The X-Ray Study of Several Reaction Products of Substituted Benzo-[1,2 : 4,5]dicyclobutene. II. 2,7-Di-*t*-butyl-11,12-dicyano-4,5,9,10-tetraphenyltetracyclo[4.4.2.$0^{1,8}$.$0^{3,6}$]dodeca-2,4,7,9-tetraene

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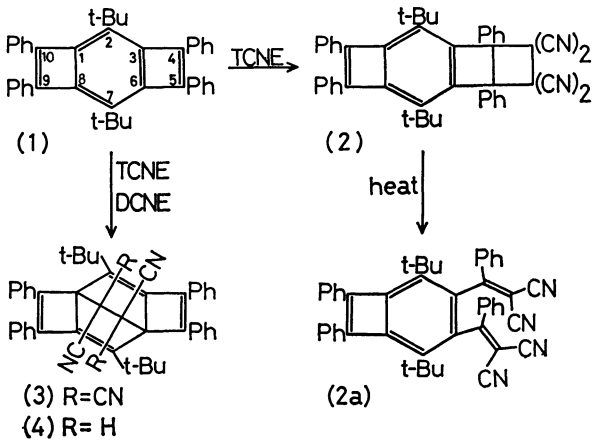
trans-1,2-Dicyanoethylene (DCNE) reacts with substituted benzo[1,2 : 4,5]dicyclobutene (**1**) to give only one adduct (**4**), the title compound, whereas tetracyanoethylene (TCNE) gives two isomers. Crystals of **4** are triclinic; space group P$\bar{1}$, $a=13.505(2)$, $b=14.118(2)$, $c=10.722(1)$ Å, $\alpha=98.87(1)$, $\beta=102.36(1)$, $\gamma=111.71(1)°$ and $Z=2$. The structure was solved by the direct method and was refined by the block-diagonal least-squares method to the final R factor of 0.055 for 5479 observed reflections. The absence of two cyano groups in **4** makes less steric hindrance than **3**. Introducing the empirical parameters, non-bonded interaction energy was calculated for the approaching model of **1** and DCNE. The result well explains the addition of DCNE to the C(1)–C(6) position of **1**.

We have investigated a series of Diels-Alder adducts formed by the reaction of substituted benzo[1,2 : 4,5]-dicyclobutene (**1**)[1] and some dienophiles. In the first two papers, we reported the crystal structures of molecules **2** and **2a**[2,3] which are the first stable compounds with an *anti*-aromatic 8π electron benzo[1,2 : 4,5]-cyclobutene skeleton, and observed some degree of electron localization in agreement with a result of molecular orbital calculation. In the third paper,[4] we presented the crystal structure of **3**, a by-product of the addition reaction of **1** and tetracyanoethylene (TCNE). The analysis revealed the stereochemical differences between the main (**2**) and by-product (**3**) of this reaction. We calculated the electronic and steric interactions between approaching **1** and TCNE, and obtained an explanation for the bifurcate reactivity.

trans-1,2-Dicyanoethylene (DCNE) gives, on the contrary, only one product **4**.[5] The present study on the X-ray analysis of **4** is, therefore, not only an assertation of the proposed molecular structure, but also the stereochemical approach to a complicated organic reaction mechanism.



Experimental and Structure Determination

Colorless needles were recrystallized from acetone–methanol solution. Oscillation and Weissenberg photographs indicated triclinic symmetry. A crystal with dimensions $0.35\times0.40\times0.40$ mm was mounted on a Rigaku automated four-circle diffratometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The crystal data are listed in Table 1. A total of 6317 independent reflections ($2\theta\leqq50°$) was obtained in which 5479 had net intensities greater than the background. The intensities were corrected for Lorentz and polarization effects. The statistical distribution of the normalized structure factors, $|E|$'s, shows that the space group is P$\bar{1}$.

