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The Crystal Structure of a Stable Benzocyclobutene. II. 2,7-Di-*t*-butyl-10,10,11,11-tetracyano-4,5,9,12-tetraphenyltetracyclo-[6.4.0.0^{3,6}.0^{9,12}]dodeca-1(8),2,4,6-tetraene

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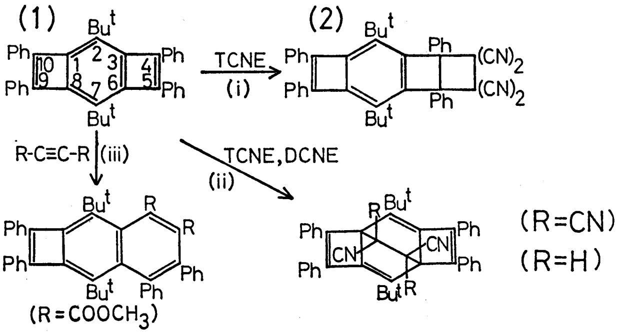
As the first step in the investigation of the reaction mechanism of a benzocyclobutene derivatives, the title compound has been determined by the X-ray diffraction method. The crystals are monoclinic; space group $P2_1/n$; $a=28.117(3)$, $b=11.148(1)$, $c=13.167(1)$ Å, and $\beta=97.26(1)°$. The asymmetric unit contains one molecule of the title compound and acetonitrile. The structure was solved by the direct method and refined by the block-diagonal least-squares method to a final R factor of 0.088 for 5456 observed reflections. The molecular framework consists of a planar ten-membered ring from benzodicyclobutene and a slightly folded four-membered ring formed by the addition of tetracyanoethylene (TCNE). Calculation has been undertaken for the non-bonded interaction energy of possible modes of approach between benzodicyclobutene and TCNE. The results are in qualitative agreement with the folding of the four-membered ring.

The Diels-Alder reactions of a benzodicyclobutene derivative (**1**)[1] with some dienophiles may be classified into three types: i) Tetracyanoethylene (TCNE) attacks the C(4)–C(5) double bond to give a "linear" adduct (**2**);[2] ii) bridged compounds across the central six-membered ring are obtained by means of a reaction with *trans*-1,2-dicyanoethylene (DCNE) and also as by-products of the reaction with TCNE,[3] and iii) some other dienophiles are added to C(1)–C(10) to produce "angular" adducts.[4] The diversity of the reactions of the molecule (**1**) should be studied stereochemically as well as electronically.



The present paper will deal with the X-ray analysis of the title compound (**2**), one of the linear adducts, as the first step in the investigation of the reaction route.

Experimental

Crystals suitable for structure determination were provided by Professor Fumio Toda of Ehime University. The crystals were orange prisms. Weissenberg photographs showed the systematic absences; ($h0l$), $h+l\neq 2n$, and ($0k0$), $k\neq 2n$, indicating that the space group was $P2_1/n$. Accurate unit-celldimensions and intensity data were obtained on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The crystal data are listed in Table 1. A total of 7404 independent reflections ($2\theta\leq 50°$) were obtained, in which 5456 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were made as usual.

Table 1. Crystal data

2,7-Di-*t*-butyl-10,10,11,11-tetracyano-4,5,9,12-tetraphenyltetracyclo[6.4.0.0^{3,6}.0^{9,12}]dodeca-1(8),2,4,6-tetraene: acetonitrile.

$C_{48}H_{38}N_4$: C_2H_3N
$F.W.=711.9$
Crystal system: monoclinic
Space group: $P2_1/n$
$a = 28.117(3)$ Å
$b = 11.148(1)$
$c = 13.167(1)$
$\beta = 97.26(1)°$
$U = 4094(1)$ Å^3
$Z = 4$
$D_m = 1.157$ g cm^{-3}
$D_x = 1.155$

Structure Determination

The structure was solved by the direct method.[5] Fourier synthesis using 545 normalized structure factors ($|E|\geq 1.7$) clearly revealed 55 non-hydrogen atoms, including those in acetonitrile. The atomic parameters were refined by the block-diagonal least-squares method. The thermal parameters of acetonitrile became twice as large as those of the other atoms. All the hydrogen atoms except for those of acetonitrile were located on a difference map. In spite of the quite large thermal parameters, the bond lengths of acetonitrile are rather reasonable. Moreover, the difference synthesis showed no large peak near the position of these atoms. Therefore, there were no difficulties in determining the occupancy of acetonitrile. At the final stage of the refinement, anisotropic temperature factors were introduced for all the non-hydrogen atoms.

