# The X-Ray Study of Several Reaction Products of Substituted Benzo-
# dicyclobutene. I. 2,7-Di-*t*-butyl-11,11,12,12-tetracyano-4,5,9,10-
# tetraphenyltetracyclo[4.4.2.0$^{1,8}$.0$^{3,6}$]dodeca-2,4,7,9-tetraene

Harumichi Tsukada,* Hirotaka Shimanouchi, and Yoshio Sasada

*Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

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As a part of the studies of the reaction mechanism of a substituted benzodicyclobutene (**1**), the X-ray analysis of the title compound was carried out. The crystals are monoclinic; space group P2$_1$/a, $a=23.159(3)$, $b=20.369(3)$, $c=8.589(1)$ Å, $\beta=104.27(1)°$. The structure was solved by the direct method and was refined by the block-diagonal least-squares method to the final $R$ factor of 0.070 for 5553 observed reflections. In the molecular structure, there is a bridge-bond formed by the "cross" addition of tetracyanoethylene (TCNE) to the C(1) and C(6) sites of **1**. The intermolecular interaction was calculated so as to make clear what kind of addition reaction is preferable for the molecule **1**. The result is consistent with the observation that, in addition to the linear adduct, a cross adduct is also obtained as a by-product.

There are several theoretical approaches to organic reactions based on electronic considerations. One of the most popular and useful theories is the Woodward-Hoffmann rule[1] for a Diels-Alder reaction between some planar conjugated molecules. In the reactions affected by steric hindrance, however, the rule sometimes fails to predict the observed reaction. For example, the Diels-Alder reaction of substituted heptafulvene and tetracyanoethylene (TCNE) gives an unexpected adduct.[2] The calculation including all the valence electrons responsible for such a repulsion will require a great deal of time and effort. It may be better to deal with the non-bonded interaction using empirical parameters obtained in the investigation of the crystal packing.[3]

A series of the adducts of substituted benzodicyclobutene[4] (**1**) with some dienophiles are most profitable for such an energetic investigation of chemical reactions. This molecule undergoes many kinds of addition reactions, since there are many sites which dienophiles can attack. We can obtain "linear" adducts if dienophile adds to the C(4)–C(5) position of the molecule **1**. Addition to the C(3)–C(4) and C(1)–C(6) positions will produce "angular" and "cross" adducts respectively. TCNE reacts with **1** to give not only the linear adduct (**2**) as the main product, but also the cross adduct (**3**) as a by-product.[5,6] The structure determination of the former had been reported previously.[7] The present X-ray analysis of the latter has revealed the stereochemical difference between the main by-products, which will give some information regarding

the steric effect of the bulky substituents on the reaction.

## Experimental and Structure Determination

Crystals suitable for structure determination were provided by Professor Fumio Toda of Ehime University. The crystals were colorless needles. From the oscillation and Weissenberg photographs, the space group was uniquely assigned as P2$_1$/a. A Rigaku automated four-circle diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda=0.71069$ Å) was used for the determination of the accurate unit-cell dimensions and for the measurement of the diffraction intensities. The crystal data are listed in Table 1. A total of 6901 independent reflections ($2\theta\leq50°$) were obtained, of which 5553 had net intensities greater than the background. The intensities were corrected for the Lorentz and polarization effects, but not for the absorption and extinction.

TABLE 1. CRYSTAL DATA OF 2,7-DI-*t*-BUTYL-11,11,12,12-TETRACYANO-4,5,9,10-TETRAPHENYLTETRACYCLO-[4.4.2.0$^{1,8}$.0$^{3,6}$]DODECA-2,4,7,9-TETRAENE

