Layered Compounds. XLIV.[1] Transannular π-π Interactions in Tetracyanoethylene Complexes of [*m.n*]Paracyclophadiynes and the Related Cyclic Acetylenes

Takahiro Kaneda and Soichi Misumi

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565

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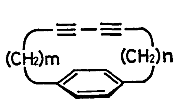
The electronic spectra of TCNE complexes of acyclic and cyclic diacetylenes and cyclic tetraacetylenes were measured. They show a maximum in the narrow region 423—431 nm regardless of ring strain in the donor molecules and proximity of two diacetylene groups. Crystalline two-to-one TCNE complexes of [*m.n*]paracyclophadiynes were prepared, the formation of one-to-one TCNE complexes in solution being established by means of the Benesi-Hildebrand plots using various molar ratios of the two components. The electronic spectra of some 1 : 1 [*m.n*]paracyclophadiyne–TCNE complexes were measured. The spectra suggest that the complexes are equilibrium mixtures consisting of three isomeric complexes, *i.e.*, a diacetylene-site complex and two pseudo-conformers of benzene-site complex. The longer wavelength band of [*m.n*]paracyclophadiyne complexes shows a marked red-shift as compared with the other bands. This is interpreted in terms of transannular π-π interaction between the diacetylene group and the benzene ring fixed closely with each other by shortening of methylene bridges. The contribution of the three isomeric complexes on the red-shift is discussed.

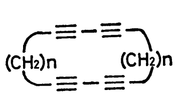
In previous papers of this series[2,3] reports were given on the syntheses and spectra of [*n*]paracyclophadiynes or [*m.n*]paracyclophadiynes $\mathbf{1}_{mn}$ where *m* and *n* are the numbers of bridging methylenes inserted between a benzene ring and a diacetylene group. Thermal and photochemical cycloadditions[4] and ^{13}C-NMR spectra[5] of $\mathbf{1}_{mn}$ and related cyclic diacetylenes were also investigated. The unusual reactions and spectral properties have been interpreted in terms of proximity interactions between the diacetylene group and the aromatic ring placed close to each other in a molecule.

Tetracyanoethylene (TCNE) complexes have often been used in studies on the relative π-base strength of various methyl-substituted benzenes[6] and transannular π-π interactions in donor molecules, *e.g.*, [*m.n*]paracyclophanes,[7] [2.2]metacyclophanes,[8] multilayered [2.2]paracyclophanes,[9] and multilayered [2.2]paracycloheterophanes.[10] The π-basicity of the donor molecules increases with an increase in the number of substituted methyl groups and/or stacking benzene rings and an increase in the face-to-face overlapping between aromatic nuclei. In contrast to the cyclophanes having symmetric donor-sites, unsymmetric cyclophanes containing non-equivalent donor sites such as 4-acetyl- and 4-methoxy-[2.2]paracyclophanes[7b] can be expected to form two isomeric one-to-one complexes with TCNE, *i.e.*, pseudo-configurational isomers. An important factor for determining which isomeric complex is more predominant or exclusive is the magnitude of ionization potentials of the constituent donor moieties. The relative orientation between an acceptor and a donor, or pseudo-conformation, is the second factor to affect transition energy of charge transfer (CT) complexes. Two pseudo-conformers were assumed for one-to-one *p*-substituted benzene–TCNE complexes and were investigated experimentally and theoretically.[11]

Since dialkyldiacetylenes have also been proved to form CT complexes with TCNE in the present study, paracyclophadiynes $\mathbf{1}_{mn}$ can be regarded as unsymmetric donor molecules having two possible donor sites. In the present work the transannular π-π interactions in $\mathbf{1}_{mn}$ and cyclic tetraacetylenes $\mathbf{2}_n$, where a suffix *n* is the number of bridging methylenes, are discussed considering geometrical effect with the aid of their TCNE complexes.



1mn



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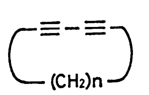

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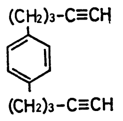

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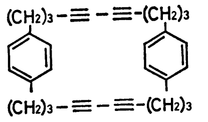

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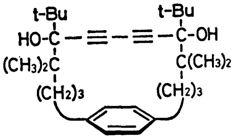

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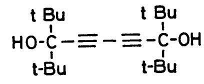

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Results and Discussion

Charge Transfer Complexes of Alkadiyne and Alkynes with TCNE. The π-donation of triple bonds have been observed in some examples,[12] *e.g.*, in the formation of hydrogen bond with hydroxylic protons[13] and of molecular complex with hydrogen chloride,[14] but not in TCNE complex. Thus we first examined alkadiyne- and alkyne–TCNE complexes in connection with the study of paracyclophadiyne–TCNE complexes.