Table 1. Crystal data

2,7-Di-*t*-butyl-11,12-dicyano-4,5,9,10-tetraphenyltetracyclo-[4.4.2.$0^{1,8}$.$0^{3,6}$]dodeca-2,4,7,9-tetraene

$C_{46}H_{40}N_2$	
M.W.	620.8
Crystal system	triclinic
Space group	P$\bar{1}$
a	13.505(2) Å
b	14.118(2) Å
c	10.722(2) Å
α	98.87(1)°
β	102.36(1)°
γ	111.71(1)°
U	1793 Å^3
D_m	1.148 g cm^{-3}
D_x	1.150 g cm^{-3}
Z	2

The structure was solved by the direct method.[6] All the 48 non-hydrogen atoms were found on the first E map calculated with 475 $|E|$'s greater than 1.6. The atomic parameters were refined by the block-diagonal least-squares method. Although hydrogen atoms were found by the difference Fourier synthesis, they were fixed at geometrically calculated positions, which were recalculated at the last stage of the refinement. Their isotropic thermal parameters were also fixed. Three reflections had $|F_o|$'s abnormally lower than $|F_c|$'s. As they seem to suffer from the secondary extinction, the final refinement was carried out without these reflections. The weighting scheme used was

$$w = 0.3 \quad \text{for } |F| = 0.0$$
$$w = 1/(1 + 0.44(4 - |F|)) \quad \text{for } 0 < |F| \leqq 4$$
$$w = 1 \quad \text{for } 4 < |F| \leqq 15$$
$$w = 1/(1 + 0.44(|F| - 15)) \quad \text{for } |F| > 15.$$

The final R factor was 0.55 for the observed reflections, and

Table 2. Fractional coordinates and equivalent isotropic temperature factors

B_{eq}'s are defined as $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$.

Atom	x	y	z	B_{eq}/Å^2
C(1)	0.2235(1)	0.4218(1)	0.1104(1)	2.58
C(2)	0.2134(1)	0.5017(1)	0.0311(1)	2.61
C(3)	0.2818(1)	0.5977(1)	0.1111(1)	2.68
C(4)	0.3411(1)	0.7135(1)	0.1348(1)	3.05
C(5)	0.4020(1)	0.7262(1)	0.2602(1)	2.93
C(6)	0.3484(1)	0.6065(1)	0.2509(1)	2.66
C(7)	0.2689(1)	0.5476(1)	0.3251(1)	2.56
C(8)	0.2072(1)	0.4501(1)	0.2459(1)	2.56
C(9)	0.1255(1)	0.3396(1)	0.2213(1)	2.79
C(10)	0.1344(1)	0.3112(1)	0.0980(1)	2.78
C(11)	0.3467(1)	0.4329(1)	0.1387(1)	3.13
C(12)	0.4246(1)	0.5472(1)	0.2321(1)	3.20
C(13)	0.1428(1)	0.4735(1)	-0.1116(1)	3.20
C(14)	0.1946(2)	0.4243(2)	-0.2022(2)	5.60
C(15)	0.1394(1)	0.5723(1)	-0.1499(1)	4.12
C(16)	0.0216(1)	0.3948(1)	-0.1332(2)	5.24
C(17)	0.2622(1)	0.5918(1)	0.4602(1)	3.21
C(18)	0.3500(2)	0.5814(2)	0.5681(2)	6.05
C(19)	0.1464(1)	0.5299(1)	0.4733(1)	4.05
C(20)	0.2798(2)	0.7071(1)	0.4807(2)	5.63
C(21)	0.3463(1)	0.7879(1)	0.0503(1)	3.74
C(22)	0.2940(1)	0.8553(1)	0.0613(2)	5.01
C(23)	0.3014(2)	0.9259(2)	-0.0175(3)	6.80
C(24)	0.3593(2)	0.9287(2)	-0.1075(2)	7.30
C(25)	0.4116(2)	0.8620(2)	-0.1208(2)	7.02
C(26)	0.4065(2)	0.7909(1)	-0.0411(2)	5.41
C(27)	0.4985(1)	0.8142(1)	0.3563(1)	3.20
C(28)	0.5250(1)	0.9177(1)	0.3469(2)	4.47
C(29)	0.6182(2)	1.0008(1)	0.4366(2)	5.52
C(30)	0.6862(2)	0.9827(1)	0.5367(2)	5.49
C(31)	0.6605(1)	0.8810(1)	0.5485(2)	5.49
C(32)	0.5677(1)	0.7978(1)	0.4587(2)	4.52
C(33)	0.0743(1)	0.2788(1)	0.3096(1)	3.05
C(34)	-0.0394(1)	0.2367(1)	0.2939(2)	4.04
C(35)	-0.0814(2)	0.1806(1)	0.3814(2)	5.19
C(36)	-0.0110(2)	0.1670(1)	0.4838(2)	5.45
C(37)	0.1024(2)	0.2087(1)	0.4999(2)	4.90
C(38)	0.1451(1)	0.2641(1)	0.4132(1)	3.98
C(39)	0.0897(1)	0.2108(1)	-0.0028(1)	3.12
C(40)	-0.0191(1)	0.1366(1)	-0.0261(1)	4.13
C(41)	-0.0627(2)	0.0428(1)	-0.1246(2)	5.31
C(42)	0.0015(2)	0.0221(1)	-0.1993(2)	5.53
C(43)	0.1097(2)	0.0943(1)	-0.1763(2)	5.25
C(44)	0.1542(1)	0.1887(1)	-0.0789(2)	4.19
C(45)	0.3627(1)	0.3528(1)	0.2027(2)	4.29
C(46)	0.5099(1)	0.6033(1)	0.1720(2)	4.34
N(1)	0.3745(1)	0.2902(1)	0.2517(2)	7.15
N(2)	0.5745(1)	0.6456(1)	0.1233(2)	6.56