The weighting scheme was $w=1/\{1+0.2(10-|F_o|)\}$ for $|F_o|<10$, $w=1$ for $10\leq|F_o|\leq 30$, and $w=1/\{1+0.8(|F_o|-30)\}$ for $|F_o|>30$, so as to make the average of $w(|F_o|-|F_c|)^2$ almost equal over all the range of $|F_o|$ values. The final R factor was 0.088 for the non-zero reflections and 0.14 for all the reflections.* The atomic scattering factors were taken from *International Tables*

TABLE 2. FINAL POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) PARAMETERS

The temperature factor has this form:

$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1636(1)	704(3)	3216(2)	33(2)	37(2)	35(2)	−2(1)	−1(1)	4(1)
C(2)	2133(1)	1038(3)	3464(2)	33(2)	35(2)	41(2)	−5(1)	3(1)	3(1)
C(3)	2321(1)	430(3)	4317(2)	30(2)	42(2)	44(2)	−6(1)	−2(1)	0(1)
C(4)	2773(1)	177(3)	5084(3)	38(2)	49(2)	45(2)	−3(2)	−7(1)	3(2)
C(5)	2535(1)	−584(3)	5620(3)	41(2)	53(2)	44(2)	−1(2)	−5(1)	5(2)
C(6)	2068(1)	−389(3)	4896(2)	41(2)	44(2)	35(2)	−2(1)	−2(1)	5(1)
C(7)	1592(1)	−679(3)	4699(2)	40(2)	45(2)	34(2)	−4(1)	5(1)	2(1)
C(8)	1386(1)	−43(3)	3795(2)	32(2)	38(2)	35(2)	−1(1)	0(1)	−3(1)
C(9)	906(1)	111(3)	3124(2)	28(1)	45(2)	39(2)	−2(1)	2(1)	−1(1)
C(10)	596(1)	1219(3)	3454(2)	35(2)	47(2)	43(2)	1(1)	3(1)	−1(2)
C(11)	926(1)	2137(3)	2916(2)	42(2)	43(2)	42(2)	0(2)	0(1)	−1(2)
C(12)	1196(1)	1010(3)	2465(2)	31(2)	39(2)	37(2)	−1(1)	3(1)	5(1)
C(13)	1154(1)	830(3)	1336(2)	42(2)	37(2)	39(2)	−8(1)	2(1)	4(1)
C(14)	1541(1)	388(3)	886(3)	54(2)	45(2)	49(2)	2(2)	8(2)	1(2)
C(15)	1494(2)	108(4)	−149(3)	81(3)	69(3)	53(2)	−3(2)	19(2)	−9(2)
C(16)	1051(2)	233(5)	−744(3)	98(3)	93(4)	43(2)	−20(3)	4(2)	−10(2)
C(17)	662(2)	617(5)	−302(3)	71(3)	90(3)	48(2)	−11(2)	−13(2)	0(2)
C(81)	707(1)	913(4)	728(3)	53(2)	70(3)	44(2)	−5(2)	−7(2)	1(2)
C(19)	662(1)	−1000(3)	2655(2)	37(2)	45(2)	40(2)	−7(1)	0(1)	3(2)
C(20)	940(1)	−1767(3)	2141(3)	57(2)	49(2)	64(2)	−8(2)	10(2)	−7(2)
C(21)	754(2)	−2849(4)	1732(4)	87(3)	61(3)	89(3)	−7(2)	9(3)	−21(3)
C(22)	285(2)	−3147(4)	1825(4)	97(4)	53(3)	107(4)	−23(3)	−16(3)	−16(3)
C(23)	9(2)	−2400(4)	2341(4)	59(3)	66(3)	110(4)	−22(2)	−14(2)	13(3)
C(24)	192(1)	−1324(4)	2757(3)	42(2)	57(2)	67(2)	−9(2)	−3(2)	10(2)
