Similarly the emission bands are also unusual from those of the benzene derivatives. These abnormal spectroscopic characteristics are attributed to strong □$_{bridge}$-□$_{ring}$ and □-□ through-space delocalization, which can result in energy transfer throughout the entire cyclophane core.[3] Pioneering work has been carried out by Bazan and co-workers in this discipline.[4] According to the contributions of these authors, the unique [2.2]paracyclophane scaffold permits creation of different chromophores at a common junction and exploration of through-space chromophore interactions.

The characteristics of the bichromophores can be explained by two states, namely ‘chromophore’ state and ‘phane’ state. The former is characterized by through-bond delocalization of charge, while the latter is best described by through-space delocalization. It has been shown that through-space □-□ interactions between the aromatic planes manifest in complete delocalization. This is known as ‘phane effect’, which leads to absorption and emission properties that are not readily described by each of the aromatic chromophores.[4] Incorporation of variety of stilbene derivatives (**23-26**, Chart 2) has led to lot of insights concerning the relation between optical properties and molecular structures.[4] The photon brings about electronic reorganization and modifies charge density within each monomer. Consequently, the electronic spectra are very much influenced.

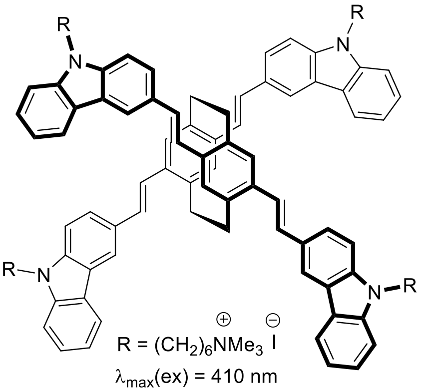
It is shown that the compound **23** with two donor and two acceptor arms displays a blue-shifted absorption at 417 nm. The N-substituted carbazole derivative **24** has been shown to exhibit a red-shifted fluorescence up to 45 nm. The shifts are consistent with increasing the electron-accepting properties of the pendant quaternary ammonium salts.[3,4c]

Chart 2



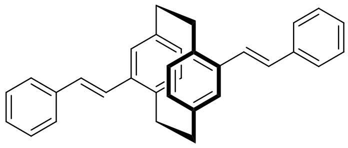
λ_{max}(ex) = 417 nm
λ_{max}(em) = 690 nm

23



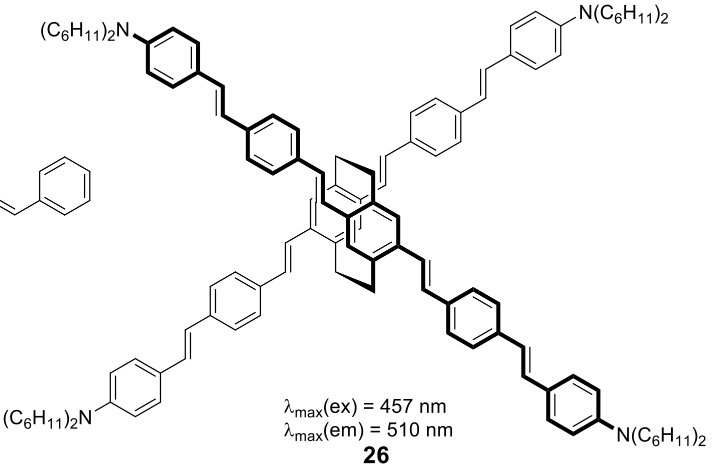
λ_{max}(ex) = 410 nm
λ_{max}(em) = 505 nm

24



λ_{max}(ex) = 307 nm
λ_{max}(em) = 412 nm

25

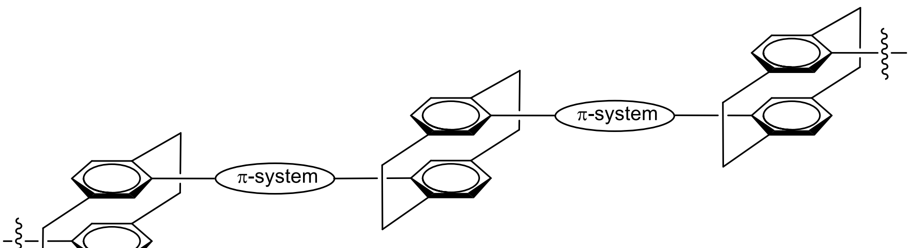


λ_{max}(ex) = 457 nm
λ_{max}(em) = 510 nm

26

As far as conducting polymers are concerned, [2.2]paracyclophane has gained a lot of importance. Incorporation of [2.2]paracyclophane unit on the conjugated polymer backbones has been shown to lead to □-stacked through-space conjugated polymers, cf. **27-29**, Chart 3.[5] Apart from these wide range of applications, [2.2]paracyclophane derivatives have also been extensively used as biosensors in biomedical research.[14]

Chart 3



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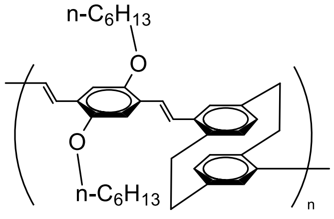