The equilibrium constants of 5-decyne- and 5,7-dodecadiyne–TCNE complexes were determined at 25°C in dichloromethane with the Benesi-Hildebrand equation[15]

$$\frac{(\mathrm{A})l}{\log I_0/I} = \frac{1}{K\varepsilon}\cdot\frac{1}{[\mathrm{D}]} + \frac{1}{\varepsilon} \tag{1}$$

where (A), l, [D], ε, and K are molar concentration of TCNE, light path length, mole fraction of the alkyne, apparent molar extinction coefficient, and the equilibrium constant, respectively. Plots of $(\mathrm{A})l/(\log I_0/I)$ against $1/[\mathrm{D}]$ give straight lines for both complexes, demonstrating that a 1 : 1 complex is formed between

Table 1. Absorption maxima and equilibrium constants of alkyne–TCNE complexes (CH_2Cl_2, 25 °C)

Alkyne	λ (nm)	K (ε)
5,7-Dodecadiyne	424	7.0(1100)
5-Decyne	370	3.9(500)
3-Octyne	367	—

the alkyne and TCNE in the solution. The observed values of λ_{mn} and K given in Table 1 indicate 5,7-dodecadiyne to be a much stronger π-base to TCNE than 5-decyne.

Electronic Spectra of Cyclic Di- and Tetraacetylene–TCNE Complexes. The electronic spectra of $\mathbf{2}_n$– and $\mathbf{3}_n$–TCNE complexes exhibit absorption bands with a maximum in the narrow region 423—431 nm as well as the one-to-one 5,7-dodecadiyne–TCNE complex, suggesting that each spectrum is associated with the transition of one-to-one complex.

The TCNE complexes of two cyclic diacetylenes, strained $\mathbf{3}_9$ and $\mathbf{3}_{10}$, show the absorption maxima at the same position. This suggests a slight strain effect on the CT-transition of diacetylene–TCNE complexes. The cyclic tetraacetylene $\mathbf{2}_3$ in which a pair of diacetylene groups are closely fixed shows an abnormal spectrum[20b)] due to transannular electronic interaction as compared with the other homologs $\mathbf{2}_n$. Thus, the $\mathbf{2}_3$–TCNE complex is also expected to exhibit transannular π-π electronic interaction differing from the other $\mathbf{2}_n$-TCNE complexes. However, it reveals a spectrum similar to those of the others, indicating that the proximity of the two diacetylene groups is not important for CT-transition energy of cyclic tetraacetylene–TCNE complexes.

Composition and Geometry of Paracyclophadiyne–TCNE Complexes. Crystalline TCNE complexes of both $\mathbf{1}_{34}$ and $\mathbf{1}_{44}$ were isolated and confirmed to consist of two moles of donors and one mole of TCNE. Harata *et al.* reported the crystal structure of the latter complex, where a TCNE molecule is sandwiched between the two benzene rings of two $\mathbf{1}_{44}$ molecules but not complexed with diacetylene group-site (Fig. 1).[16)]

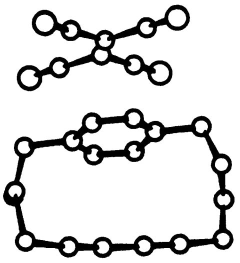


Fig. 1. Crystal structure of two-to-one [4.4]paracyclophadiyne–TCNE complex.[16)]

In solution, on the other hand, [*m.n*]paracyclophadiynes $\mathbf{1}_{mn}$ are found to form one-to-one TCNE complex by the following experiments. When molar ratios of $\mathbf{1}_{33}$ and $\mathbf{1}_{44}$ *vs.* TCNE in dichloromethane are changed in the ranges 16—1/19 and 12—1/13, respectively, the position of absorption maximum and the shape of absorption curve remain unchanged for both the complex solution.