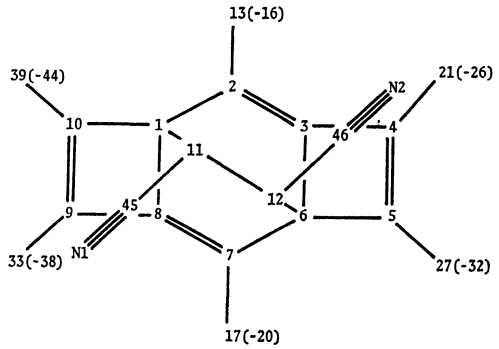


Fig. 1. Numbering scheme. Numbers in parentheses indicate the atoms of the substituents.

0.067 for all the reflections.† The atomic scattering factors were taken from "International Tables for X-ray Crystallography."[7] The final atomic parameters are listed in Table 2. The crystallographic numbering scheme is shown in Fig. 1.

Description of the Structure

Crystal structure viewed along the a axis is shown in Fig. 2. Stereoscopic views of the molecular framework are given in Fig. 3. There is no intermolecular distance shorter than van der Waals contacts. Bond lengths and angles are listed in Tables 3 and 4, respectively. As previously assigned from spectroscopic studies,[5] **4** has a framework formed by an addition of DCNE to C(1) and C(6) position of **1**. Although two isomers of cross

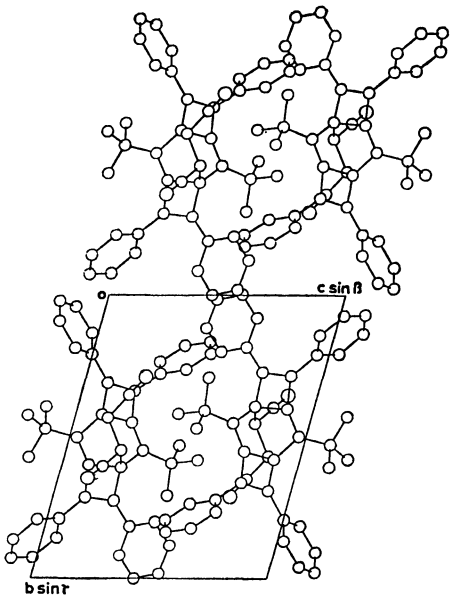


Fig. 2. Crystal structure projected along the a axis.

Table 3. Bond lengths (l/Å)

Standard deviations are given in parentheses.

