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New Cycloaddition Reactions of some Ethenyl and Ethinyl[2.2]paracyclophanes with some Dienophiles

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Abstract: 4-Ethenyl[2.2]paracyclophane (1), 4,12-, (13), 4,15-, (16) and 4,16-diethenyl[2.2]paracyclophane (18) as well as, 4-ethinyl-[2.2]paracyclophane (20) undergo[2+2]cycloaddition reactions with tetracyanoethylene (TCNE). These reactions involve the formation of a charge-transfer complex as an initial step. With 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), bromanil (BRL) as well as 4-phenyl-1,2,4-triazoline-3,5-dione and 4-ethenyl[2.2]paracyclophane (1) as the diene,[2+4]cycloadditions took place. The reaction between 4,12-, (13), 4,15-, (16) and 4,16-, diethenyl[2.2]paracyclophane (18) and TCNE are influenced by the transannular electronic interactions.

Introduction:

The multi-bridged[2_n]phanes act as diene systems and undergo[4+2]Diels-Alder cycloaddition reactions with dienophiles under relatively mild conditions[1,2]. This activity has been rationalized by the high inherent strain of the phanes and the strain release which takes place in the course of the cycloaddition.

On the other hand styrene derivatives react with tetracyanoethylene (TCNE) to give stable cyclobutane derivatives[3,4] by a [2+2]cycloaddition between the dienophile and the vinyl group, the aromatic π-electrons are not being involved.

In the present investigation some vinyl substituted[2.2]paracyclophanes have been prepared and used as exo-olefinic systems in reactions with dienophiles such as TCNE, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), bromanil

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(BRL) and 4-phenyl-1,2,4-triazoline-3,5-dione to compare the behaviour of the cyclophanes, in which transannular electronic interactions exist, with that of conventional aromatic compounds lacking these interactions.

Results and Discussion

[2+2]Cycloaddition reactions (Figures 1 and 2)

Addition of 4-ethenyl[2.2]paracyclophane (1)[5] to TCNE in toluene gave a CT complex absorbing at λ_{max} = 542 nm in dichlorometane (Table 1). On heating the reaction mixture for five hours a cyclobutane derivative 2 was formed in 72% yield. However, on heating the reaction mixture for three days at 100 °C, 1,1-dicyano-2-(4-[2.2]paracyclophanyl) ethene (3) was obtained. Heating 2 in toluene afforded 3 (Fig. 1) as well, indicating that this adduct is an intermediate in the route from 1 to 3.

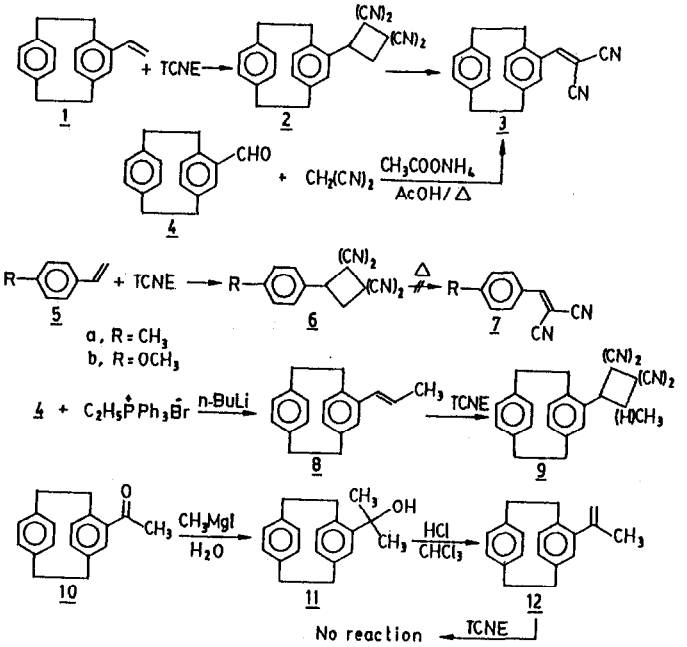

Fig.1

The reaction between TCNE and both p-methyl and p-methoxy styrene (5) under the same condition gave only the cyclobutane derivatives 6 and the benzylidene malononitriles were not formed on prolonged heating. Evidently, the transannular interactions in 1 enhances its cycloaddition reactivity with TCNE as compared by 5, since in spite of the fact that 1 is sterically more hindered than p-methyl and p-methoxy styrene (5), the former undergoes the cycloaddition reaction easily. Moreover, styrene itself does not react with TCNE under these conditions. The structure of 3 was further confirmed by

an independent synthesis from 4-formyl[2.2]paracyclophane (4)[6] with malononitrile and ammonium acetate in acetic acid at 110 °C (see Experimental Section).

Analogously TCNE forms a CT complex with 4-(β-methylethenyl)[2.2]paracyclophane (8) at λ_{max} = 556 nm in dichloromethane (Table 1). On heating a mixture of the donor and the acceptor in toluene a cyclobutane derivative 9 was formed. In contrast to 1, the reaction product 9 is not affected by heat, possibly due to the steric effect of the methyl group.

