

Thermal Rearrangement of 2,5-Bis(dicyanomethylene)bicyclo[4.2.0]oct-7-ene and 2,5-Bis(dicyanomethylene)bicyclo[4.2.0]octa-3,7-diene. Unexpected Formation of 2,6-Bis(dicyanomethylene)bicyclo[3.3.0]octa-1(5)-ene and -octa-3,7-diene, New Electron Acceptors

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Upon heating at 200 °C in *o*-dichlorobenzene, 2,5-bis(dicyanomethylene)bicyclo[4.2.0]octa-3,7-diene gave rise to 2,6-bis(dicyanomethylene)bicyclo[3.3.0]octa-3,7-diene by a rearrangement as a sole isolable product in modest yield, and no trace of 5,8-bis(dicyanomethylene)cycloocta-1,3,6-triene, the expected product, was detected. On the other hand, 2,5-bis(dicyanomethylene)bicyclo[4.2.0]octa-7-ene underwent a thermal reaction at lower temperature (110 °C in toluene) to give 5,8-bis(dicyanomethylene)-1,3-cyclooctadiene, the normal ring-opened product, and 2,6-bis(dicyanomethylene)bicyclo[3.3.0]octa-1(5)-ene, a rearranged product, in about 1:1 ratio. The rearranged product has a planar 1,1,6,6-tetracyanohexatriene structure (X-ray analysis), and shows a considerably lower electron affinity than that of tetracyanoethylene and 7,7,8,8-tetracyano-*p*-quinodimethane. The electron acceptor also formed a crystalline 1:1 charge transfer complex with tetrathiafulvalene, of which electronic conductivity was near insulating ($1.1 \times 10^{-7} \text{ S cm}^{-1}$). We have proposed a possible mechanism for the rearrangements involving the zwitterionic intermediates.

Polycyanosubstituted π -electron systems have attracted much attention because of their unique properties as excellent electron acceptors. Particularly, tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) have been widely modified to acquire insight into the relationship between the structure and the electronic properties.^{1–4} However, 5,8-dicyanomethylene-1,3,6-cyclooctatriene (**1**), a simple eight-membered ring vinylog of TCNQ, has remained unknown to date. Although most are probably inferior to TCNQ as an electron acceptor, **1** would still be worth studying from structural and physicochemical points of view.

It is well known that a thermal ring opening of bicyclo[4.2.0]oct-7-ene produces cycloocta-1,3-diene, and that cyclooctatetraene is in equilibrium with a valence isomer, bicyclo[4.2.0]octa-2,4,7-triene, at around room temperature.⁵ Taking advantage of these transformations, we synthesized a number of novel eight-membered-ring conjugated compounds by thermal ring openings of the corresponding bicyclic valence isomers (Chart 1).^{6–10} Among them, 5,8-dimethylene-1,3,6-cyclooctatriene (**2**) and its derivatives **3–4** were prepared by a thermal reaction of 2,5-dimethylenebicyclo[4.2.0]octa-3,7-dienes **5–7** in good yields.^{8–10} In contrast to the successful synthesis, a thermal reaction of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (**9**) failed to yield cycloocta-2,5,7-triene-1,4-dione (**8**), giving tropone instead, involving decarbonylation.¹¹ However, a slight structural modification changed the course of the thermal reaction, and thus bicyclo[4.2.0]octa-7-ene-2,5-dione (**10**), the 7,8-dihydro compound of **9**, underwent a clean ring opening to cycloocta-5,7-diene-1,4-dione (**11**). The synthesis of **8** was attained by the bromination and dehy-

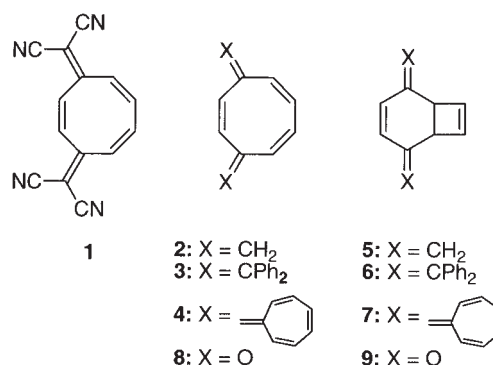
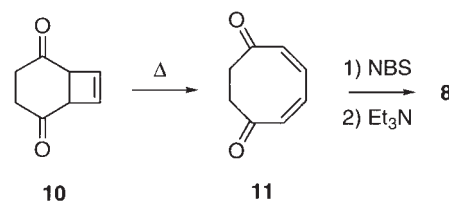


Chart 1.