C(1)–C(2)	1.541(3)	C(17)–C(20)	1.528(4)
C(1)–C(8)	1.531(3)	C(21)–C(22)	1.384(3)
C(1)–C(10)	1.543(3)	C(21)–C(26)	1.397(4)
C(1)–C(11)	1.568(3)	C(22)–C(23)	1.393(4)
C(2)–C(3)	1.342(3)	C(23)–C(24)	1.362(5)
C(2)–C(13)	1.520(3)	C(24)–C(25)	1.378(5)
C(3)–C(4)	1.481(3)	C(25)–C(26)	1.408(4)
C(3)–C(6)	1.534(3)	C(27)–C(28)	1.395(3)
C(4)–C(5)	1.363(3)	C(27)–C(32)	1.390(3)
C(4)–C(21)	1.482(3)	C(28)–C(29)	1.387(4)
C(5)–C(6)	1.549(3)	C(29)–C(30)	1.377(4)
C(5)–C(27)	1.461(3)	C(30)–C(31)	1.380(4)
C(6)–C(7)	1.545(3)	C(31)–C(32)	1.385(4)
C(6)–C(12)	1.573(3)	C(33)–C(34)	1.386(3)
C(7)–C(8)	1.340(3)	C(33)–C(38)	1.398(3)
C(7)–C(17)	1.521(3)	C(34)–C(35)	1.398(4)
C(8)–C(9)	1.481(3)	C(35)–C(36)	1.378(4)
C(9)–C(10)	1.365(3)	C(36)–C(37)	1.382(4)
C(9)–C(33)	1.484(3)	C(37)–C(38)	1.390(4)
C(10)–C(39)	1.467(3)	C(39)–C(40)	1.394(3)
C(11)–C(12)	1.582(3)	C(39)–C(44)	1.396(3)
C(11)–C(45)	1.468(3)	C(40)–C(41)	1.392(4)
C(12)–C(46)	1.473(3)	C(41)–C(42)	1.376(4)
C(13)–C(14)	1.535(4)	C(42)–C(43)	1.378(4)
C(13)–C(15)	1.528(3)	C(43)–C(44)	1.391(4)
C(13)–C(16)	1.542(3)	C(45)–N(1)	1.137(4)
C(17)–C(18)	1.536(4)	C(46)–N(2)	1.138(4)
C(17)–C(19)	1.533(3)		

† The tables of the structure factors and the other atomic parameters are kept as Document No. 8124 at the Chemical Society of Japan.

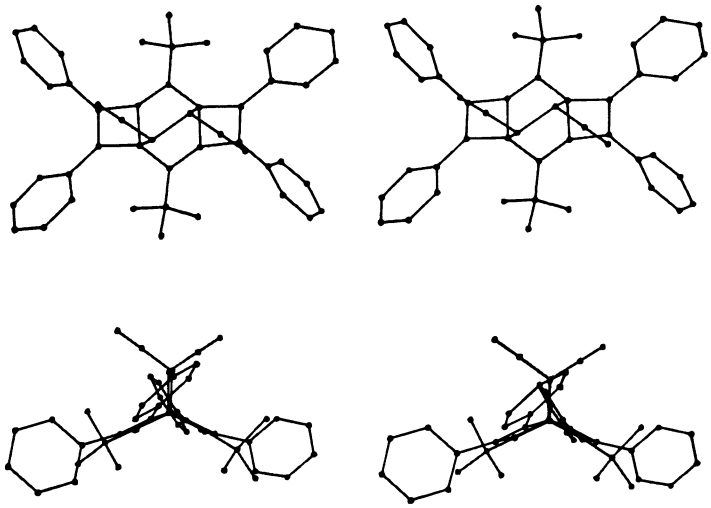
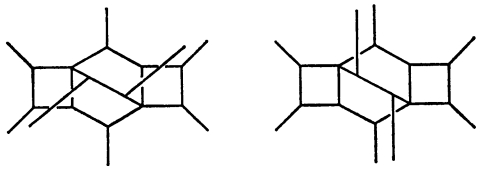


Fig. 3. Stereoscopic views.

TABLE 4. BOND ANGLES (ϕ/°)
Standard deviations are given in parentheses.