Reaction of 4-(α-methylethenyl)[2.2]paracyclophane (12) with TCNE did not lead to any reaction. Furthermore, the initialy formed CT complex was unstable and dissociated into its components in a few minutes. The presence of the methyl group in the α-position is responsible for such behaviour, since it tends to decrease the resonance between the olefinic and the aromatic π-electrons through distortion and deviation from planarity. Moreover, the presence of methyl groups in such positions results in increasing the steric hindrance making the interaction between both donor and acceptor less effective.

Interaction between 4,12-diethenyl[2.2]paracyclophane (13)[7] and excess TCNE is similar to that between 1 and TCNE, only one vinyl group being involved to provide 14 and 15 (Fig. 2). The reduced reactivity of 14 may be explained by the electron withdrawing cyano groups, which tend to deactivate the other half of the molecule by transannular electronic interactions.

The effect of transannular electronic interactions in 1 is illustrated in Fig. 3. As is apparent from this figure, these electronic interactions tend to increase the electron donating character of the vinyl substituted half of the molecule, and consequently the acceptor will complex with this half followed by cycloaddition reaction. As a result of this effect, the unsubstituted half will be deactivated correspondingly.

On the basis of the structural environment and the orientation of the two vinyl groups in the pesudo-geminal isomer, 4,15-diethenyl[2.2]paracyclophane (16)[7], it prefers to undergo an intramolecular[2+2]cycloaddition reaction to give 17 rather than reacting with TCNE. Heating 16 alone in toluene results in formation of 17. The spectral properties of 17 are in good agreement with those of the well known compound prepared by photolysis of 16[8].

The behaviour of the pesudo-ortho isomer, 4,16-diethenyl[2.2]paracyclophane (18)[7] towards TCNE is similar to its pesudo-para isomer, only formation of a mono cyclobutane ring derivative, being observed.

Surprisingly, 4-ethinyl[2.2]paracyclophane (20)[7] reacts with TCNE to give product 21 (Fig. 2). A mechanism of its formation is proposed in Fig. 4.

The formation of stable CT complexes of all mono, diethenyl and mono-ethinyl[2.2]paracyclophanes with TCNE was also observed. The electronic spectral data of some representive examples 1, 8 and 20 were recorded in

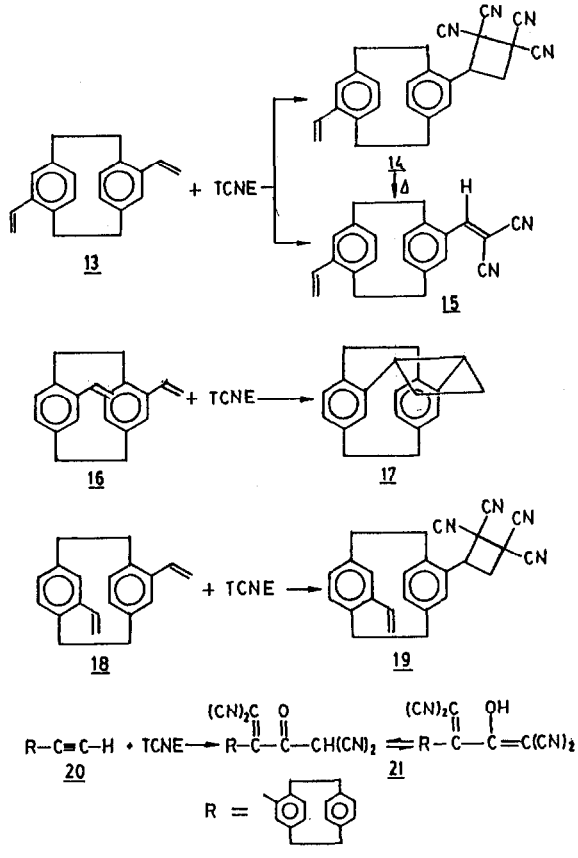
CN
CN
CN
CN
+ TCNE
13
14
Δ
H
CN
CN
15
+ TCNE
16
17
CN
CN
CN
CN
+ TCNE
18
19
(CN)2C
O
R–C≡C–H + TCNE → R–C–C–CH(CN)2
20
(CN)2C
OH
⇌ R–C–C=C(CN)2
21
R =