| |
|---|
| C$_{48}$H$_{38}$N$_4$ |
| Molecular weight 670.9 |
| Crystal system: monoclinic |
| Space group: P2$_1$/a |
| $a=23.159(3)$ Å |
| $b=20.369(3)$ |
| $c=8.589(1)$ |
| $\beta=104.27(1)°$ |
| $U=3927(1)$ Å$^3$ |
| $Z=4$ |
| $D_m=1.135$ g cm$^{-3}$ |
| $D_x=1.135$ |
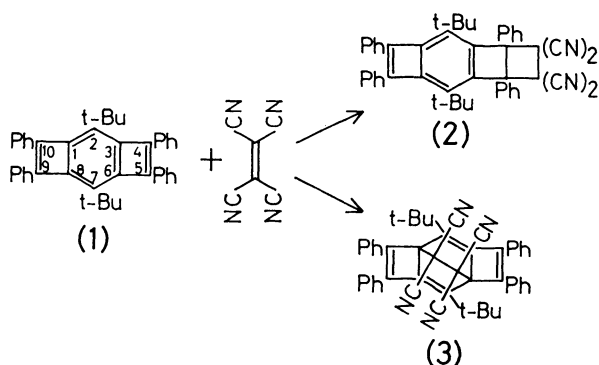
The structure was solved by the direct method.[8] The E map, calculated from 450 normalized structure factors ($E\geq 1.7$) with determined signs, clearly revealed 52 non-hydrogen atoms. Fourier synthesis including all these atoms showed no other spurious peaks at all. The atomic parameters were refined by the block-diagonal least-squares method. After the convergence of the positional and isotropic thermal parameters, the contribution from hydrogen atoms located geometrically was included. At the subsequent stage of the refinement, with the introduction of anisotropic thermal parameters for the nonhydrogen atoms, the parameters of the



(1)



(2)



(3)

hydrogen atoms were not shifted, but their positions were recalculated at the last stage. The weighting scheme was; $w=0.8$ for $|F|=0$, $w=1.0$ for $0<|F|\leq30$, and $w=1/\{1+0.14(|F|-30)\}$ for $|F|>30$. The final $R$ factor was 0.070 for 5553 observed reflections. In the final cycle of the least-squares, no shifts exceeded one tenth of their e.s.d's. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography.[9]" The final atomic parameters are listed in Table 2,[10] while the crystallographic numbering scheme is shown in Fig. 1.

TABLE 2. ATOMIC COORDINATES ($\times 10^4$)

| | X | Y | Z |
|---|---|---|---|
| C(1) | 1553( 1) | 2336( 1) | 7917( 3) |
| C(2) | 2123( 1) | 2357( 1) | 9309( 3) |
| C(3) | 2429( 1) | 1808( 1) | 9174( 3) |
| C(4) | 2952( 1) | 1382( 1) | 9712( 3) |
| C(5) | 2771( 1) | 947( 1) | 8485( 3) |
| C(6) | 2183( 1) | 1325( 1) | 7791( 3) |
| C(7) | 1548( 1) | 1113( 1) | 7831( 3) |
| C(8) | 1245( 1) | 1669( 1) | 7910( 3) |
| C(9) | 694( 1) | 2017( 1) | 7982( 4) |
| C(10) | 936( 1) | 2623( 1) | 7922( 3) |
| C(11) | 1753( 1) | 2377( 1) | 6275( 3) |
| C(12) | 2146( 1) | 1724( 1) | 6186( 3) |
| C(13) | 2251( 1) | 2864( 1) | 10656( 3) |
| C(14) | 2265( 2) | 3563( 2) | 10034( 4) |
| C(15) | 1757( 2) | 2812( 2) | 11566( 4) |
| C(16) | 2848( 2) | 2725( 2) | 11819( 5) |
| C(17) | 1349( 2) | 405( 2) | 7966( 5) |
| C(18) | 1708( 3) | 134( 2) | 9604( 7) |
| C(19) | 703( 2) | 376( 2) | 7923(11) |
| C(20) | 1491( 2) | -40( 2) | 6712( 7) |
| C(21) | 3503( 1) | 1424( 1) | 11028( 3) |
| C(22) | 3515( 1) | 1154( 2) | 12519( 4) |
| C(23) | 4029( 2) | 1205( 2) | 13762( 4) |
| C(24) | 4520( 2) | 1517( 2) | 13498( 5) |
| C(25) | 4513( 2) | 1784( 2) | 12017( 5) |
| C(26) | 4000( 1) | 1734( 2) | 10772( 4) |
| C(27) | 3078( 1) | 398( 1) | 7941( 3) |
| C(28) | 3533( 1) | 66( 1) | 9019( 4) |
| C(29) | 3857( 1) | -423( 2) | 8506( 4) |
| C(30) | 3734( 1) | -595( 2) | 6895( 4) |
| C(31) | 3286( 2) | -271( 2) | 5813( 4) |
| C(32) | 2957( 2) | 221( 2) | 6316( 4) |
| C(33) | 89( 1) | 1809( 2) | 8056( 5) |
| C(34) | -28( 2) | 1669( 2) | 9530( 6) |
| C(35) | -606( 2) | 1488( 3) | 9584( 9) |
| C(36) | -1043( 2) | 1443( 3) | 8217(10) |
| C(37) | -933( 2) | 1578( 3) | 6752( 9) |
| C(38) | -363( 2) | 1771( 2) | 6669( 6) |
| C(39) | 678( 1) | 3281( 1) | 7767( 3) |
| C(40) | 152( 1) | 3404( 2) | 8249( 4) |
| C(41) | -115( 1) | 4019( 2) | 8034( 4) |
| C(42) | 136( 1) | 4523( 2) | 7351( 4) |
| C(43) | 653( 1) | 4412( 2) | 6859( 4) |
| C(44) | 919( 1) | 3795( 1) | 7065( 4) |
| C(45) | 2108( 1) | 2967( 1) | 6181( 3) |
| C(46) | 1215( 1) | 2400( 2) | 4929( 3) |
| C(47) | 2755( 1) | 1901( 2) | 6091( 4) |
| C(48) | 1875( 2) | 1344( 2) | 4730( 4) |
| N(1) | 2392( 1) | 3419( 1) | 6118( 4) |
| N(2) | 795( 1) | 2422( 2) | 3904( 4) |
| N(3) | 3232( 1) | 2013( 2) | 6057( 4) |
| N(4) | 1668( 2) | 1058( 2) | 3591( 4) |