Scheme 1.

drobromination of **11** (Scheme 1).¹² Based on this background information, we attempted the synthesis of **1** through a thermal reaction of either 2,5-bis(dicyanomethylene)bicyclo[4.2.0]octa-3,7-diene (**12**) or its 3,4-dihydro derivative **13**. However, the attempts failed and instead we found novel rearrangements of **12** and **13**, and studied the physicochemical

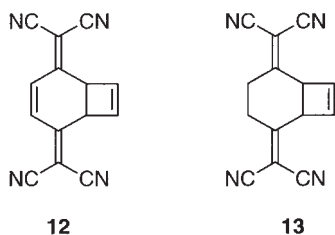


Chart 2.

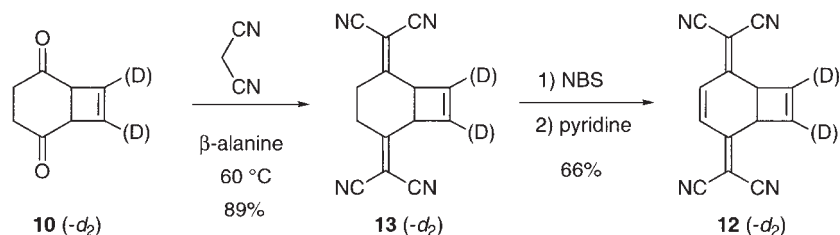
properties of the resulting rearranged products as electron acceptors (Chart 2).

Results and Discussion

Synthesis of Precursors. Compound **13** was prepared by the Knoevenagel condensation of the dione **10**¹³ with malononitrile in 89% yield. The bromination and dehydrobromination of **13** in a similar fashion to the synthesis of TCNQ^{14,15} gave

12 in 66% yield (Scheme 2). Dideuterated compounds **12-d₂** and **13-d₂** were prepared similarly from **10-d₂**, obtained by the photochemical cycloaddition of 2-cyclohexene-1,4-dione¹⁶ with dideuterioacetylene.

Thermal Reactions. Because the pyrolytic reaction of **12** at 500 °C by a flow method¹⁷ resulted in extensive decomposition, thermal reactions were examined in solution. The heating of **12** in *o*-dichlorobenzene at 180 °C for 5 h afforded a pale-yellow compound **14** in 22% yield as a sole isolated product. The structure of **14** was assigned to 2,6-bis(dicyanomethylene)bicyclo[3.3.0]octa-3,7-diene, based on an elemental analysis and spectral data (Table 1). The ¹H NMR spectrum of **14** is composed of three signals with the same intensity for two sets of olefinic protons and a set of aliphatic protons. The spectral data indicate *C₂* or *C_i* symmetry of the molecule and the presence of two sets of conjugated dicyanomethylenecyclopentenes. When the reaction was monitored by ¹H NMR in deuterated bromobenzene, the decrease of **12** es-

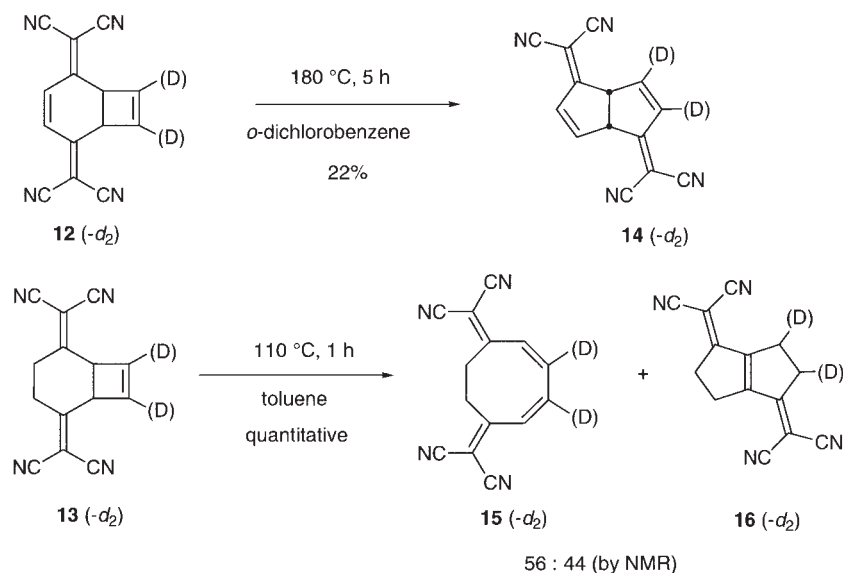


Scheme 2.