Fig. 2

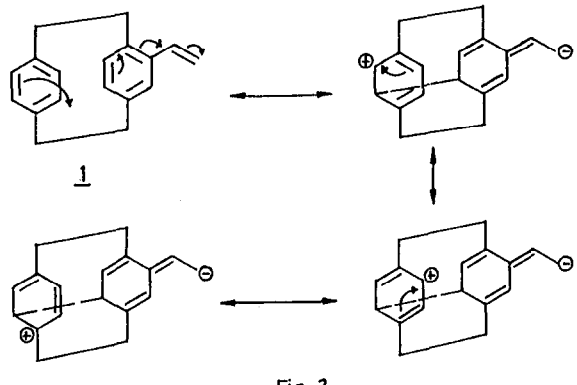
1

Fig. 3

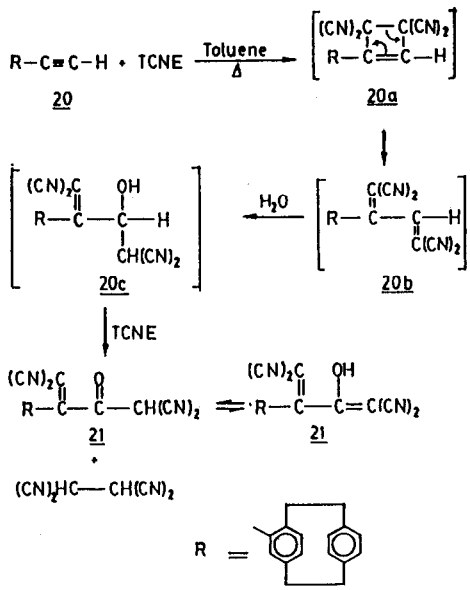

Fig. 4

Table 1

Maximum Absorption Wavelengths λ_{max} (nm), Molar Extinction Coefficients ε_{max} ($L.mol^{-1} cm^{-1}$), Association Constants K_{CT} ($L.mol^{-1}$) and the Transition Energies E(e.V.) for Compounds 1, 8 and 20 with TCNE.

Donor	λ_{max}(nm)	ε_{max} ($L.mol^{-1} cm^{-1}$)	K_{CT}($L.mol^{-1} cm^{-1}$)	E (e.V.)
1	542	333	12.67	2.29
8	556	286	15.98	2.23
20	522	250	6.40	2.38

Table 1. It is suggested that a stable charge-transfer complex is necessary as an intermediate step for such cycloaddition reactions with TCNE, since these compounds (as examples) formed stable CT-complex with TCNE that can be easily investigated, whereas 12 as an example cannot. At the same time these compounds gave adducts of cycloaddition products, whereas 12 did not react at all. The association constant (K_{CT}) values of such complex were determined using the Benesi-Hildebrand equation[9].

It is concluded from the data in Table 1 that, although 4-(β-methyl -etheny)[2.2]paracyclophane (8) forms a more stable CT complex than 4-ethenyl-[2.2]paracyclophane (1), which is related to the inductive effect of the methyl group, as mentioned before this methyl group itself has a steric effect during the chemical reaction. At the same time, 1 forms a more stable CT complex than 12 and this is due to the higher reactivity of the vinyl group compared with the isopropenyl one, and that is in agreement with the suggetion that the CT complex is an intermediate step for such cycloaddition reactions.

[4+2]Cycloaddition reactions (Fig. 5).

Heating 4-ethenyl[2.2]paracyclophane (1) with DDQ in acetic acid afforded product 22. According to the mass spectrum of the reaction product two alternative structures 22 and 23 are possible. However the ^{1}H-NMR spectrum did not show the m-coupling for H_a in 13, whereas the H_b and H_c protons appear as (dd) at δ = 6.69 (J = 7 Hz.) and at δ = 6.62 (J = 6.8 Hz.). Also, H_d and H_e show a multiplet at δ = 4.32-4.29, whereas H_f and H_g appear as multiplets at δ = 4.06-4.01. Besides the other aromatic and bridged protons, the spectrum includes two singlets at δ = 2.49 and at δ = 2.40 for the two methyl groups, suggesting that acetylation of the enol form of the DDQ by acetic acid had taken place.

The behaviour of BRL as dienophile differs from that of DDQ. Thus, it reacts with 1 to give adduct 24, which then eliminates two molecules of HBr to yield 25.

Similarly, 4-phenyl-1,2,4-triazoline-3,5-dione reacts with 1 in acetic acid following a [2+4]cycloaddition mode to form 26 (Fig. 5).