C(25)	3286(1)	537(3)	5300(2)	37(2)	59(2)	40(2)	−3(2)	−8(1)	9(2)
C(26)	3639(1)	−235(4)	5063(3)	47(2)	78(3)	67(3)	10(2)	−5(2)	−10(2)
C(27)	4120(1)	28(5)	5388(4)	44(2)	134(5)	71(3)	23(3)	−2(2)	−12(3)
C(28)	4241(1)	1052(5)	5928(3)	42(2)	132(4)	65(3)	−21(3)	−7(2)	−6(3)
C(29)	3896(2)	1826(5)	6154(4)	60(3)	93(4)	100(4)	−21(3)	−14(3)	−23(3)
C(30)	3414(1)	1577(4)	5847(4)	49(2)	74(3)	91(3)	−2(2)	−10(2)	−23(3)
C(31)	2708(1)	−1266(4)	6553(3)	43(2)	59(2)	50(2)	−4(2)	−4(2)	14(2)
C(32)	2920(2)	−2369(4)	6488(4)	109(4)	65(3)	68(3)	20(3)	−5(3)	12(2)
C(33)	3112(2)	−2980(5)	7374(4)	131(5)	86(4)	88(4)	27(4)	−11(3)	31(3)
C(34)	3093(2)	−2495(6)	8314(4)	108(4)	116(5)	75(3)	13(4)	−19(3)	44(3)
C(35)	2885(2)	−1395(6)	8386(4)	127(5)	148(6)	51(3)	24(4)	−16(3)	15(3)
C(36)	2695(2)	−760(5)	7509(3)	100(4)	96(4)	56(3)	23(3)	−15(2)	4(3)
C(37)	2422(1)	1938(3)	2896(3)	41(2)	47(2)	55(2)	−11(2)	4(2)	8(2)
C(38)	2118(1)	2706(4)	2085(3)	59(2)	53(2)	60(2)	−10(2)	0(2)	17(2)
C(39)	2807(1)	1246(4)	2392(4)	51(2)	71(3)	93(3)	−6(2)	30(2)	14(2)
C(40)	2677(1)	2819(4)	3693(3)	65(3)	57(3)	74(3)	−27(2)	−10(2)	11(2)
C(41)	1354(1)	−1558(4)	5369(3)	46(2)	62(2)	47(2)	−7(2)	4(2)	19(2)
C(42)	822(1)	−1756(4)	5034(3)	53(2)	93(3)	67(3)	−25(2)	5(2)	29(2)
C(43)	1614(2)	−2758(4)	5377(5)	85(3)	61(3)	139(5)	−6(3)	23(3)	39(3)
C(44)	1403(2)	−1053(5)	6470(3)	79(3)	138(5)	40(2)	−33(3)	8(2)	10(3)
C(45)	677(1)	2973(3)	2177(3)	45(2)	48(2)	62(2)	7(2)	7(2)	3(2)
C(46)	1231(1)	2869(3)	3669(3)	52(2)	49(2)	54(2)	−3(2)	12(2)	−6(2)
C(47)	100(1)	1302(3)	2931(3)	40(2)	49(2)	62(2)	5(2)	9(2)	2(2)
C(48)	597(1)	1387(3)	4563(3)	47(2)	55(2)	51(2)	0(2)	14(2)	0(2)
N(1)	499(1)	3626(3)	1581(3)	64(2)	74(2)	88(3)	20(2)	10(2)	28(2)
N(2)	1459(1)	3461(3)	4242(3)	77(2)	71(2)	77(2)	−13(2)	1(2)	−24(2)
N(3)	−274(1)	1386(3)	2509(3)	38(2)	82(3)	90(3)	7(2)	−3(2)	7(2)
N(4)	610(1)	1496(4)	5420(3)	90(3)	92(3)	53(2)	7(2)	21(2)	−8(2)
C(49)	694(3)	4696(6)	6280(7)	160(7)	93(5)	201(8)	8(5)	81(6)	1(5)
C(50)	261(3)	5446(5)	6204(5)	192(7)	83(4)	111(5)	−38(4)	71(5)	−17(4)
N(5)	−79(3)	6063(5)	6144(5)	207(6)	105(4)	140(5)	−8(4)	75(5)	−24(4)