Table 1. Spectral Properties of New Compounds

	IR ($\nu_{\text{CN}}/\text{cm}^{-1}$)	UV-vis ^{a)} ($\lambda_{\text{max}}/\text{nm}$ (log ϵ))	¹ H NMR ^{b)} (δ/ppm)	¹³ C NMR ^{c)} (δ/ppm)
12	2230	253 (3.26)	4.45 (s, 2H)	43.33
		262 (3.18)	6.34 (s, 2H)	87.98
		332sh (4.46)	7.25 (s, 2H)	110.37
		348 (4.56)		111.14
		366 (4.44)		
13	2230	254 (4.40)	3.06 (m, 4H)	29.20
		333 (3.01)	4.48 (s, 2H)	48.16
		354 (3.23)	6.32 (s, 2H)	86.54
		372 (3.29)		110.57
		395 (3.12)		
14	2230	265sh (4.28)	4.66 (ddd, <i>J</i> = 1.2, 1.7, 2.2 Hz, 2H)	56.09
		302 (4.50)	6.81 (dd, <i>J</i> = 1.7, 5.4 Hz, 2H)	79.85
		320sh (4.30)	7.15 (ddd, <i>J</i> = 1.2, 2.2, 5.4 Hz, 2H)	110.83
		370sh (3.20)		111.87
15	2226	228 (4.03)	3.07 (s, 4H)	33.07
		274 (4.00)	6.49 (AA'BB', 2H)	87.68
		343 (4.07)	6.68 (AA'BB', 2H)	110.82
		tailing to 430 nm		111.28
16	2224	337 (4.15)	3.09 (m, 4H)	26.55
		355 (4.44)	3.50 (m, 4H)	37.63
		373 (4.60)		80.54
		395 (4.51)		111.63

a) In dichloromethane. b) In CDCl₃, 270 MHz. c) In CDCl₃, 67.5 MHz.



Scheme 3.

entially obeyed first-order kinetics, although the unidentifiability of the majority of products (>70%) makes the kinetics questionable. Assuming validity of the first-order kinetics, the rate constant at 150 °C was calculated to be $1.9 \times 10^{-5} \text{ s}^{-1}$ and the free energy of activation $\Delta G^\ddagger = 143.1 \pm 0.8 \text{ kJ mol}^{-1}$. The energy value is slightly smaller than that for the ring opening of the tetraphenyl derivative **6** to **3** ($\Delta G^\ddagger = 153 \text{ kJ mol}^{-1}$).⁸ The thermal reaction was completed in 3 h at 180 °C in benzonitrile, giving **14** in a similar yield, thus suggesting that some acceleration had occurred in this more dipolar solvent.

On the other hand, compound **13** underwent thermal reactions more easily and cleanly than **12**; upon heating **13** in deuterated toluene at 110 °C, the ¹H NMR signal of the aliphatic protons of **13** at 3.06 ppm completely disappeared in only 1 hour. The disappearance of **13** also obeyed first-order kinetics with the following kinetic and thermodynamic parameters: k (80 °C) = $1.40 \times 10^{-4} \text{ s}^{-1}$; $\Delta G^\ddagger = 118.4 \pm 0.4 \text{ kJ mol}^{-1}$. The NMR spectrum of the resulting reaction mixture indicated a clean formation of two new products with a 56:44 ratio. One of the products tended to decompose upon chromatographic separation both on alumina and silica gel, but these products can be separated by fractional crystallization. Thus, upon standing the reaction mixture in toluene at room temperature, a fine yellow solid **15** precipitated first of all in 44% yield, and then yellow needles of **16** crystallized out in 22% yield from the concentrated filtrate. The reaction was about 1.9-times faster in more dipolar acetonitrile [k (80 °C) = $2.65 \times 10^{-4} \text{ s}^{-1}$]. In acetonitrile, however, while the yield of **16** remained almost the same as in toluene, the yield of **15** became very poor (4%). The poor yield of **15** in acetonitrile seems to correlate with its instability on alumina, and in fact **15** decomposed in hot acetonitrile, giving a complex mixture. Both **15** and **16** have the same molecular formula with **13**, but no interchange between the products was observed when they were each heated in toluene.