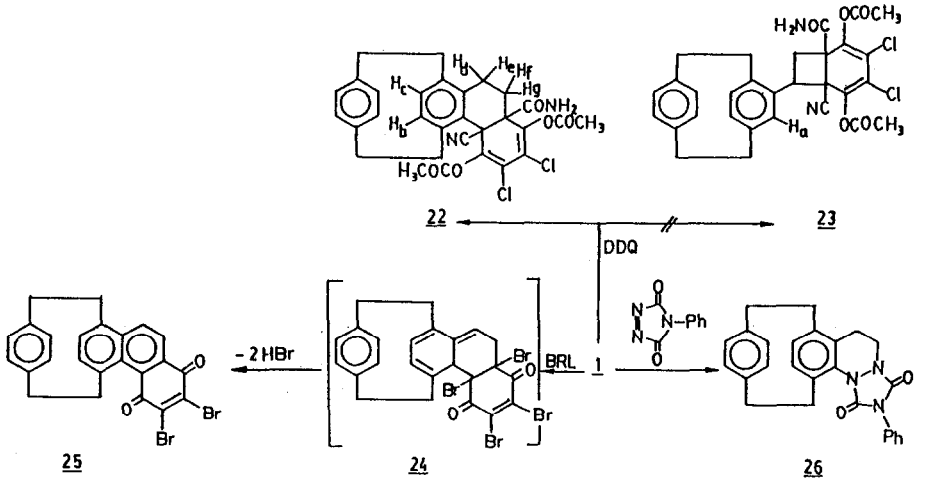

Fig. 5

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained on 320 FT IR spectrometer (KBr pellet and film). UV Spectra were performed on a Beckman UV 350 spectrophometer. ^{1}H-NMR and ^{13}C-NMR were determined on Bruker WM 400 (400.1 MHz.) spectrometer. Low resolution mass spectra were recorded on a Finnigan MAT 8430 instrument, at 70 eV.

Silica gel (Merck, 60 PF 254) was used for preparative thin layer plates chromatography.

TCNE (Merck) was recrystallized from chlorobenzene and sublimed, DDQ (Aldrich) was recrystallized from benzene/chloroform (2:3) and BRL (Merck) was recrystallized several times from benzene. Toluene, dichloromethane and acetonitrile were purified following ref. 10, dried and distilled.

Stock solutions (1×10^{-2} M) of TCNE and donors (1,8 and 16) were prepared for determination of stoichiometry by using Job's method[11].

1,1,2,2,-Tetracyano-3-(4-[2.2]paracyclophanyl)cyclobutane (2).

A mixture of 0.468 g (2 mmol) of 1 and 0.256 g (2 mmol) of TCNE in 100 ml of toluene was stirred at reflux temperature under N_2 for 5 hours. The solution was then concentrated and the residue was applied on chromatographic thin layer plates using dichloromethane as eluent. A solid colorless product was obtained, which recrystallized from benzene to give 2; yield 0.52 g (72%); m.p. 138 °C. IR(KBr); 3029-3007 (Ar-CH); 2928-2856 (aliph,-CH) ; 2246 cm^{-1} (C≡N). ^{1}H-NMR (CD_3COCD_3) δ = 2.90-3.70 (m, 10H, CH_2-CH_2 and $\underline{CH}_2$ -C(CN)$_2$), 5.05-5.15 (q, 1H, $\underline{CH}$-CH_2C (CN)$_2$), 6.25-6.60 (m, 7H, PC* -H). ^{13}C-NMR (CD_3COCD_3) δ = 31.97, 34.57,34.69,35.50,35.68,43.02,45.06, 50.58,115.59,115.89,116.12,116.42,131.51,132.61,133.19,133.90,133.94,134.22, 134.51,136.39,139.50,140.27,141.47,141.59. MS,m/z(rel. intensity), 362(M^+,14), 234(18), 115(22), 129(100), 104(58). Anal. Calcd. for $C_{24}H_{18}N_4$ (362.38) C, 79.54; H.5.01; N,15.45, found C,79.39; H,4.95; N, 15.40.

1,1-Dicyano-2-(4-[2.2]paracyclophanyl) ethene (3).

3 Was obtained by one of the following procedures:

(1) By applying the former procedure, with heating the reaction mixture for 3 days. The solvent was evaporated and the residue was recrystallized from ethanol to give 3; yield 0.36 g (63%), m.p. 125 °C. IR(KBr); 3041-3008(Ar-CH), 2959-2930 (aliph.-CH), 2227 cm^{-1} (C≡N). UV(CH_2Cl_2), λ_{max} = 362, 276 nm. ^{1}H-NMR($CDCl_3$) δ = 2.90-3.50(m,8H.CH_2 -CH_2), 6.39-7 .4 (m,7H, PC-H); 7.82(s,1H,-$\underline{CH}$=C(CN)$_2$). ^{13}C-NMR($CDCl_3$) δ = 33.67,34.93,35.19, 35.36,81.42,112.98,114.40,131.34,131.74,132.25,132.51,132.91, 133.17, 135.80,138.34,139.08,139.75,141.59,143.74,156.64. MS,m/z(rel. intensity),

* PC stands for paracyclophanyl.

284(M^+,4), 259(6), 142(16), 104(100). Anal. Calcd. for $C_{20}H_{16}N_2$(284.33) C,84.48; H,5.67; N,9.85, found C,84.32; H,5.62; N,9.90.

(2) By heating 0.362 g(1 mmol) of 2 under reflux in 50 ml toluene for 3 days. The yield; 0.20 g (70%).

(3) An authentic sample of 3 was prepared by heating a mixture of 0.472 g (2 mmol) of 4, 0.132 g(2 mmol) of malononitrile and 0.308 g(4 mmol) of fused amm. acetate in 50 ml glacial acetic acid under reflux for 10 hrs. The yield; 0.43 g(71%).

1,1,2,2-Tetracyano-3-p-tolylcyclobutane (6a).