C(2)–C(1)–C(8)	110.9(1)	C(2)–C(13)–C(16)	111.6(2)
C(2)–C(1)–C(10)	128.1(2)	C(14)–C(13)–C(15)	108.8(2)
C(2)–C(1)–C(11)	107.2(1)	C(14)–C(13)–C(16)	109.2(2)
C(8)–C(1)–C(10)	84.5(1)	C(15)–C(13)–C(16)	107.8(2)
C(8)–C(1)–C(11)	105.8(1)	C(7)–C(17)–C(18)	109.3(2)
C(10)–C(1)–C(11)	115.8(1)	C(7)–C(17)–C(19)	110.1(2)
C(1)–C(2)–C(3)	106.2(2)	C(7)–C(17)–C(20)	111.6(2)
C(1)–C(2)–C(13)	125.4(2)	C(18)–C(17)–C(19)	108.7(2)
C(3)–C(2)–C(13)	128.4(2)	C(18)–C(17)–C(20)	110.1(2)
C(2)–C(3)–C(4)	151.4(2)	C(19)–C(17)–C(20)	107.0(2)
C(2)–C(3)–C(6)	119.0(2)	C(4)–C(21)–C(22)	121.4(2)
C(4)–C(3)–C(6)	89.2(1)	C(4)–C(21)–C(26)	119.2(2)
C(3)–C(4)–C(5)	93.4(2)	C(22)–C(21)–C(26)	119.5(2)
C(3)–C(4)–C(21)	134.1(2)	C(21)–C(22)–C(23)	120.5(2)
C(5)–C(4)–C(21)	132.0(2)	C(22)–C(23)–C(24)	120.3(3)
C(4)–C(5)–C(6)	93.0(2)	C(23)–C(24)–C(25)	120.3(3)
C(4)–C(5)–C(27)	133.5(2)	C(24)–C(25)–C(26)	120.4(3)
C(6)–C(5)–C(27)	132.2(2)	C(21)–C(26)–C(25)	119.0(3)
C(3)–C(6)–C(5)	84.4(1)	C(5)–C(27)–C(28)	120.8(2)
C(3)–C(6)–C(7)	110.2(1)	C(5)–C(27)–C(32)	121.3(2)
C(3)–C(6)–C(12)	105.8(1)	C(28)–C(27)–C(32)	117.9(2)
C(5)–C(6)–C(7)	128.9(2)	C(27)–C(28)–C(29)	120.6(2)
C(5)–C(6)–C(12)	115.1(1)	C(28)–C(29)–C(30)	120.6(3)
C(7)–C(6)–C(12)	107.5(1)	C(29)–C(30)–C(31)	119.6(3)
C(6)–C(7)–C(8)	105.9(2)	C(30)–C(31)–C(32)	119.9(2)
C(6)–C(7)–C(17)	126.8(2)	C(27)–C(32)–C(31)	121.4(2)
C(8)–C(7)–C(17)	127.3(2)	C(9)–C(33)–C(34)	123.1(2)
C(1)–C(8)–C(7)	119.4(2)	C(9)–C(33)–C(38)	117.8(2)
C(1)–C(8)–C(9)	89.2(1)	C(34)–C(33)–C(38)	119.1(2)
C(7)–C(8)–C(9)	151.1(2)	C(33)–C(34)–C(35)	119.8(2)
C(8)–C(9)–C(10)	93.0(1)	C(34)–C(35)–C(36)	120.8(3)
C(8)–C(9)–C(33)	132.3(2)	C(35)–C(36)–C(37)	119.8(3)
C(10)–C(9)–C(33)	133.4(2)	C(36)–C(37)–C(38)	120.0(3)
C(1)–C(10)–C(9)	93.2(1)	C(33)–C(38)–C(37)	120.6(2)
C(1)–C(10)–C(39)	132.0(2)	C(10)–C(39)–C(40)	120.4(2)
C(9)–C(10)–C(39)	134.3(2)	C(10)–C(39)–C(44)	120.9(2)
C(1)–C(11)–C(12)	107.0(1)	C(40)–C(39)–C(44)	118.7(2)
C(1)–C(11)–C(45)	111.7(2)	C(39)–C(40)–C(41)	120.4(2)
C(12)–C(11)–C(45)	110.1(2)	C(40)–C(41)–C(42)	120.3(3)
C(6)–C(12)–C(11)	107.6(1)	C(41)–C(42)–C(43)	119.9(3)
C(6)–C(12)–C(46)	111.3(2)	C(42)–C(43)–C(44)	120.4(3)
C(11)–C(12)–C(46)	109.7(2)	C(39)–C(44)–C(43)	120.2(2)
C(2)–C(13)–C(14)	109.1(2)	C(11)–C(45)–N(1)	179.6(3)
C(2)–C(13)–C(15)	110.3(2)	C(12)–C(46)–N(2)	178.7(3)