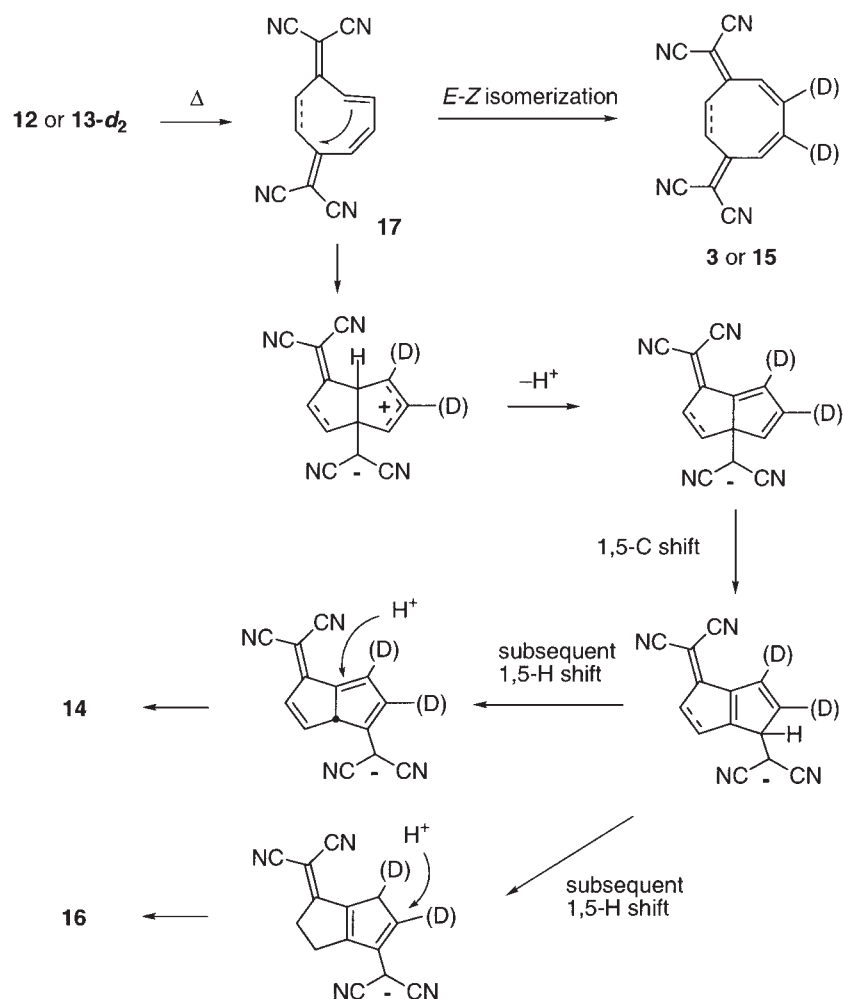
Compound **15** was determined to be 5,8-bis(dicyanomethylene)-1,3-cyclooctadiene from the spectral data, and **16** to

be 2,6-bis(dicyanomethylene)bicyclo[3.3.0]octa-1(5)-ene from analytical and spectral data and confirmed by X-ray crystallographic analysis. These results are markedly different from the thermal reactions of other dimethylenebicyclo[4.2.0]octa-(3),7-(di)enes **5–7** (Scheme 3).

The deuterated compounds **14-d₂**, **15-d₂** and **16-d₂** were also obtained by the thermal reaction of **12-d₂** and **13-d₂**, whose ¹H NMR spectra are informative for elucidating the mechanism of these rearrangements to some extent. The integral of the peaks for both olefinic protons of **14-d₂** are reduced to almost half of those of the aliphatic peaks, and both of the signals for aliphatic protons of **16-d₂** are equal in intensity. These results indicated that two deuteriums in these compounds are located adjacently. Moreover, the signals at 6.49 ppm for inner olefinic protons of **15** are absent in the spectrum of **15-d₂**, suggesting that the formation proceeds through a thermal ring opening of the cyclobutene ring of **13**.

Similar to the reaction mechanisms of the known 2,4-dimethylenebicyclo[4.2.0]octenes, we assumed as a probable mechanism that the rearrangements start with the thermal ring opening to form the strained cyclooctadienes **17**, which converted competitively to dimethylenecyclooctadiene **15** via *E–Z* bond isomerization and to bicyclo[3.3.0]octane skeletons via zwitterionic intermediates, as shown in Scheme 4. The strong electron-withdrawing property of dicyanomethylene groups seems to play an important role in determining the reaction pathway to bicyclic compounds **14** and **16**. The desired product **1** might form from **12** as a transient species in the mechanism because of the modest yield. However, little decisive evidence has been obtained to date.

Properties of New Acceptors. New compounds **12**, **15** and **16**, having tetracyanohexatriene or -octatetraene moieties, are regarded as vinylogs of TCNE, and are therefore of interest from the viewpoint of new electron acceptors. Therefore, the electrochemical properties were examined by cyclic voltammetry (Table 2). While **12** and **16** show two sets of well-reversible one-electron reduction waves, **15** showed poorly reversible reduction waves, probably owing to the nonplanar

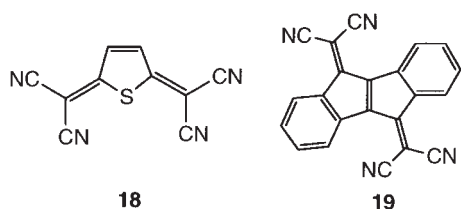


Scheme 4. A possible mechanism of the rearrangements via thermal ring opening.