Standard deviations are given in parentheses.
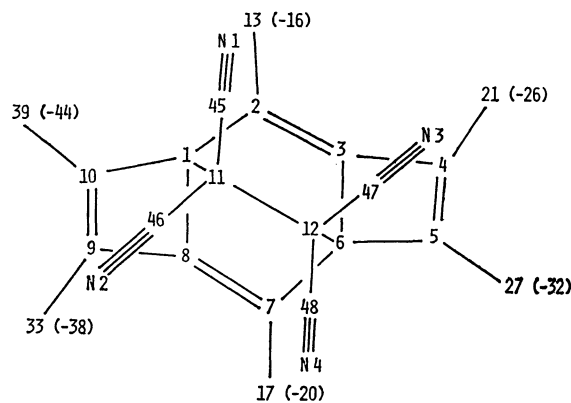


Fig. 1. Numbering scheme. Numbers in parentheses indicate the atoms of the substituents.

## Description of the Structure

A stereoview of the crystal structure is shown in Fig. 2. The intermolecular contacts are normal, judging from the relevant van der Waals radii. Two perspective views of a single molecule are given in Fig. 3. This structure is consistent with that presumed by the spectroscopic study.[6] The molecular framework contains a bridge bond formed by the addition of TCNE at the bridge heads C(1) and C(6) for which the name "cross adduct" is suitable. It consists of three planar parts, which all include the C(1)–C(6) interatomic vector. The deviations of the atoms from the least-squares planes and the dihedral angles between these planes are given in Table 3. The chemically equivalent planes, I and II, make a dihedral angle of 125.0°, which is bisected by the plane, III, formed by the addition of TCNE.

Although these three planes have no significant distortion, the four-membered rings annelated to those parts are slightly but significantly folded, the C(4) atom approaching the cyano groups. On the other hand, the $t$-butyl groups are kept away from the cyano groups, the deviation of the tertiary carbon atoms from the planes, I and II, being 0.13 Å. These trends may be attributed to the steric effects of the bulky substituents, which may play an important role in the addition reaction.

The bond lengths and angles are listed in Tables 4 and 5 respectively. As this molecule has an approximate two-fold axis, average values are used in the following discussion. The lengths of two double bonds, C(2)=C(3)
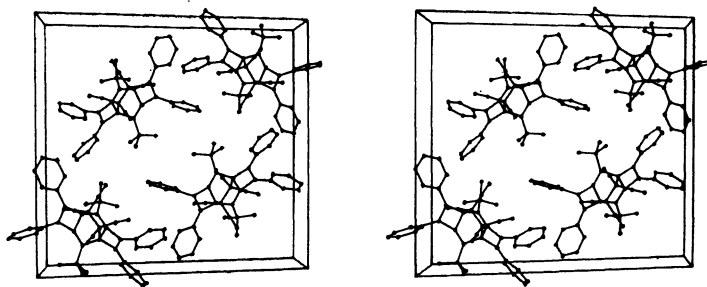