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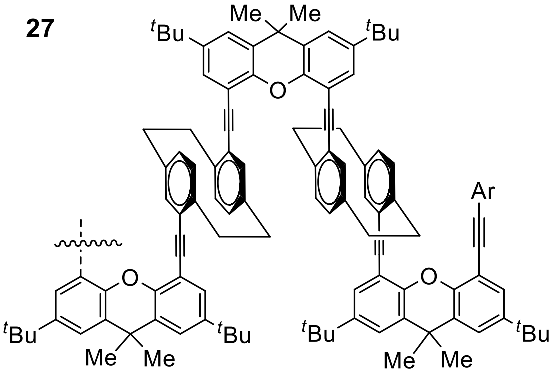
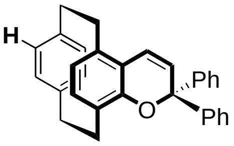


29

Because of the remarkable phane effect, [2.2]paracyclophane can also influence the spectrokinetic properties of chromene annulated to it. Investigation of the effects of through-space delocalization on reactive intermediate is of significant importance from the standpoints of both fundamental understanding and practical applications. The logically designed cyclophane-based chromenes (cyclophanochromenes) **30** in Chart 4 is synthesized and examined the extent to which the covalently-bound and cofacially-oriented arenes influence thermal reversion kinetics or persistence of photogenerated o-quinonoid intermediates. Herein, the remarkable ‘phane’ effects allow the happening of photochromism to be observed at room temperature.

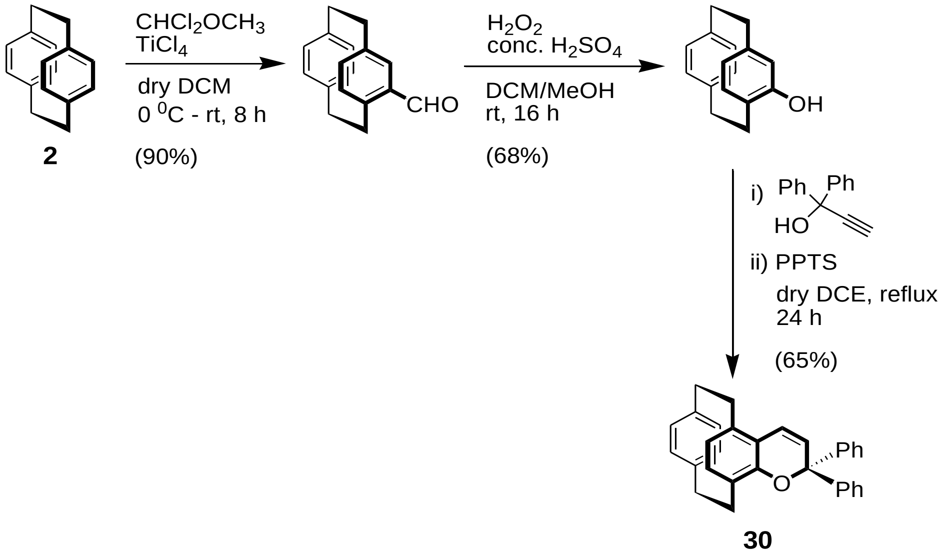
Chart 4



30

The [2.2]paracyclophane-based chromene **30** was in turn synthesized starting from suitably substituted hydroxycyclophanes, as shown below in Scheme 4. The required monohydroxycyclophane was prepared from mono-formylcyclophane by Dakin reaction with H_2O_2 and conc. H_2SO_4. The mono-formylcyclophane was prepared from commercially available [2.2]paracyclophane by formylation with dichloromethyl methyl ether in the presence of $TiCl_4$ in dry DCM.[15] The hydroxycyclophane, thus derived was subjected to cyclocondensation with 1,1-diphenylpropargyl alcohol using pyridinium-p-toluenesulfonate (PPTS) as the catalyst to get **30**.

Scheme 4



Upon photolysis the solutions of chromenes **30** turned reddish-brown; which is very important from the view point of their applications in ophthalmic plastic lenses. In Figure 2 the absorption spectrum of the solution before and after irradiation is shown; the spectrum was recorded at room temperature, i.e., 298 K. The spectrum in Figure 2 clearly reveals that the photogenerated intermediate of cyclophanochromene exhibits absorption property in the visible region. The absorption in this case is characterized by a sharp band at ca. 417-420 nm followed by a broad band that spans from 450 nm to 700 nm. The reddish-brown color of the photolysate was found to disappear in 2-3 min upon standing in dark.

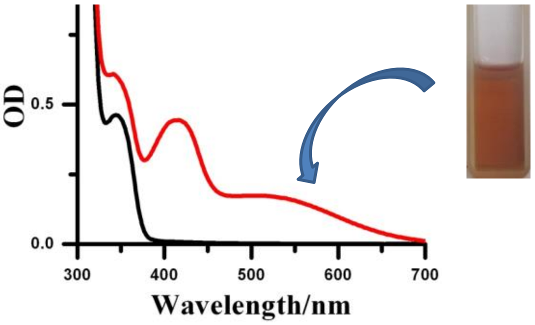


Figure 2. The absorption spectrum of chromene 30 before (black) and after (red) irradiation at 298 K.

CONCLUSIONS

Among vast number of organic molecules, cyclophanes, especially [2.2]paracyclophane derivatives are the novel types of molecules which are used as important functional materials. The 'phane effect' of this novel molecule is nicely exploited in various derivatives of [2.2]paracyclophane and thus it become a very important scaffold for various advanced materials as applied to photochromic molecule, sensor, asymmetric organocatalyst, solar cell, light emitting devices (OLED), chiroptical material, etc. The extent to which 'phane effect' influences the properties of the cyclophane molecules is an active area of research at present time. In case of photo active material, the phane effect is evident involving through-space delocalization between the aryl and the photogenerated o-quinonoid chromophores and show amazing stabilization. In future there are a lot to explore the cyclophane derivatives as potentially important functional material used in various kinds of applications.

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