Table 2. Reduction Potentials^{a)} of **12**, **15**, **16**, Together with TCNE, TCNQ, **18** and **19**

Compounds	$E_{1/2}^1$	$E_{1/2}^2$
12	-0.34	-0.73
15	-0.47	-1.47*
16	-0.52	-0.90
TCNE	0.22	-0.76
TCNQ	0.18	-0.37
18 ^{b)}	0.07	-0.54
19 ^{c)}	0.10	-0.3

a) V vs Ag/Ag⁺, in 0.1 mol dm⁻³ Et₄NClO₄/CH₃CN, sweep rate 100 mV s⁻¹. b) Ref. 18. c) Ref. 19. *Peak potential.



conformation and chemical liability of the unsaturated eight-membered ring. Their electron affinities ($E_{1/2}^1 = -0.34$ to -0.52 V) are considerably weaker than TCNE (0.22 V), TCNQ (0.18 V), thiophene derivative **18** (0.07 V)¹⁸ and dibenzopentalene derivative **19** (0.10 V),¹⁹ probably due to the electron-donating properties of the alkyl groups.

Good single crystals of a molecular complex of the acceptor **16** with toluene (1:1) suitable for X-ray analysis were obtained as yellow plates by mixing **16** with toluene in chloroform. Almost no change in the infrared absorption of the cyano groups ($\nu = 2224$ cm⁻¹) suggests that the complex is nonionic. The ORTEP drawing of **16** in Fig. 1a shows a planar structure of the molecule. The length of the dicyanomethylene double bonds ($1.35 \text{ \AA} = 135 \text{ pm}$) is slightly shorter than those of neutral TCNQ ($1.362 \text{ \AA}$)²⁰ or BenzoTCNQ ($1.384 \text{ \AA}$),²¹ but quite similar to those of the molecular complex of 2-chlorotetracyanoanthraquinodimethane with benzene ($1.344 \text{ \AA}$).²² The packing diagram of the complex in Figs. 1b and 1c shows that the disordered toluene molecule is interposed by acceptors in the upper and lower layers, and are captured by Y-shaped dicyanomethylene groups of the adjacent acceptors, which lie on an almost coplane with toluene.²³ No short contacts within van der Waals distance were observed. The shortest intermolecular contact between acceptors is $3.37 \text{ \AA}$ (C7-C7*), and acceptor

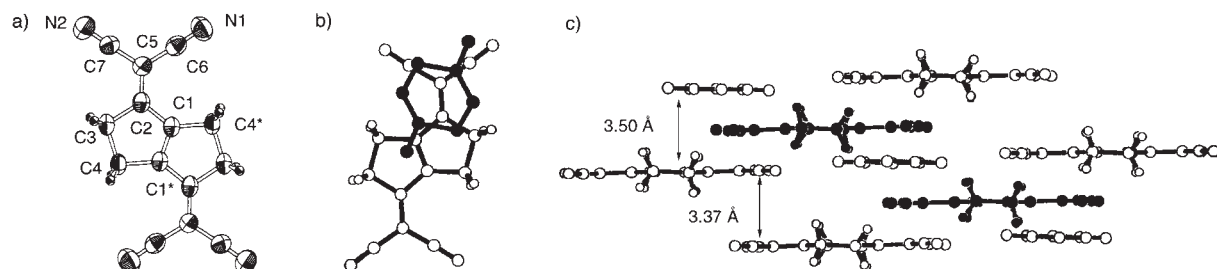


Fig. 1. a) ORTEP view of **16** in the complex showing the atom numbering scheme. b) Molecular overlap in **16**·C₇H₈ showing the disordered atomic position for the methyl groups. c) Molecular arrangement in the **16**·C₇H₈ crystal.

Table 3. Crystal Data for C-T Complex of **16** and Toluene

	16 ·C ₇ H ₈
Formula	C ₁₄ H ₈ N ₄ ·C ₇ H ₈
Formula weight	324.37
Crystal system	Triclinic
Space group	<i>P</i> 1̄(#2)
Z	2
<i>a</i> /Å	8.252(3)
<i>b</i> /Å	8.442(3)
<i>c</i> /Å	7.762(1)
α /°	102.23(3)
β /°	112.40(2)
γ /°	62.17(2)
Volume/Å ³	441.7(3)
ρ_{calcd} /g cm ⁻³	1.746
<i>F</i> ₀₀₀	240.00
μ (Mo K α)/cm ⁻¹	1.11
No. of observation	965
<i>R</i>	0.064
<i>R</i> _w	0.065
G.F.I.	2.63

and toluene is 3.50 Å (C6–C9). Thus, the toluene molecule can be regarded as an inclusion of a network of acceptors (Table 3–5).