A mixture of 2.56 g(20 mmol) of TCNE and 2.36 g(20 mol) of p-methyl styrene (5a) in 100 ml toluene was heated under reflux in N_2 atmosphere for 3 days. The mixture was concentrated and the residue was chromatographed on tlc plates using dichloromethane as an eluent. A solid colorless product was obtained which recrystallized from EtOH/CH_2Cl_2 to give 1.16 g(24%) of 6a; m.p. 183-4 °C. IR(KBr), 3010-3000 cm^{-1} (Ar-CH), 2980-2890 (aliphi-CH), 2220 cm^{-1} (C≡N). ^{1}H-NMR (CD_3COCD_3) δ = 2.33(m,3H); 3.36-3.60(m,2H); 4.83 (m,1H); 7.30(m,4H). The remaining spectra were as given in ref. 4.

1,1,2,2-Tetracyano-3-p-anisylcyclobutane (6b).

5b Was prepared as described above from 2.68 g(20 mmol) of p-methoxy styrene (5b) and 2.56 g(20 mmol) of TCNE in 100 ml toluene. Colorless crystals, 1.08 g(21%), m.p. 195 °C. IR(KBr), 3000-2990(Ar-CH), 2970-2920(aliph. -CH), 2225 cm^{-1} (C≡N): ^{1}H-NMR (CD_3COCD_3), δ =3.39-3.62 (m,2H); 3.64(s,3H); 4.85(m,1H); 7.29(m,4H). The other spectra were as given in ref. 4.

4-(β-Methylethenyl[2.2]paracyclophane (8).

To a stirred suspension of 9.275 g(25 mmol) of ethyltriphenylphosphonium bromide in 100 ml absolute THF, cooled to 0°C, 20 ml (24 mmol) n-butyllithium (1.2 M in hexane) was added dropwise. After stirring for 2 hours at room temperature the mixture was then cooled again to 0 °C and 0.944 g(4.0 mmol) of 4-formyl[2.2]paracyclophane (4) in 30 ml absolute THF was added with stirring. Stirring was continued for 2 days at room temperature, then the mixture was hydrolysed with water. Extraction with chloroform and recrystallization from n-hexane gave 8 as colorless crystals; yield 0.65 g(61%); m.p. 65 °C. IR(KBr); 3010-3000(Ar-CH), 2940-2890(aliph.-CH), 1590 cm^{-1} Ar-C=C). ^{1}H-NMR ($CDCl_3$) δ = 2.07 (d,3H,CH_3), 2.91-3.38(m,8H,CH_2-CH_2); 5.12(m, 1H, = CH-CH_3), 5.17 (m,1H,-CH=CH-CH_3), 6.32-6.65(m,7H,PC-H). ^{13}C-NMR($CDCl_3$) δ = 23.96, 34.46,35.32,35.28,35.47,115.42,130.16,130.69,132.21,132.27,132.39, 133.01,133.07,135.48,136.81,139.26,139.74,143.00,145.37. MS, m/z(rel. intensity) 248(M^+,20), 144(20), 143(100), 129(46), 128(28), 104(8). Anal. Calcd. for $C_{19}H_{20}$(248.35) C,91.88; H,8.12, found C,91.75; H,8.10.

3-Methyl-4-(4-[2.2]paracyclophanyl)-1,1,2,2-tetracyanocyclobutane (9).

A mixture of 0.496 g(2 mmol) of 8 and 0.256 g(2 mmol) of TCNE in 50 ml

toluene was heated under reflux for 3 days. The solution was concentrated and the residue was then recrystallized from EtOH to give the product 9 as colorless crystals; yield 0.50 g (67%), m.p. 220 °C. IR(KBr); 3130-2967(Ar-CH); 2960-2931 (aliph.-CH), 2250 cm^{-1} (C≡N). UV(CH_2Cl_2), λ_{max} = 280, 242 (nm). ^{1}H-NMR (CD_3COCD_3) δ= 1.84(d,3H,CH_3), 2.95-3.43(m,8H,CH_2-CH_2), 3.64-3.73(m,1H,CH-CH_3), 4.54(d,1H,-CH-$CHCH_3$); 6.30-6.70(m,7H,PC-H). ^{13}C-NMR (CD_3COCD_3) δ = 18.73,34.48,34.66,35.45,35.67,38.59,48.28,51.42,65.65,119.82, 113.93,114.19,115.72,130.98,131.80,133.20,133.90,133.97,134.10,134.26,136.90, 139.40,140.28,140.49,142.00. MS m/z(rel. intensity) 376(M^+,20), 365 (40), 248(22), 247(18), 143(60), 129(64), 104(50). Anal. Calcd. for $C_{25}H_{20}N_4$ (376.41) C,79.77; H,5.36; N,14.88, found C,79.65; H,5.31; N,14.83.

4-Isopropanoyl[2.2]paracyclophane (11).