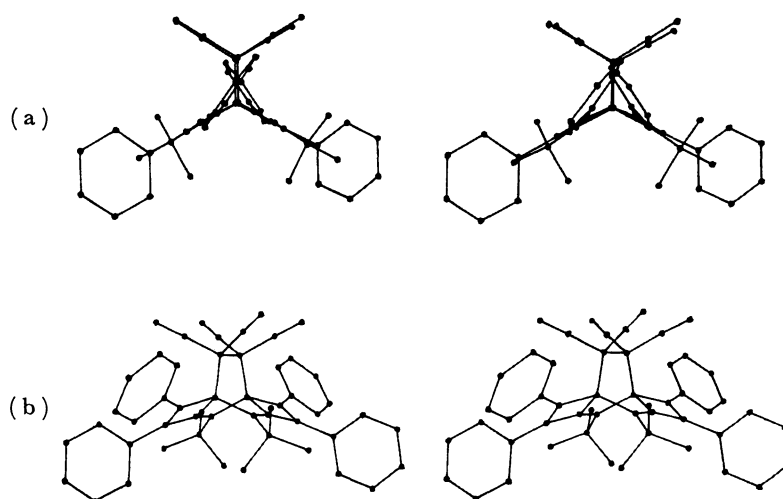Fig. 2. Crystal structure viewed along the c axis.

Fig. 3.   Stereoscopic views.   (a) viewed along the C(1)–C(6) direction.
(b) viewed along the midpoints of C(1)–C(2) and C(6)–C(7).

TABLE 3.   DEVIATIONS ($l/\text{Å}$) OF THE ATOMS FROM THE
LEAST-SQUARES PLANES AND THE DIHEDRAL
ANGLES ($\phi/°$) BETWEEN THEM

(Asterisks indicate the atoms defining the best plane.)

| Plane I | | Plane II | | Plane III | |
|---|---|---|---|---|---|
| C(1)* | −0.002 | C(1)* | 0.002 | C(1)* | −0.005 |
| C(2)* | 0.005 | C(8)* | −0.005 | C(11)* | 0.009 |
| C(3)* | −0.005 | C(7)* | 0.004 | C(12)* | −0.009 |
| C(6)* | 0.003 | C(6)* | −0.002 | C(6)* | 0.005 |
| C(13) | −0.134 | C(17) | −0.130 | | |
| C(4) | 0.014 | C(9) | 0.001 | | |

| Plane IV | | Plane V | |
|---|---|---|---|
| C(3)* | −0.012 | C(1)* | 0.014 |
| C(4)* | 0.014 | C(8)* | −0.014 |
| C(5)* | −0.013 | C(9)* | 0.016 |
| C(6)* | 0.012 | C(10)* | −0.015 |
| C(2) | −0.070 | C(7) | −0.065 |
| C(21) | −0.023 | C(33) | 0.041 |
| C(27) | −0.209 | C(39) | −0.155 |

| | II | III | IV | V |
|---|---|---|---|---|
| I | 125.0 | 117.2 | 2.1 | 124.6 |
| II | | 117.9 | 124.7 | 1.9 |
| III | | | 117.4 | 118.4 |
| IV | | | | 124.1 |

TABLE 4. BOND LENGTH ($l/\text{Å}$)