The planar acceptor **16** also formed an 1:1 charge-transfer (C-T) complex with 2,2',5,5'-tetrathiafulvalene (TTF) as fine and black needles by a diffusion method. The complex was, however, slight ionic based on the infrared absorption of nitrile groups (2222 cm⁻¹; $\Delta\nu = 2$ cm⁻¹), and the conductivity, measured on a compressed pellet with a two-probe method at room temperature, was near insulating (1.1×10^{-7} S cm⁻¹). The weak C-T interaction may be due to the considerably poorer electron affinity compared with TCNQ.

Although the other tetracyanohexatriene, **12** and -octatetraene **15**, have a similar electron affinity to **16**, no C-T complex has been obtained so far.

Conclusion

Whereas 2,5-dimethylenebicyclo[4.2.0]octa-3,7-dienes gave rise to normal ring-opened products, the dicyanomethylidene derivative **12** afforded a rearranged product **14** as a sole isolable product in moderate yield. The normal ring-opened product **1** might form as a transient species, judging from the modest yield; however, no evidence for the formation has been obtained so far. On the other hand, the dihydro compound **13** un-

Table 4. Fractional Coordination and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms with Esd's in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} ^{a)}
N(1)	−0.3761(5)	0.5599(5)	0.3220(5)	6.2(1)
N(2)	−0.0583(5)	0.8747(5)	0.6231(5)	6.2(1)
C(1)	−0.0559(5)	0.5063(4)	0.0480(5)	3.45(9)
C(2)	−0.0344(5)	0.6207(5)	0.2119(5)	3.77(9)
C(3)	0.1156(7)	0.6805(6)	0.2203(6)	4.4(1)
C(4)	0.1696(7)	0.6033(6)	0.0417(6)	4.3(1)
C(5)	−0.1277(5)	0.6700(5)	0.3378(5)	3.83(9)
C(6)	−0.2675(6)	0.6081(5)	0.3247(5)	4.3(1)
C(7)	−0.0883(6)	0.7851(5)	0.4946(6)	4.4(1)
C(8)	0.368(1)	0.991(1)	1.082(2)	12.2(3)
C(9)	0.391(1)	0.905(1)	0.932(1)	10.4(3)
C(10)	0.507(1)	0.9094(9)	0.850(1)	10.6(2)
C(11)	0.536(1)	0.839(1)	0.706(1)	16.3(4)

a) $B_{\text{eq}} = 4/3 \sum \sum \beta_{ij} a_i \cdot a_j$.

Table 5. Selected Bond Lengths (Å), and Bond Angles (deg) of **16** for **16**·C₇H₈

C(1)–C(1)*	1.348(6)	C(1)–C(1)*–C(2)*	111.1(4)
C(1)–C(2)	1.432(4)	C(1)–C(1)*–C(4)	112.7(4)
C(1)–C(4)*	1.504(4)	C(2)–C(1)–C(4)*	136.1(3)
C(2)–C(3)	1.516(5)	C(1)–C(2)–C(3)	107.0(3)
C(2)–C(5)	1.350(5)	C(1)–C(2)–C(5)	128.0(3)
C(3)–C(4)	1.537(5)	C(3)–C(2)–C(5)	124.9(3)
C(5)–C(6)	1.437(5)	C(2)–C(3)–C(4)	106.5(3)
C(5)–C(7)	1.423(5)	C(1)*–C(4)–C(3)	102.4(3)
N(1)–C(6)	1.137(4)	C(2)–C(5)–C(6)	122.8(3)
N(2)–C(7)	1.138(4)	C(2)–C(5)–C(7)	120.9(3)
		C(6)–C(5)–C(7)	116.3(3)
		N(1)–C(6)–C(5)	177.3(4)
		N(2)–C(7)–C(5)	177.9(4)

derwent a thermal reaction at a relatively lower temperature to give a normal ring-opened product **15** together with a rearranged product **16**. An interruption of conjugation on the six-membered ring would decrease the activation energy of the ring opening to allow the formation of **15** competitively. The rearranged product **16**, having a planar 1,1,6,6-tetracyanohexatriene structure, shows moderate electron affinity compared with TCNE and TCNQ. The results expand the variety of the chemistry of the polycyanosubstituted π -electron systems.