adducts of **1** and DCNE, **4** and **4a**, would be possible, the present analysis revealed that the former is the correct one. This stereoselectivity of the addition reaction will be discussed later.



4 4a

The present structure is quite similar to that of **3** except that the latter has two more cyano groups on the central bridge. Therefore, the framework of **4** without terminal substituents also consists of three planar parts, which include C(1)–C(6) interatomic vector in common. Least-squares planes and deviations of the atoms from the planes are given in Table 5. Dihedral angles between these planes are shown in Table 6. The planes I and II make an angle of 125.7°. The plane III, formed by the addition of DCNE, bisects this dihedral angle. These were also the case in **3**; the corresponding value is 125.0°. But the detailed observation of the planarity and dihedral angle indicates some characteristic differences between **3** and **4**. A slight folding of the four-membered ring observed in **3** is reduced in **4**. Mean deviation from these planes is 0.014 Å in **3** and 0.007 Å in **4**. On the contrary, coplanarity between I and this four-membered ring is poorer in **4**; the dihedral angle between them is 4.6° in **4**, whereas it is 2.0° in **3**. The direction of this bending is upward to the cyano group just above the four-membered ring. However, the largest difference between these molecules is the deviation of *t*-butyl groups. The trend observed in **3** in which the *t*-butyl groups are bent away from the plane I opposite to the cyano group just above is greatly reduced in **4**. The mean deviation of C(13) of the *t*-butyl group from the plane I is up to 0.13 Å in **3**, and it is 0.048 Å in **4**.

Table 5. Deviations (l/Å) of the atoms from the least-squares planes

Asterisks indicate the atoms defining the best plane.

Plane I		Plane II		Plane III	
C(1)*	−0.001	C(1)*	−0.006	C(1)*	0.015
C(2)*	0.001	C(8)*	0.012	C(11)*	−0.023
C(3)*	−0.001	C(7)*	−0.011	C(12)*	0.023
C(6)*	0.001	C(6)*	0.006	C(6)*	−0.015
C(13)	−0.049	C(17)	−0.048		
C(4)	−0.133	C(9)	0.138		
Plane IV		Plane V			
C(3)*	0.003	C(1)*	0.010		
C(4)*	−0.002	C(8)*	−0.011		
C(5)*	0.003	C(9)*	0.012		
C(6)*	−0.003	C(10)*	−0.012		
C(2)	−0.092	C(7)	0.033		
C(21)	−0.155	C(33)	0.274		
C(27)	−0.208	C(39)	0.096		

Table 6. Dihedral angles (ϕ/°)

	II	III	IV	V
I	125.7(1)	117.1(1)	4.9(1)	128.7(1)
II		117.2(1)	127.9(1)	4.3(1)
III			114.6(1)	114.1(1)
IV				130.6(1)

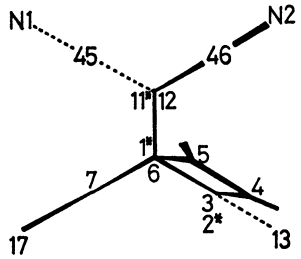


Fig. 4. Schematic drawing of the molecule projected along the C(1)–C(6) direction.