for X-Ray Crystallography.[6] The final atomic parameters are listed in Table 2,* while the crystallographic numbering scheme is shown in Fig. 1.

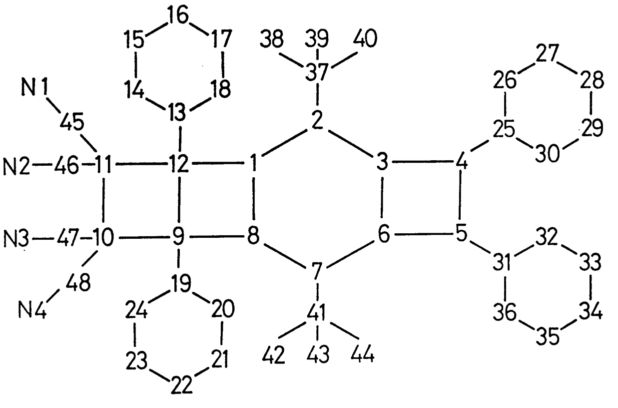


Fig. 1. Crystallographic numbering scheme.

Results and Discussion

The crystal structure is shown in Fig. 2, the molecular framework is shown in Fig. 3, and the bond lengths and angles are listed in Table 4. Ten atoms of the molecular framework, which are originally the skeleton of **1**, are nearly coplanar (Table 3). By the addition of TCNE, a new cyclobutane ring is formed, which makes a dihedral angle (109.0°) with the ten-membered ring. The corresponding dihedral angle of perchloro-3, 4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane[7] is 115°. In the cyclobutane ring, all the bond lengths exceed 1.60 Å, considerably longer than the usual C(sp^3)–C(sp^3) lengths. Such an elongation effect of the four-membered ring may be attributed to the strong repulsion between the non-bonded atoms. For example, the C–C bond length is 1.56 Å in cyclobutane and 1.583 Å in *cis*-3,4-dichloro-1-cyclobutene.[8] Also elongated is that in the

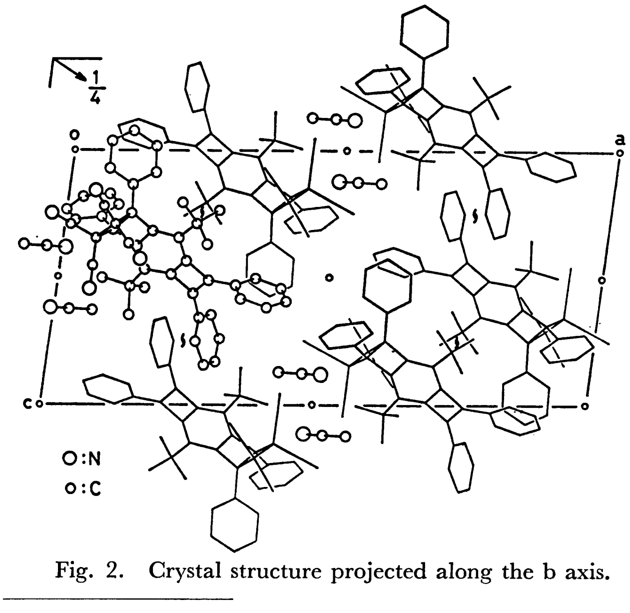
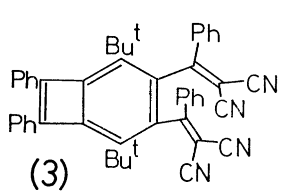


Fig. 2. Crystal structure projected along the b axis.