Experimental

General. The melting points were recorded on a Yanaco MP 500D apparatus and uncorrected. FAB- and EI-High resolution mass spectra were measured on a JEOL JMS-SX 102 instrument. ^1H NMR spectra (tetramethylsilane; 0 ppm as an internal standard) and ^{13}C NMR spectra (CDCl_3 ; 77.0 ppm as an internal standard) were recorded on JEOL EX-270 and JEOL GSX-400 instruments. The chemical shifts are given in ppm. IR spectra were obtained by a Perkin-Elmer 1650 spectrometer. Microanalyses were performed at the Elemental Analysis Center, Faculty of Science, Osaka University. Electronic spectra (UV-vis) were obtained on a Hitachi U-3400 instrument. Column chromatography was performed with a Merck Kiesel-gel 60.

Cyclic voltammograms were recorded on a BAS 100B/W (CV-50W) Voltammetric Analyzer and Electrochemical Workstation. All electrochemical measurements were carried out in acetonitrile solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (nakarai Tesque Inc.) at 25°C under an argon atmosphere.

All of the reactions were carried out under a nitrogen or argon atmosphere unless otherwise noted. Diethyl ether and THF were distilled from sodium diphenylketyl prior to use. DMF was distilled from CaH_2 and stored over MS 4A under a nitrogen atmosphere. Dichloromethane and acetonitrile were distilled from P_4O_{10} . Malononitrile, β -alanine and *N*-bromosuccinimide were commercially available and used without further purification.

7,8-Dideuteriobicyclo[4.2.0]oct-7-ene-2,5-dione ($10\text{-}d_2$): Dideuterioacetylene, generated by the slow addition of deuterium oxide (40 cm^3) into a suspension of calcium carbide (64 g, 1 mol) with DMF (100 cm^3), was bubbled into a solution of 2-cyclohexene-1,4-dione (3.3 g, 30 mmol) in dichloromethane (250 cm^3) under cooling at -60°C . After half of the D_2O was consumed, the solution, saturated with dideuterioacetylene, was irradiated (Pyrex photoreactor and 400 W-Hg lamp was used) at -60°C with bubbling for 3 hours, and then allowed to warm to rt. After stirring for 12 hours, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed on silica gel with CH_2Cl_2 to give a dideuterated compound $10\text{-}d_2$ (3.40 g, 82%). MS (EI) m/z (%) 138 (M^+ ; 43), 138 (6), 84 (100).

2,5-Bis(dicyanomethylene)bicyclo[4.2.0]oct-7-ene (13): To a preheated mixture of 10 (1.36 g, 10 mmol) and malononitrile (1.52 g, 23 mmol) at 80°C in an oil bath was added a 20 cm^3 of a 0.1 M (0.1 mol dm^{-3}) aqueous solution of β -alanine with stirring. After 30 min, the mixture was diluted with water (100 cm^3), and cooled to room temperature. The precipitated crude product was collected by filtration, and dissolved in CH_2Cl_2 (50 cm^3). The filtrate was extracted with CH_2Cl_2 ($2 \times 20 \text{ cm}^3$). The CH_2Cl_2 solutions were combined, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel with CH_2Cl_2 to give bis(dicyanomethylene) compound 13 (2.40 g, 89%). Recrystallization from CH_2Cl_2 -hexane gave pale-yellow prisms; mp $124\text{--}125^\circ\text{C}$; MS (EI) m/z (%) 232 (M^+ ; 59), 231 (33), 204 (100); Found: C, 72.40; H, 3.43; N, 24.07%. Calcd for $\text{C}_{14}\text{H}_8\text{N}_4$: C, 72.40; H, 3.47, N, 24.12%.

7,8-Dideuterio-2,5-bis(dicyanomethylene)bicyclo[4.2.0]oct-7-ene ($13\text{-}d_2$): MS (EI) m/z (%) 234 (M^+ ; 65), 233 (32), 206 (92), 18 (100).