These differences may be consistently explained as follows. Figure 4 is a schematic drawing of the molecule projected along the C(1)–C(6) direction. Absence of the two cyano groups on the central bridge in the case of **4** reduces the repulsion with *t*-butyl groups and the latter can be nearly on the plane I. At the same time, the torsion angle along the C(11)–C(12) bond will be changed to be favourable against the other steric effect. The torsion angle C(1)–C(11)–C(12)–C(6) in **4** [121.2(1)°] is greater than that of **3** by 2.5°. Then the four-membered ring, C(3)–C(4)–C(5)–C(6), below this cyano group may slightly go upward so as to avoid the repulsion between the *t*-butyl group which is attached to the other plane II.

The lack of the two cyano groups also reduces the steric hindrance in the central bridge bond. The mean bond length C(1)–C(11) in **4** is 1.571 Å, which is 0.016 Å shorter than that of **3**. Moreover, the difference of the C(11)–C(12) distances between **3** and **4** is 0.042 Å. This shortening is partly due to the elimination of an electron withdrawing cyano group, but more important is the reduction of the repulsion between the cyano groups in the eclipse conformation.

Discussion

In a previous paper,[4] we have shown a new approach to a reaction mechanism of complicated molecules. Its interaction energy was divided into two parts, a stabilization energy in the intermediate state[8] of the approaching molecules, and a steric effect of the bulky substituents estimated from the empirical non-bonded interaction parameters.[9] The former was calculated in the reaction intermediate of unsubstituted benzo[1,2 : 4,5]dicyclobutene and TCNE or ethylene. The preference of the cross addition of TCNE is expected from this result. However, it is overcome by the repulsion between the bulky substituents. These results are in good agreement with the observed reaction of **1** and TCNE. It is, therefore, quite important to carry out the same kind of calculation for the reaction of **1** and DCNE which is

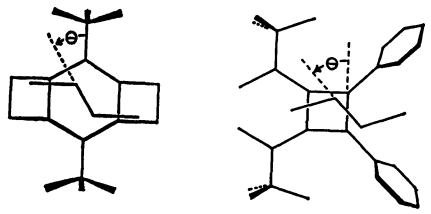


Fig. 5. Relative orientation θ in the (a) cross, and (b) linear approaching mode.

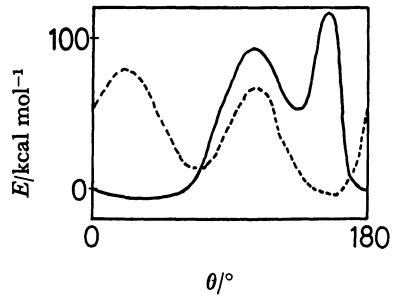


Fig. 6. Variations of the non-bonded interaction energy with the relative orientation θ at a constant distance (3.4 Å).

expected to be less repulsive than TCNE. The procedure is almost the same as that in the previous report. Since the electronic interaction energy was calculated without bulky substituents, the result is also applicable to that of DCNE. Relative orientation θ in the reaction intermediate is defined in Fig. 5. Non-bonded interaction energy in the case where the interplane distance is 3.4 Å is shown in Fig. 6. The solid curve refers to the cross addition (Fig. 5a). Its minimum is -6.6 kcal mol^{-1}†† at about 50° of θ. The dashed curve indicates the energy value of the linear addition (Fig. 5b). It has a minimum energy -5.0 kcal mol^{-1} when θ is $-10°$. In order to reduce the total number of parameters, terminal substituents are fixed as those in Fig. 5, which may be regarded as least repulsive conformations. Both of the minimum energy and the shape of the potential groove indicate that the cross approaching mode is less hindered than that of the linear approach. Taking the electronic interaction energy into account, we conclude that the cross addition is much preferable to the linear addition, and it is consistent with the reaction of **1** and DCNE.

The present calculation also explains why **4**, not a possible isomer **4a**, was actually formed. They correspond to the adducts with the θ value of 60° and 120° respectively. There is a local minimum at 120° in Fig. 6, but the energy value is high because of the repulsion between *t*-butyl groups and cyano groups.

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†† 1 kcal mol^{-1}=4.184 kJ mol^{-1}.

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