(3)

TABLE 3. DEVIATIONS (l/Å) FROM THE PLANE THROUGH THE TEN-MEMBERED RING

C(1)*	−0.040
C(2)*	0.011
C(3)*	0.008
C(4)*	0.010
C(5)*	−0.005
C(6)*	−0.009
C(7)*	0.001
C(8)*	0.003
C(9)*	0.016
C(12)*	0.005
C(10)	1.489
C(11)	1.556
C(37)	0.074
C(41)	−0.008
C(25)	0.044
C(31)	0.007

Asterisks are used to define the best plane.

TABLE 4a. BOND LENGTHS (l/Å)
Standard deviations are given in parentheses.

C(1)–C(2)	1.442(4)	C(19)–C(20)	1.390(5)
C(1)–C(8)	1.381(4)	C(19)–C(24)	1.392(5)
C(1)–C(12)	1.522(4)	C(20)–C(21)	1.394(6)
C(2)–C(3)	1.360(5)	C(21)–C(22)	1.381(7)
C(2)–C(37)	1.543(5)	C(22)–C(23)	1.374(8)
C(3)–C(4)	1.548(5)	C(23)–C(24)	1.390(7)
C(3)–C(6)	1.435(5)	C(25)–C(26)	1.379(6)
C(4)–C(5)	1.336(5)	C(25)–C(30)	1.387(6)
C(4)–C(25)	1.488(5)	C(26)–C(27)	1.399(8)
C(5)–C(6)	1.536(5)	C(27)–C(28)	1.365(8)
C(5)–C(31)	1.475(5)	C(28)–C(29)	1.360(8)
C(6)–C(7)	1.370(5)	C(29)–C(30)	1.391(7)
C(7)–C(8)	1.442(5)	C(31)–C(32)	1.374(7)
C(7)–C(41)	1.529(5)	C(31)–C(36)	1.384(7)
C(8)–C(9)	1.526(5)	C(32)–C(33)	1.399(8)
C(9)–C(10)	1.604(5)	C(33)–C(34)	1.358(9)
C(9)–C(12)	1.612(5)	C(34)–C(35)	1.368(9)
C(9)–C(19)	1.509(5)	C(35)–C(36)	1.401(9)
C(10)–C(11)	1.605(5)	C(37)–C(38)	1.540(5)
C(10)–C(47)	1.479(5)	C(37)–C(39)	1.547(6)
C(10)–C(48)	1.471(5)	C(37)–C(40)	1.546(6)
C(11)–C(12)	1.619(5)	C(41)–C(42)	1.519(6)
C(11)–C(45)	1.461(5)	C(41)–C(43)	1.523(7)
C(11)–C(46)	1.472(5)	C(41)–C(44)	1.545(7)
C(12)–C(13)	1.490(5)	C(45)–N(1)	1.139(5)
C(13)–C(14)	1.393(5)	C(46)–N(2)	1.136(5)
C(13)–C(18)	1.406(5)	C(47)–N(3)	1.130(5)
C(14)–C(15)	1.387(6)	C(48)–N(4)	1.131(6)
C(15)–C(16)	1.391(7)	C(49)–C(50)	1.471(12)
C(16)–C(17)	1.370(7)	C(50)–N(5)	1.172(10)
C(17)–C(18)	1.386(7)		

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* The tables of structure factors and the atomic parameters of the hydrogen atoms are kept as Document No. 7809 at the Chemical Society of Japan.

TABLE 4b. BOND ANGLES (ϕ/°)

Standard deviations are given in parentheses.