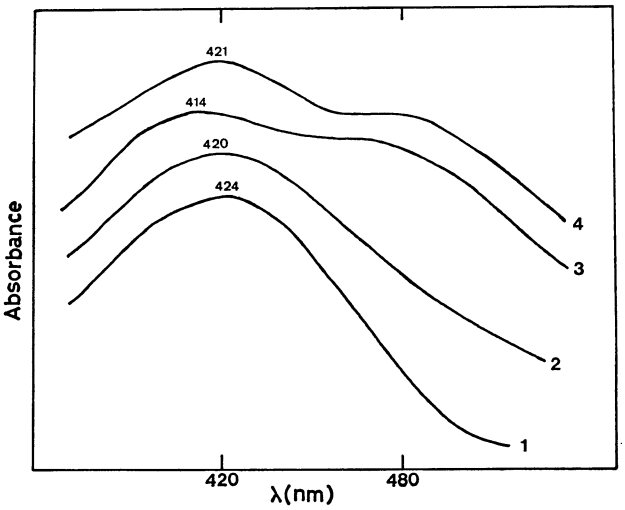
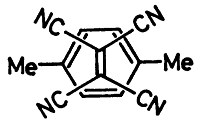


Fig. 2. Electronic spectra of TCNE complexes (CH_2Cl_2, room temp): curve 1, 5,7-dodecadiyne; 2, a 1:6:6 mixture of TCNE, **4**, and 5,7-dodecadiyne; 3, **4**; 4, **6**. * λ_{max} in nm.

Two possible pseudo-configurational isomers are expected for the one-to-one complex of $\mathbf{1}_{mn}$, *viz.*, a diacetylene-site complex $\mathbf{10}_{mn}$ and a benzene-site complex for which two conformational isomers $\mathbf{11}_{mn}$ and $\mathbf{12}_{mn}$ are theoretically anticipated for *p*-xylene–TCNE complex.[11c),17)]

In studying the electronic spectra of $\mathbf{1}_{mn}$–TCNE complexes, it is advantageous to examine those of TCNE complexes of *p*-di(4-pentynyl)benzene **4** and [5.5]-paracyclophadiyne derivative **6** bearing bulky groups at the propargyl positions. The spectra are shown in Fig. 2. A mixture of TCNE and 1-alkyne or 1,1,6,6-tetra-*t*-butyl-2,4-hexadiyne-1,6-diol **7** having similar bulky groups at the propargyl positions exhibits no band in the visible region. Complexing with TCNE is considered to be difficult owing to steric hindrance of the bulky groups in the latter case. Thus the observed CT-bands of **4**– and **6**–TCNE complexes should be attributed to the benzene-site complex, but not to the diacetylene-site one. The shorter- and longer-wavelength bands of these complexes are assigned to "perpendicular" and "parallel" complexes, respectively, according to the assignment (**8** and **9**)[11c)] for *p*-xylene–TCNE complex. As seen in Fig. 2, a mixture of TCNE, **4**, and 5,7-dodecadiyne of a 1:6:6 ratio shows a spectrum which is characterized as a superposition of the spectra due to the two independent complexes. It is quite reasonable that there are three isomeric complexes $\mathbf{10}_{mn}$—$\mathbf{12}_{mn}$ in the equilibrium mixture of $\mathbf{1}_{mn}$–TCNE complex (Scheme 1).



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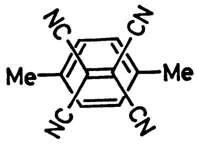

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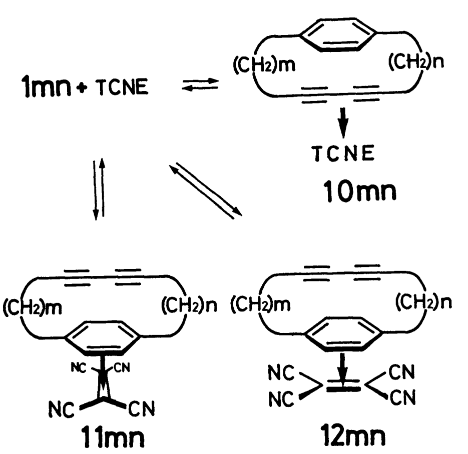

Scheme 1.