2,5-Bis(dicyanomethylene)bicyclo[4.2.0]octa-3,7-diene (12): Bis(dicyanomethylene) 13 (707 mg, 3.0 mmol) and *N*-bromosuccinimide (600 mg, 3.4 mmol) were dissolved in a mixture of

CH_2Cl_2 (10 cm^3) and acetonitrile (2 cm^3). The solution was cooled below -50°C in an ethanol-dry ice bath under a N_2 atmosphere and added dropwise was a solution of pyridine (289 mg, 3.65 mmol) and CH_2Cl_2 (2 cm^3) over 2 min with stirring. After the addition, the mixture was allowed to warm up to room temperature, stirred overnight and then water (20 cm^3) and CH_2Cl_2 (10 cm^3) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 ($2 \times 10 \text{ cm}^3$). The extracts were combined, washed with water and brine, dried (MgSO_4) and concentrated under reduced pressure. The residue was chromatographed on silica gel with CH_2Cl_2 to give 12 (460 mg, 66%). Recrystallization from CH_2Cl_2 -hexane gave pale yellow prisms; mp $168\text{--}169^\circ\text{C}$; MS (EI) m/z (%) 230 (M^+ ; 38), 229 (18), 203 (69), 165 (62), 18 (100); Found: C, 73.15; H, 2.58; N, 24.24%. Calcd for $\text{C}_{14}\text{H}_6\text{N}_4$: C, 73.04; H, 2.63; N, 24.34%.

7,8-Dideuterio-2,5-bis(dicyanomethylene)bicyclo[4.2.0]octa-3,7-diene ($12\text{-}d_2$): MS (EI) m/z (%) 232 (M^+ ; 74), 231 (31), 205 (100), 167 (95).

Thermal Rearrangement of 12 : A solution of 12 (100 mg, 1 mmol) in *o*-dichlorobenzene (20 cm^3) was heated at 180°C in an oil bath for 3 h. The solvent was removed in vacuo. Chromatography of the residue on silica gel with CH_2Cl_2 at 0°C gave 14 (22 mg, 22%). Recrystallization from CH_2Cl_2 gave a pale-yellow powder; mp $168\text{--}169^\circ\text{C}$; MS (EI) m/z (%) 230 (M^+ , 100), 203 (87), 165 (50); Found: C, 73.00; H, 2.88; N, 24.27%. Calcd for $\text{C}_{14}\text{H}_6\text{N}_4$: C, 73.04; H, 2.63; N, 24.34%.

Thermal Rearrangement of 13 : A solution of 13 (1.0 g, 4.3 mmol) in toluene (40 cm^3) was heated at reflux for 2 h under a N_2 atmosphere, and then allowed to cool and stand at room temperature overnight. The yellow needles which precipitated were collected by filtration to give nearly pure 15 (435 mg, 44%). The filtrate was concentrated under reduced pressure until an orange solid appeared. The yellow suspension was heated until a homogeneous solution was obtained, and the resulting solution was allowed to stand at room temperature overnight to give 16 (220 mg, 22%). Recrystallization of 16 from benzene gave yellow-orange prisms; 15 : mp $210\text{--}211^\circ\text{C}$ (decomp.); MS (EI) m/z (%) 232 (M^+ , 100), 206 (46); Found: C, 72.17; H, 3.33; N, 24.06%. Calcd for $\text{C}_{14}\text{H}_8\text{N}_4$: C, 72.40; H, 3.47, N, 24.12%. 16 : mp $145\text{--}146^\circ\text{C}$; MS (FAB) m/z (%) 232 (M^+ , 43), 231 ($\text{M}^+ - 1$, 100); Found C, 72.40; H, 3.52; N, 24.07%. Calcd for $\text{C}_{14}\text{H}_8\text{N}_4$: C, 72.40; H, 3.47, N, 24.12%.

Kinetics of the Thermal Reaction of 12 and 13 : The reaction rates of the reactions were measured by monitoring the decrease in the appropriate peaks of the ^1H -NMR spectra at 150°C in $\text{C}_6\text{D}_5\text{Br}$ for 12 , and at 80°C in C_7D_8 or CD_3CN for 13 .

Complexation of 16 and TTF: A complex of 16 and TTF (1:1) was obtained as black needles from a chloroform solution by slow evaporation; mp $210\text{--}212^\circ\text{C}$; IR (KBr) 2222 cm^{-1} (CN); Found C, 54.69; H, 2.82; N, 12.76; S, 29.20%. Calcd for $\text{C}_{14}\text{H}_8\text{N}_4 \cdot \text{C}_6\text{H}_4\text{S}_4$: C, 55.02; H, 2.77, N, 12.83, S 29.38%.

Crystal and Experimental Data for Complex of 16 and Toluene: A single crystal was grown by the slow evaporation of a saturated solution of 16 in chloroform and small portion of toluene and its size was ca. $0.2 \times 0.3 \times 0.4 \text{ mm}^3$ (mp 150°C , decomp). The intensity data ($2\theta < 60^\circ$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), and the structure was solved by direct methods. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. All of the

hydrogens were located by calculations. The larger temperature factor for carbons of toluene should be due to disorder. The final cycle of the full-matrix least-squares refinement was based on 965 observed reflections ($I > 3\sigma$) and 134 variable parameters.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC-211186.

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