A solution of 4.3 g(17.2 mmol) of 10 in 70 ml dry ether was added with stirring during ½ hr to the Grignard reagent[0.5 g(20.48 mmol) Mg in 20 ml dry ether + 1.3 ml (20.48 mmol) CH_3I in 25 ml dry ether]. The reaction mixture was stirred at R.T for 5 hrs. Thereafter 100 ml dry benzene was added to the reaction mixture and was refluxed for 6 hrs. After hydrolysis, extraction with dichloromethane and chromatographic purification the product 11 was obtained as yellow oil; yield 4.0 g (87%). IR(KBr), 3500-3300(OH), 3020-3009(Ar-CH), 2985-2975 cm^{-1} (aliph.-CH). ^{1}H-NMR($CDCl_3$) δ = 1.50 (s,3H, CH_3), 1.60(s,3H,CH_3), 2.20-3.40(m,8H,CH_2-CH_2), 6.3-6.8(m,7H). ^{13}C-NMR($CDCl_3$) δ = 16.54, 17.43,30.71,31.25,33.43,35.55,55.37,129.02,130.33,138.73,134.21, 135.44,135.85,136.08,136.24,136.56,136.71,137.14,139.80. MS, m/z(rel. intensity) 266(M^+,25), 251(62), 147(100), 104(12). Anal. Calcd. for $C_{19}H_{22}O$ (266.37) C,85.67; H,8.33, found C,85.53; H,8.29.

4-(α-Methylethenyl)[2.2]paracyclophane (12).

4.7 g(17.67 mmol) of 11 was dissolved in 30 ml $CHCl_3$ and added dropwise to stirred 30 ml HCl (4N) at R.T. Stirring was continued for 24 hrs at R.T. The organic layer was then extracted with $CHCl_3$, neutralized with $NaHCO_3$, washed several times with H_2O and dried over anhydrous $CaCl_2$.$CHCl_3$ was evaporated and the residue was recrystallized from toluene/petroluem ether to afford the product 12 as colorless crystals; 3.8 g(87%), m.p. 73 °C. IR(KBr), 3050-2995(Ar-CH), 2993-2980(aliph.-CH), 1595 cm^{-1} (Ar-C=C). ^{1}H-NMR($CDCl_3$) δ = 2.10(s,3H,CH_3), 2.80-3.2(m,8H,CH_2-CH_2), 5.10(s,2H,CH_2), 6.3-6.7(m,7H,PC-H). ^{13}C-NMR($CDCl_3$)δ = 23.90, 34.52,35.30,35.34,35.54,115,25,130.17,130.67, 130.71,132.24,132.37,132.97,133.04,135.44,136.76,139.21,139.32,139.69,143.02. MS, m/z(rel. intensity), 248(M^+,38), 144(22), 143(100), 129(50), 128(28), 105(17), 104(9). Anal. Calcd. for $C_{19}H_{20}$(248.35), C,91.88; H,8.12, found C,91.73; H,8.13.

12-Ethenyl-4-(2',2',3',3'-tetracyanocyclobutyl)[2.2]paracyclophane (14).

A mixture of 0.52 g(2 mmol) of 13 and 0.512 g(4 mmol) of TCNE in 100 ml

dry toluene was heated under reflux for 5 hrs. The solution was concentrated and chromatographed on prep. tlc plates using dichloromethane as eluent. Recrystallization from $CHCl_3$/EtOH gave 14 as colorless crystals; yield 0.45 g (58%); m.p. 142 °C. IR(KBr), 3020-3010 (Ar-CH); 2940-2920(aliph.-CH); 2235 cm^{-1} (C≡N). ^{1}H-NMR(CD_3COCD_3) δ = 2.85-3.75(m,10H, CH_2-CH_2 and CH_2-$C(CN)_2$); 5.10-5.20(t,1H,CH-CH_2-$C(CN)_2$); 5.38(dd,1H), 5.60(dd,1H), CH=CH_2; 6.40-7.42(m,7H, PC-H) and CH=CH_2). ^{13}C-NMR (CD_3COCD_3) δ = 31.59,34.62,34.73,35.70,35.94, 42.80,43.17,50.70,113.00,113.60,114.20,114.80,115.38,130.04,130.66,131.41, 132.75,133.78,134.51,134.72,135.85,138.06,138.22,138.55,141.20,143.55. MS, m/z(rel. intensity) 388(M^+,30), 235(19), 104(60). Anal. Calcd. for $C_{26}H_{20}N_4$ (388.42) C,80.39; H,5.19; N,14.42, found C,80.28; H,5.15; N,14.39.

4-(2',2'-Dicyanoethenyl)-12-ethenyl[2.2]paracyclophane (15).