C(2)-C(1)-C(8)	125.3 (3)	C(12)-C(13)-C(18)	120.8 (3)
C(2)-C(1)-C(12)	140.7 (3)	C(14)-C(13)-C(18)	118.1 (3)
C(8)-C(1)-C(12)	93.7 (3)	C(13)-C(14)-C(15)	121.0 (3)
C(1)-C(2)-C(3)	108.8 (3)	C(14)-C(15)-C(16)	119.8 (4)
C(1)-C(2)-C(37)	127.8 (3)	C(15)-C(16)-C(17)	119.9 (5)
C(3)-C(2)-C(37)	123.4 (3)	C(16)-C(17)-C(18)	120.8 (5)
C(2)-C(3)-C(4)	146.3 (3)	C(13)-C(18)-C(17)	120.4 (4)
C(2)-C(3)-C(6)	126.1 (3)	C(9)-C(19)-C(20)	116.8 (3)
C(4)-C(3)-C(6)	87.6 (3)	C(9)-C(19)-C(24)	124.1 (3)
C(3)-C(4)-C(5)	92.0 (3)	C(20)-C(19)-C(24)	119.0 (3)
C(3)-C(4)-C(25)	140.5 (3)	C(19)-C(20)-C(21)	121.0 (4)
C(5)-C(4)-C(25)	127.5 (3)	C(20)-C(21)-C(22)	119.3 (5)
C(4)-C(5)-C(6)	91.7 (3)	C(21)-C(22)-C(23)	120.2 (5)
C(4)-C(5)-C(31)	129.2 (3)	C(22)-C(23)-C(24)	120.8 (5)
C(6)-C(5)-C(31)	139.1 (3)	C(19)-C(24)-C(23)	119.7 (4)
C(3)-C(6)-C(5)	88.8 (3)	C(4)-C(25)-C(26)	119.7 (4)
C(3)-C(6)-C(7)	126.0 (3)	C(4)-C(25)-C(30)	120.4 (4)
C(5)-C(6)-C(7)	145.2 (3)	C(26)-C(25)-C(30)	119.5 (4)
C(6)-C(7)-C(8)	108.7 (3)	C(25)-C(26)-C(27)	119.8 (4)
C(6)-C(7)-C(41)	122.1 (3)	C(26)-C(27)-C(28)	120.2 (5)
C(8)-C(7)-C(41)	129.2 (3)	C(27)-C(28)-C(29)	120.4 (5)
C(1)-C(8)-C(7)	125.0 (3)	C(28)-C(29)-C(30)	120.4 (5)
C(1)-C(8)-C(9)	95.0 (3)	C(25)-C(30)-C(29)	119.8 (4)
C(7)-C(8)-C(9)	140.0 (3)	C(5)-C(31)-C(32)	120.7 (4)
C(8)-C(9)-C(10)	113.6 (3)	C(5)-C(31)-C(36)	120.3 (4)
C(8)-C(9)-C(12)	84.9 (2)	C(32)-C(31)-C(36)	118.9 (4)
C(8)-C(9)-C(19)	117.9 (3)	C(31)-C(32)-C(33)	120.6 (5)
C(10)-C(9)-C(12)	89.8 (2)	C(32)-C(33)-C(34)	120.7 (6)
C(10)-C(9)-C(19)	120.6 (3)	C(33)-C(34)-C(35)	119.1 (6)
C(12)-C(9)-C(19)	121.6 (3)	C(34)-C(35)-C(36)	121.2 (6)
C(9)-C(10)-C(11)	90.4 (2)	C(31)-C(36)-C(35)	119.5 (5)
C(9)-C(10)-C(47)	115.8 (3)	C(2)-C(37)-C(38)	114.7 (3)
C(9)-C(10)-C(48)	115.7 (3)	C(2)-C(37)-C(39)	108.9 (3)
C(11)-C(10)-C(47)	108.6 (3)	C(2)-C(37)-C(40)	108.1 (3)
C(11)-C(10)-C(48)	115.4 (3)	C(38)-C(37)-C(39)	109.8 (3)
C(47)-C(10)-C(48)	109.8 (3)	C(38)-C(37)-C(40)	106.6 (3)
C(10)-C(11)-C(12)	89.5 (2)	C(39)-C(37)-C(40)	108.6 (3)
C(10)-C(11)-C(45)	116.4 (3)	C(7)-C(41)-C(42)	114.3 (3)
C(10)-C(11)-C(46)	112.1 (3)	C(7)-C(41)-C(43)	108.8 (4)
C(12)-C(11)-C(45)	117.3 (3)	C(7)-C(41)-C(44)	108.3 (4)
C(12)-C(11)-C(46)	114.7 (3)	C(42)-C(41)-C(43)	109.2 (4)
C(45)-C(11)-C(46)	106.5 (3)	C(42)-C(41)-C(44)	107.0 (4)
C(1)-C(12)-C(9)	86.3 (2)	C(43)-C(41)-C(44)	109.1 (4)
C(1)-C(12)-C(11)	103.4 (3)	C(11)-C(45)-N(1)	177.2 (4)
C(1)-C(12)-C(13)	125.0 (3)	C(11)-C(46)-N(2)	178.1 (4)
C(9)-C(12)-C(11)	89.6 (2)	C(10)-C(47)-N(3)	178.0 (4)
C(9)-C(12)-C(13)	118.2 (3)	C(10)-C(48)-N(4)	177.9 (4)
C(11)-C(12)-C(13)	119.2 (3)	C(49)-C(50)-N(5)	178.7 (8)
C(12)-C(13)-C(14)	120.3 (3)		