Electronic Spectra of Paracyclophadiyne–TCNE Complexes. The absorption curves and their apparent maxima of $\mathbf{1}_{mn}$– and **5**–TCNE complexes are given in Fig. 3 and Table 2. All the complexes show a maximum in the narrow region 425—431 nm, $\mathbf{1}_{33}$–TCNE complex exhibiting an additional, strong maximum at 555 nm. The other curves are unsymmetric, suggesting an additional band submerged in longer wavelength region. We have resolved the curves into two components on the assumption that they consist approximately of two CT-bands, since the shorter wavelength band (λ_{max} *p*-xylene 415 nm;[6] [*m.n*]paracyclophane 416—430 nm)[7a] of the two maxima of *p*-xylene derivative–TCNE complexes and the absorption band (421—431 nm) of diacetylene–TCNE complex appear at nearly the same position. The results of curve analyses are given in Table 2. The $\mathbf{1}_{24}$–, $\mathbf{1}_{44}$–, and $\mathbf{1}_{55}$–TCNE complexes exhibit a longer wavelength band at 470 or 480 nm in addition to a shorter wavelength band. From the fact that the absorption curves of these complexes are very similar to curve 2 in Fig. 2, one may reason as follows: the shorter wavelength band is possibly attributed both to the diacetylene-site complex $\mathbf{10}_{mn}$ and the benzene-site "perpendicular" complex $\mathbf{11}_{mn}$, and the longer wavelength band to the "parallel" complex $\mathbf{12}_{mn}$. It is also shown that in the cases of the three $\mathbf{1}_{mn}$–TCNE complexes, there is no appreciable transannular π-π interaction between the two chromophores in the donor molecules.

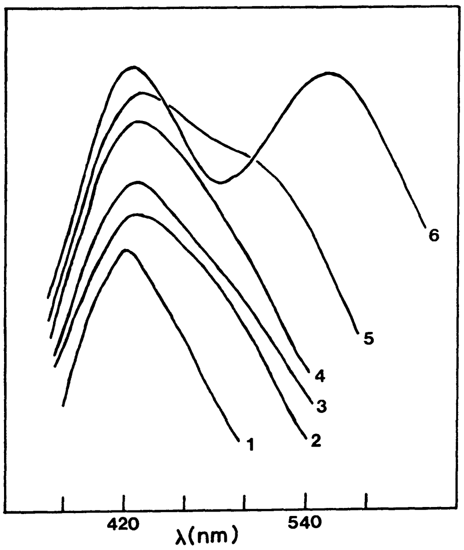

Fig. 3. Electronic spectra of [*m.n*]paracyclophadiyne–TCNE complexes (CH_2Cl_2, room temp): curve 1, **5**; 2, $\mathbf{1}_{24}$; 3, $\mathbf{1}_{55}$; 4, $\mathbf{1}_{44}$; 5, $\mathbf{1}_{34}$; 6, $\mathbf{1}_{33}$.

TABLE 2. CT-BAND POSITIONS OF CYCLOPHANE– AND *p*-XYLENE–TCNE COMPLEXES(CH_2Cl_2, ROOM TEMP)

Donor	λ_{max} (nm)[a]	
$\mathbf{1}_{33}$	427 (425)	555 (555)
$\mathbf{1}_{34}$	431 (415)	(510)
$\mathbf{1}_{24}$	430 (402)	(470)
$\mathbf{1}_{44}$	429 (410)	(480)
$\mathbf{1}_{55}$	426 (410)	(480)
5	425 (415)	(480)
p-xylene[b]	426 (408)	(490)
p-xylene[c]	415	460
[3.3] paracyclophane[d]	486	599
[3.4] paracyclophane[d]	470	538

a) Values in parentheses denote curve-resolved maximum. b) Ref. 11c ($CHCl_3$). c) Ref. 6. d) Ref. 7a.

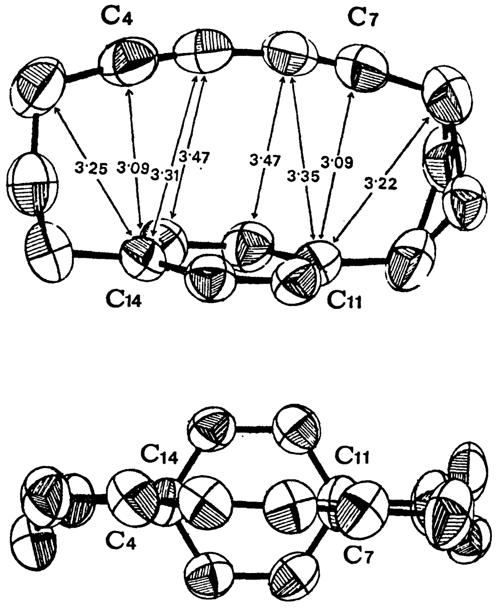

Fig. 4. Crystal structure of [3.3]paracyclophadiyne.[18]