15 was obtained by each of the following procedures:

(a) By the same procedure described above, using the same molar ratios of the rectants, but the time under reflux in toluene was extended to 3 days. Recrystallization from ethanol afforded 15 as pale-green crystals ; yield 0.45 g(73%), m.p. 145 °C. IR(KBr), 3081-3011(Ar-CH), 2934-2858 (aliph-CH); 2227 cm^{-1} (C≡N). UV(CH_2Cl_2) λ_{max} = 336,268,262,256,250(nm). ^{1}H-NMR($CDCl_3$) δ = 2.86-3.58(m,8H,CH_2-CH_2); 5.38(dd,1H); 5.60(dd,1H), CH=CH_2; 6.35-7.38(m,7H,PC-H and CH=CH_2); 7.83(s,1H,-CH=$C(CN)_2$). ^{13}C-NMR ($CDCl_3$) δ = 32.76,33.29,33.95,34.90.81.55,113.03,114.44,115.32,129.83, 130.04,130.66,131.41,131.73,132.75,133.78,134.72,135.85,138.22,138.55, 141.20,143.55,157.00. MS, m/z(rel. intensity) 310(M^+,8), 181(10), 130 (84), 129(100), 115(22). Anal. Calcd. for $C_{22}H_{18}N_2$(310.36) C,85.13;H, 5.85; N,9.02, found C,85.07; H,5.82; N,9.00.

(b) A solution of 0.388 g(1 mmol) of 14 in 30 ml dry toluene was heated under reflux for 3 days. Recrystallization from ethanol afforded the product 15 as colorless crystals; yield 0.30 g(96%), m.p. 142 °C. The spectral data were as the same as given in procedure (a).

4,15-(cis-1,2-cyclobutylene)[2.2]paracyclophane (17).

A mixture of 0.52 g(2 mmol) of 16 and 0.512 g(4 mmol) of TCNE was heated under reflux (under N_2) for 3 days. The solution was concentrated and chromatographed on prep. tlc plates using dichloromethane as eluent; two products were separated. One of them is TCNE (identified by an authentic sample). The other was recrystallized from ethanol to give 17 as colorless plates; yield 0.18 g(35%), m.p. 219 °C. IR(KBr); 3020-3000(Ar-CH); 2980-2920 cm^{-1} (aliph.-CH). ^{1}H-NMR($CDCl_3$) δ = 2.42-2.61(m,6H,CH_2-CH_2), 3.95-3.20 (m,6H,CH_2-CH_2), 4.43-4.56(m,2H,CH-CH_2), 6.19-6.46(m,6H,PC-H). The other spectral data were the same as reported in ref. 7.

16-Ethenyl-4-(2',2',3',3'-tetracyanocyclobutyl)[2.2]paracyclophane (19).

A mixture of 0.52 g(2 mmol) of 18 and 0.512 g(4 mmol) of TCNE in 100 ml

of toluene was heated for 3 days. The solution was concentrated and recrystallized from $CHCl_3$/EtOH to give 19 as colorless crystals; yield 0.42 g (54%); m.p. 250 °C. IR(KBr), 3010-3000(Ar-CH); 2980-2940(aliph.-CH), 2225 cm^{-1} (C≡N). UV(CH_2Cl_2) λ_{max} = 278,276,268,262,250(nm). ^{1}H-NMR(CD_3COCD_3) δ = 2.75-3.80(m,10H,CH_2-CH_2 and CH_2-$C(CN)_2$); 5.12-5.22(t,1H, CH-CH_2-$C(CN)_2$); 5.30(dd, 1H); 5.50(dd,1H), CH=CH_2; 6.30-7.42(m,7H,PC-H and CH=CH_2). ^{13}C-NMR (CD_3COCD_3) δ = 31.80,34.61,34.93,35.81,35.96,42.90,48.18,50.71,113.10,113.50, 114.20,114.80,115.22,130.08,130.80,131.30,132.70,133.80,134.61,134.83,135.42, 138.17,138.34,138.61,142.32,154.38. MS. m/z(rel. intensity) 388(M^+, 100), 362(20), 361(48), 360(34), 334(60), 105(59). Anal. Calcd. for $C_{26}H_{20}N_4$ (388.42) C,80.39; H,5.19; N,14.42, found C, 80.25, H,5.13; N,14.44.

2-(4-[2.2]paracyclophanyl)-1,1,5,5-tetracyanopenta-1,4-diene-3-one (21).

A mixture of 0.464 g(2 mmol) of 20 and 0.256 g(2 mmol) of TCNE in 80 ml dry toluene was heated under reflux for 3 days. The solution was then concentrated and the residue was applied on prep. tlc plates using dichloromethane as eluent. Recrystallization from ethanol gave the product 21 as red crystals; yield 0.39 g(50%) m.p. 210 °C (decom.). IR(KBr), 3080-3005 (Ar-CH),2995-2930 (aliph.-CH), 2223(=N), 1745 cm^{-1} (CO). UV(CH_2Cl_2) λ_{max} = 484, 374,344(nm). ^{1}H-NMR(CD_3COCD_3), δ = 1.30(br,1H,OH), 2.95-3.60(m,8H,CH_2-CH_2), 6.30-7.20(m,7H,PC-H). ^{13}C NMR(CD_3COCD_3) δ = 32.64,33.70,34.80,35.40,82.40, 84.70,112.30,113.92,114.35,114.71,132.80,133.41,133 .60,133.91,134.63,136.84, 137.45,138.30,139.12,139.80,140.19,142.40,206.20. MS, m/z(rel.intensity), 376(M^+,10), 119(18), 105(32), 104(100). Anal. Calcd. for $C_{25}H_{16}N_4O$ (388.38) C,77.31; H,4.15; N,14.42, found C,77.22, H,4.17; N,14.45.