unsaturated four-membered ring of the benzocyclobutene derivative (**3**),[9] a compound formed by the heat isomerization of the present compound. Our results, however, show much longer values than these compounds, indicating that the elongation effect is fortified by the bulky substituents. This suggests that this cyclobutane ring is easily cleaved. The bond between the *t*-butyl group and the skeleton is also affected by the repulsion. The averaged value, 1.54 Å, is comparable to that of the **3** molecule. The contraction of the C(1)–C(2)–C(37) and C(3)–C(2)–C(37) angles is 4.4°, and the C(1)–C(2)–C(3) angle is 108.8°. The corresponding values of the **3** molecule are 7 and 109° respectively. Although **2** and **3** are different about the cleaved ring, the resemblance in conformation of the *t*-butyl groups between **2** and **3** shows that the steric effects of the surrounding substituents are similar to each other. A detailed comparison indicates that, in **2**, one of the

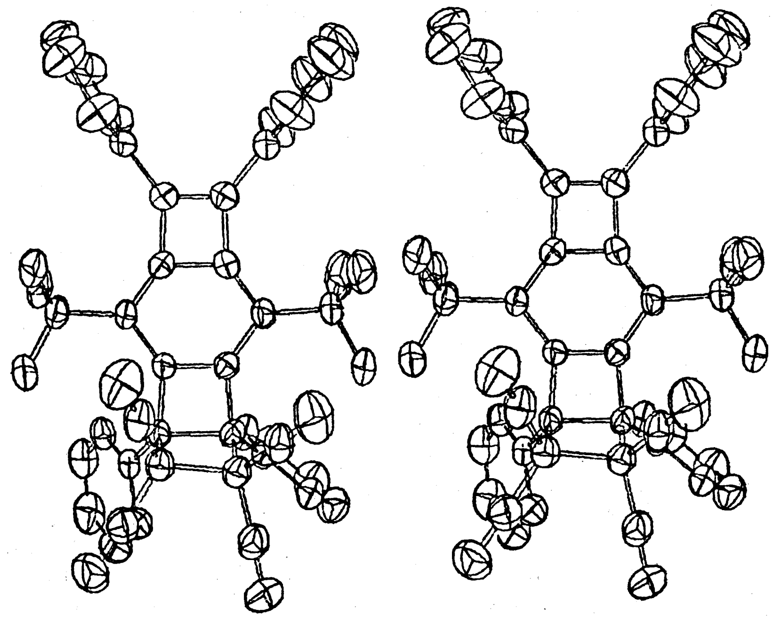

Fig. 3. A stereoscopic view perpendicular to the tenmembered ring.

methyl groups of the *t*-butyl group lies close to the skeletal plane. This is quite reasonable because, in the case of **3**, the cyano and phenyl groups jamming the in-plane methyl groups from both sides of the skeletal plane may have more freedom in their conformation than in the case of **2**. Phenyl groups attached to the unsaturated four-membered ring are rotated around the connecting bonds in both **2** and **3** molecules. The rotation angles of **2** are 80.2 and 91.7°, greater than those of **3**, 61 and 74°. These relatively large values, which may be attributed to the steric effect of the out-of-plane methyl groups, will serve to protect the reaction of one more TCNE to the unsaturated four-membered ring.