The longer wavelength band of $\mathbf{1}_{33}$–TCNE complex appears with a red-shift of 75 nm as compared to those of complexes of $\mathbf{1}_{44}$ and $\mathbf{1}_{55}$. The crystal structure of $\mathbf{1}_{33}$ shows a remarkable distortion of the diacetylene group and a slight bending of the benzene ring from their normal arrangements as seen in Fig. 4.[18] Since the positions of CT-absorption maxima are little affected by such distortions of benzene ring[7a,b] and of diacetylene group as described for $\mathbf{3}_9$ and $\mathbf{3}_{10}$, the marked red-shift of $\mathbf{1}_{33}$–TCNE complex should be interpreted in terms of considerable transannular π-electron donation from the non-complexed diacetylene group to the complexed benzene ring in the parallel complex $\mathbf{12}_{33}$. On the other hand, the shorter wavelength band can be assigned to the complex $\mathbf{10}_{33}$ and $\mathbf{11}_{33}$, provided that both complexes are in an equilibrium as shown in Scheme 1. Since the maximum of this band appears at nearly the same position as the corresponding maxima of the other complexes $\mathbf{10}_{mn}$ and $\mathbf{11}_{mn}$ having different number of bridged methylene, it is suggested that the transannular π-π interaction does not make a very important contribution to the CT-tansitions of both complexes $\mathbf{10}_{33}$ and $\mathbf{11}_{33}$.

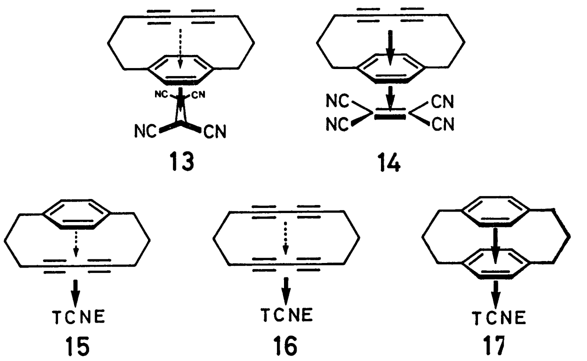

Fig. 5. Transannular π-π interaction in cyclic donor–TCNE complexes; thick and dotted arrows in the donor molecules indicate effective and unobserved interactions, respectively.

The complex of $\mathbf{1}_{34}$ shows an intermediate spectral feature between those of its homologs $\mathbf{1}_{33}$ and $\mathbf{1}_{m=n>3}$. The argument described for $\mathbf{1}_{33}$ seems to be also applicable to this complex.

Geometrical Effect of TCNE Complexes on Transannular π-π Interaction. A different π-donating character of the diacetylene group was observed between two pseudo-conformer $\mathbf{11}_{33}$ and $\mathbf{12}_{33}$ (or **13** and **14** in Fig. 5). The difference can be qualitatively accounted for according to the discussion for the spectra of two isomeric complexes of *p*-disubstituted benzenes.[11a,c] The molecular orbitals that take part in allowed CT-transitions are depicted as **18** for **13** and as **19** for **14**. In **19**, the large π-electron density at C_4, C_7, C_{11}, and C_{14} causes facile overlapping between the three chromophores as expected from the crystal structure in Fig. 4, making the charge delocalization favorable. In the alternative pseudo-conformer **18**, the π-π interaction is not favorable because of the existence of a nodal plane passing through C_4, C_7, C_{11}, and C_{14} (Fig. 6). Two bands of TCNE complexes of [3.4]paracyclophadiyne $\mathbf{1}_{34}$ and [3.3]paracyclophane[7a] are similarly explained in terms of two pseudo-conformers.

It is noteworthy that there is no appreciable transannular delocalization in the diacetylene-site complexes, **15** and **16**, and the benzene-site perpendicular complex **13** in contrast to marked delocalization in the parallel complex **14**. Unusual thermal cycloaddition reactions of [*m.n*]paracyclophadiynes with TCNE were observed to proceed *via* the complex $\mathbf{10}_{mn}$ and not *via* the more stable $\mathbf{12}_{mn}$.