Preparation of 22:

A mixture of 0.468 g(2 mmol) of 1 and 0.454 g(2 mmol) of DDQ in 200 ml acetic acid was heated under reflux for 10 hrs. The solution was then concentrated and the residue was recrystallized from benzene/petroleum ether to give 22; yield 0.32 g(28%), m.p. 110 °C. IR(KBr), 3437-3422(CONH_2), 3050-3000(Ar-CH), 2980-2950(aliph.-CH), 2237(C≡N), 1794,1739,1680 cm^{-1} (CO). ^{1}H-NMR($CDCl_3$) δ = 2.40(s,3H,$OCOCH_3$), 2.49(s,3H,$OCOCH_3$), 2.90-3.60(m,8H,CH_2-CH_2), 4.01-4.06(m,2H,H_f and H_g), 4.29-4.32(m,2H,H_d and H_e), 6.20-6.69(m,8H;$CONH_2$, 6H,PC-H). ^{13}C-NMR($CDCl_3$) δ = 28.20,29.40,32.40,34.50,35.76,35.96,40.08,40.20, 114.15,125.40,126.30,129.82,130.42,130.56,131.18,132.10,132.39,133.18,133.50, 134.40,134.53,134.96,135.01,135.18,136.72,138.01,139.35,165.80,170.80,171.20, MS, m/z(rel. intensity) 566(M+1,24), 565(M^+,37), 562(32), 527(30), 522(40), 520(58), 469(12), 467(38), 462(64), 460(100), 425(19), 338(8), 234(22), 233 (86), 129(90), 104(58). Anal. Calcd. for $C_{30}H_{26}Cl_2N_2O_5$(565.51) C,63.71, H, 4.63; Cl,12.56; N,4.95, found C,63.75; H,4.62; Cl,12.60; N,5.00.

Preparation of 25:

A mixture of 0.468 g(2 mmol) of 1 and 0.848 g(2 mmol) of BRL in 150 ml

acetic acid was refluxed for 3 days. The solution was then concentrated and the residue was recrystallized from benzene/petroleum ether to give the product 25 as colorless plates; yield 0.58 g(32%), m.p. 120°C. IR(KBr) 3081-3006(Ar-CH), 2955-2929(aliph.-CH), 1690 cm^{-1} (CO). UV(CH_2Cl_2) λ_{max} = 240 , 328,320,236(nm). ^{1}H-NMR($CDCl_3$) δ = 2.75-3.43(m,8H,CH_2-CH_2), 6.38-6.55(m,4H, PC-H),6.72-6.75(d,2H,PC-H), 7.62-7.65(d,2H,Ar-H). ^{13}C-NMR($CDCl_3$) δ= 33.79, 34.57,35.13,35.42,129.28,130.25,131.77,132.03,132 .10,133.12,133.65,133.92, 134.88,136.69,137.92,139.22,139.39,139.20,139.79,140.03,141.15,168.14. MS, m/z(rel. intensity) 496(M^+,22),392(100), 390(60), 292(36), 232(54),145(100) , 128(60), 104(70). Anal. Calcd. for $C_{24}H_{16}Br_2O_2$(496.36) C,58.07; H,3.25;Br, 32.23, found C,57.93; H,3.22; Br, 32.20.

Preparation of 26:

In 100 ml acetic acid, a mixture of 0.468 g(2 mmol) of 1 and 0.35 g (2 mmol) of 4-phenyl-1,2,4-triazolin-3,5-dione was refluxed for 5 days. Acetic acid was then evaporated and the residue was applied on tlc plates using CH_2Cl_2 as eluent. Recrystallization from ethyl acetate afforded 26 as colorless crystals; yield 0.52 g(64%), m.p. 300 °C. IR(KBr)3010-3000(Ar-CH), 2980-2950(aliph.-CH), 1710 cm^{-1} (CO). ^{1}H-NMR(DMSO-d_6) δ =2.35-4.22(m,12H,CH_2-CH_2), 6.10-6.50(m,6H,PC-H), 7.30-7.63(m,5H,Ar-H). ^{13}C-NMR(DMSO-d_6) δ= 32.20, 33.84,34.28,36.15,40.17,42.29.129.16,129.22,130.38,132.25,134.37,135.45, 135.98,136.01,136.27,136.56,138.15,139.47.140.07,140.18,141.59,141.64, 142.30,151.30,152.80. MS, m/z(rel. intensity) 409(M^+,22), 105(16), 104 (100). Anal. Calcd. for $C_{26}H_{23}N_3O_2$(409.44) C,76.26; H,5.66; N,10.26, found C, 76.15; H,5.58; N,10.25.

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