The central six-membered ring of the **2** molecule takes a shallow boat form, whereas the **3** molecule has a flattened crown conformation in which atoms deviate alternately from the plane. The four-membered rings annelated to the central six-membered ring are almost co-planar in **2**. However, the cyclobutane ring formed by the addition of TCNE is significantly non-planar. The dihedral angle between the C(9)–C(10)–C(11) and C(9)–C(12)–C(11) planes is 8.5°. The torsion angle C(9)–C(10)–C(11)–C(12) is 6.6°. This small, but significant, non-planarity may be regarded as a result of the steric effect of the bulky substituents. This effect, which also causes the elongation and distortion of some bond lengths and angles presented above, may play an intermediate role in the addition reaction as well. Therefore, we have calculated the non-bonded interaction energy for all the possible modes of approach between the **1** molecule and TCNE.

First, it was assumed that, in the stable conformation of the **1** molecule, four phenyl groups are rotated by 60° around the connecting bonds. This assumption is supported by the observation that some compounds with many phenyl groups have similar conformations; that of hexaphenylbenzene is 67.2°, for example.[10] Second, it was assumed that the plane of TCNE is parallel to that of the cyclobutene ring of **1** and that the center of the former approaches through the normal, passing the midpoint of the reactive double bond of the latter so as to make the overlap of the π-orbitals the maximum. For energy calculation, the distance between the double bonds and also the relative orientation were taken as variables. The former was varied from 4.0 to 3.4 Å, which is the van der Waals contact. The latter was every 10° of rotation up to 180° around the axis through the midpoints of both the double bonds. Some possible conformational changes of **1** in the reaction were

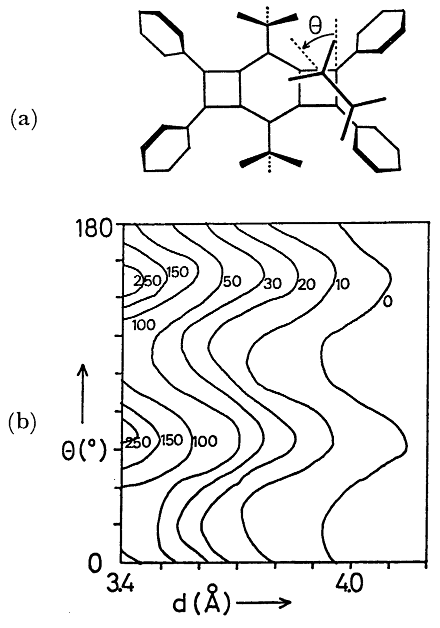

Fig. 4. (a) Relative orientation of the two molecules. (b) Two dimensional map of the non-bonded interaction energy (kcal mol^{-1}).

excluded from these calculations so as to reduce the number of parameters. For the same reason, the non-parallel approach of the two molecules was not considered. The potential functions used were those of Giglio.[11] The results are shown in Fig. 4. There are two potential grooves at the torsion angles of 20 and 110°, the former having a large overlap of the π-orbital. Therefore, the former mode of approach is preferable in the addition reaction. When the new cyclobutane is formed, strong intramolecular repulsion may modify the structure of **2** from the assumed one. However, the distortion of this cyclobutane ring, expressed in terms of the interedge angle (6.6°), is in qualitative agreement with the probable mode of approach. This indicates that such a calculation of the intermolecular interaction may be useful for the investigation of the reaction route of the **1** molecule with some dienophiles. The analyses of the other Diels-Alder adducts are in progress.

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