| | | | | | |
|---|---|---|---|---|---|
| C(1) | −C(2) | 1.547( 4) | C(17) | −C(20) | 1.504( 8) |
| C(1) | −C(8) | 1.535( 4) | C(21) | −C(22) | 1.388( 4) |
| C(1) | −C(10) | 1.546( 4) | C(21) | −C(26) | 1.378( 5) |
| C(1) | −C(11) | 1.590( 4) | C(22) | −C(23) | 1.393( 5) |
| C(2) | −C(3) | 1.344( 4) | C(23) | −C(24) | 1.368( 6) |
| C(2) | −C(13) | 1.523( 4) | C(24) | −C(25) | 1.380( 7) |
| C(3) | −C(4) | 1.469( 4) | C(25) | −C(26) | 1.391( 6) |
| C(3) | −C(6) | 1.539( 4) | C(27) | −C(28) | 1.394( 4) |
| C(4) | −C(5) | 1.361( 4) | C(27) | −C(32) | 1.401( 5) |
| C(4) | −C(21) | 1.483( 4) | C(28) | −C(29) | 1.383( 5) |
| C(5) | −C(6) | 1.551( 4) | C(29) | −C(30) | 1.387( 5) |
| C(5) | −C(27) | 1.461( 4) | C(30) | −C(31) | 1.378( 5) |
| C(6) | −C(7) | 1.540( 4) | C(31) | −C(32) | 1.390( 5) |
| C(6) | −C(12) | 1.584( 4) | C(33) | −C(34) | 1.388( 7) |
| C(7) | −C(8) | 1.342( 4) | C(33) | −C(38) | 1.381( 7) |
| C(7) | −C(17) | 1.526( 5) | C(34) | −C(35) | 1.402( 9) |
| C(8) | −C(9) | 1.477( 4) | C(35) | −C(36) | 1.351(11) |
| C(9) | −C(10) | 1.362( 4) | C(36) | −C(37) | 1.372(12) |
| C(9) | −C(33) | 1.479( 5) | C(37) | −C(38) | 1.396(10) |
| C(10) | −C(39) | 1.460( 4) | C(39) | −C(40) | 1.402( 4) |
| C(11) | −C(12) | 1.625( 4) | C(39) | −C(44) | 1.392( 4) |
| C(11) | −C(45) | 1.471( 4) | C(40) | −C(41) | 1.389( 5) |
| C(11) | −C(46) | 1.476( 4) | C(41) | −C(42) | 1.381( 5) |
| C(12) | −C(47) | 1.477( 4) | C(42) | −C(43) | 1.382( 5) |
| C(12) | −C(48) | 1.473( 5) | C(43) | −C(44) | 1.391( 5) |
| C(13) | −C(14) | 1.525( 5) | C(45) | −N(1) | 1.140( 4) |
| C(13) | −C(15) | 1.541( 5) | C(46) | −N(2) | 1.140( 5) |
| C(13) | −C(16) | 1.519( 5) | C(47) | −N(3) | 1.134( 5) |
| C(17) | −C(18) | 1.549( 7) | C(48) | −N(4) | 1.137( 6) |
| C(17) | −C(19) | 1.488(10) | | | |

Standard deviations are given in parentheses.

and C(4)=C(5), are, though normal, somewhat different from each other. The atomic chain of C(2)=C(3)–C(4)=C(5) lies nearly on a plane and has almost the same bond lengths as those of *trans*-butadiene.[11] The two single bonds connecting the phenyl and the four-membered rings have significantly different lengths. This may be related to the dihedral angle between the four-membered and phenyl rings; one dihedral angle is 86.4°, and the other, 25.6°. The shorter single bond, C(5)–C(27), is accompanied by the smaller dihedral angle, indicating a conjugation effect between the* $\pi$ electron systems of the skeleton and the phenyl ring.

As for the other single bonds, it should be mentioned that they are stretched to some extent. In particular,

C(11)–C(12) is 1.625 Å, about 0.09 Å longer than the normal $C_{sp^3}$–$C_{sp^3}$ bond length.[12] These elongations may be partly the result of the electron-withdrawing effect of the cyano group; at the same time, the nearly eclipse conformation around this bond, the average torsion angle being 2.1°, may greatly affect the bond length. This is also the case with the compound 2 previously reported,[7] the corresponding values being 1.612 Å and 5.8° respectively.

### Discussion

The theoretical approaches are quite difficult for the various chemical reactions of complicated organic molecules. We have treated interactions between the reacting molecules by dividing them into two parts: the electronic interaction between the active sites of both the pertinent molecules, and the non-bonded steric effect of the bulky substituents.