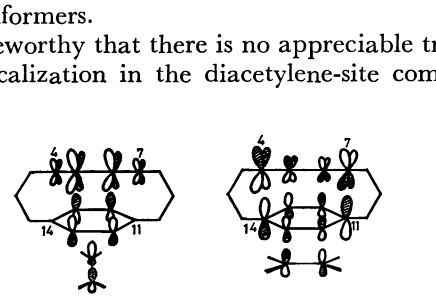

Fig. 6. Orbital sets of [3.3]paracyclophadiyne–TCNE complex.

Experimental

Materials. Five [*m.n*]paracyclophadiynes $\mathbf{1}_{mn}$, cyclic tetraacetylenes $\mathbf{2}_n$ (n=9 and 10), cyclic diacetylenes $\mathbf{3}_n$, diethynyl compound **4**, and paracyclophatetrayne **5** were prepared previously.[2] The diacetylene derivatives having bulky group at propargyl positions **6** and **7**,[19] cyclic tetraacetylenes $\mathbf{2}_n$ (n=3 and 4),[20] 5,7-dodecadiyne,[21] 5-decyne, and 3-octyne[22] were synthesized respectively according to the corresponding methods.

Tetracyanoethylene was recrystallized from chlorobenzene and sublimed twice at 125 °C/1 mmHg. TCNE was dissolved without coloration in dichloromethane (E. Merck Co. spectrograde) used as a solvent.

Electronic Spectra and Determination of Equilibrium Constants. All the spectra were measured on a Hitachi EPS-3T autorecording spectrophotometer using a 10 mm cell at room temperature within a few minutes after preparation of the solution.

Dichloromethane solutions of $\mathbf{1}_{mn}$- and **5**-TCNE complexes were prepared by a method similar to that for [*m.n*]paracyclophane–TCNE complexes.[7a] The observed maximum absorbances were 0.57—0.72 for $\mathbf{1}_{mn}$-complexes and 0.36 for **5**-complex. From the solutions of $\mathbf{1}_{33}$- and $\mathbf{1}_{44}$-complexes the donors were recovered by chromatography on alumina using hexane–ether (2: 1) as an eluent.

The spectra of $\mathbf{2}_n$- and $\mathbf{3}_n$-TCNE complexes were measured as follows: concentration of donor, 0.005—0.022 M; concentration of TCNE, 0.022—0.032 M; molar concentration ratio, 0.3—0.9. The observed maximum absorbances were in the range 0.20—0.42.

The Benesi-Hildebrand method[19] was used to determine the molar extinction coefficients and equilibrium constants for 5,7-dodecadiyne- and 5-decyne-TCNE complexes in dichloromethane at 25 °C. In these determinations the mole fraction of the donors was varied from 0.018 to 0.044, while the concentration of TCNE was held between 0.007 and 0.011 M. A straight line was obtained through the four measured points for each complex. The values of K and ε in Table 1 were calculated by the least-squares method.

Preparation of Crystalline Paracyclophadiyne–TCNE Complexes. The two-to-one complexes of [3.4]- and [4.4]-paracyclophadiynes over TCNE were prepared as follows.

A mixture of 0.1 g of $\mathbf{1}_{34}$ and 0.03 g of TCNE was dissolved in 0.5 ml of ethyl acetate, and then 3 ml of pentane was added. The solution was cooled to −20 °C to yield dark-red rhombic plates, which were collected and dried. $\mathbf{1}_{34}$–TCNE 2: 1 complex, mp 96—102 °C. Found: C, 83.84; H, 6.37; N, 9.69%. Calcd for $C_{40}H_{36}N_4$: C, 83.88; H, 6.34; N, 9.78%.

A solution of $\mathbf{1}_{44}$ (0.1 g) and TCNE (0.02 g) in 0.5 ml of ethyl acetate was cooled to −20 °C to give red crystals. The crystals were dissolved in a minimum amount of ethyl acetate, and the solution was allowed to stand overnight at room temperature. During this period the solvent was nearly completely evaporated to give reddish-orange rhombic plates, which were collected, washed quickly with petroleum ether containing a small amount of ethyl acetate, and dried. $\mathbf{1}_{44}$–TCNE 2: 1 complex, mp 117—128 °C. Found: C, 83.88; H, 6.71; N, 9.42%. Calcd for $C_{42}H_{40}N_4$: C, 83.96; H, 6.71;

N, 9.33%.

The infrared spectra of these crystalline complexes were illustrated as a superposition of those due to the two components.

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