Table 5. Bond angles $(\phi/°)$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(2) | -C(1) | -C(8) | 109.5( 2) | C(2) | -C(13) | -C(14) | 112.6( 3) |
| C(2) | -C(1) | -C(10) | 126.9( 2) | C(2) | -C(13) | -C(15) | 108.0( 3) |
| C(2) | -C(1) | -C(11) | 107.8( 2) | C(2) | -C(13) | -C(16) | 110.4( 3) |
| C(8) | -C(1) | -C(10) | 84.6( 2) | C(14) | -C(13) | -C(15) | 108.9( 3) |
| C(8) | -C(1) | -C(11) | 106.2( 2) | C(14) | -C(13) | -C(16) | 108.0( 3) |
| C(10) | -C(1) | -C(11) | 117.0( 2) | C(15) | -C(13) | -C(16) | 108.9( 3) |
| C(1) | -C(2) | -C(3) | 106.2( 2) | C(7) | -C(17) | -C(18) | 107.6( 4) |
| C(1) | -C(2) | -C(13) | 125.0( 2) | C(7) | -C(17) | -C(19) | 110.9( 5) |
| C(3) | -C(2) | -C(13) | 128.4( 2) | C(7) | -C(17) | -C(20) | 113.0( 4) |
| C(2) | -C(3) | -C(4) | 151.2( 3) | C(18) | -C(17) | -C(19) | 108.5( 5) |
| C(2) | -C(3) | -C(6) | 119.7( 2) | C(18) | -C(17) | -C(20) | 105.8( 4) |
| C(4) | -C(3) | -C(6) | 89.1( 2) | C(19) | -C(17) | -C(20) | 110.7( 5) |
| C(3) | -C(4) | -C(5) | 94.0( 2) | C(4) | -C(21) | -C(22) | 119.9( 3) |
| C(3) | -C(4) | -C(21) | 133.8( 2) | C(4) | -C(21) | -C(26) | 120.0( 3) |
| C(5) | -C(4) | -C(21) | 132.1( 3) | C(22) | -C(21) | -C(26) | 120.1( 3) |
| C(4) | -C(5) | -C(6) | 92.7( 2) | C(21) | -C(22) | -C(23) | 119.8( 3) |
| C(4) | -C(5) | -C(27) | 131.6( 3) | C(22) | -C(23) | -C(24) | 119.7( 4) |
| C(6) | -C(5) | -C(27) | 135.1( 2) | C(23) | -C(24) | -C(25) | 120.9( 4) |
| C(3) | -C(6) | -C(5) | 84.2( 2) | C(24) | -C(25) | -C(26) | 119.6( 4) |
| C(3) | -C(6) | -C(7) | 109.6( 2) | C(21) | -C(26) | -C(25) | 119.9( 4) |
| C(3) | -C(6) | -C(12) | 105.9( 2) | C(5) | -C(27) | -C(28) | 120.5( 3) |
| C(5) | -C(6) | -C(7) | 127.2( 2) | C(5) | -C(27) | -C(32) | 121.4( 3) |
| C(5) | -C(6) | -C(12) | 116.3( 2) | C(28) | -C(27) | -C(32) | 117.9( 3) |
| C(7) | -C(6) | -C(12) | 108.5( 2) | C(27) | -C(28) | -C(29) | 121.3( 3) |
| C(6) | -C(7) | -C(8) | 106.1( 2) | C(28) | -C(29) | -C(30) | 120.3( 3) |
| C(6) | -C(7) | -C(17) | 125.1( 3) | C(29) | -C(30) | -C(31) | 119.1( 3) |
| C(8) | -C(7) | -C(17) | 128.4( 3) | C(30) | -C(31) | -C(32) | 121.0( 3) |
| C(1) | -C(8) | -C(7) | 120.0( 3) | C(27) | -C(32) | -C(31) | 120.3( 3) |
| C(1) | -C(8) | -C(9) | 88.8( 2) | C(9) | -C(33) | -C(34) | 119.9( 4) |
| C(7) | -C(8) | -C(9) | 151.2( 3) | C(9) | -C(33) | -C(38) | 120.2( 4) |
| C(8) | -C(9) | -C(10) | 93.8( 2) | C(34) | -C(33) | -C(38) | 119.9( 4) |
| C(8) | -C(9) | -C(33) | 134.6( 3) | C(33) | -C(34) | -C(35) | 119.2( 5) |
| C(10) | -C(9) | -C(33) | 131.6( 3) | C(34) | -C(35) | -C(36) | 120.4( 7) |
| C(1) | -C(10) | -C(9) | 92.7( 2) | C(35) | -C(36) | -C(37) | 120.9( 8) |
| C(1) | -C(10) | -C(39) | 134.8( 2) | C(36) | -C(37) | -C(38) | 119.7( 7) |
| C(9) | -C(10) | -C(39) | 132.3( 3) | C(33) | -C(38) | -C(37) | 119.8( 5) |
| C(1) | -C(11) | -C(12) | 106.8( 2) | C(10) | -C(39) | -C(40) | 120.1( 3) |
| C(1) | -C(11) | -C(45) | 112.4( 2) | C(10) | -C(39) | -C(44) | 122.1( 3) |
| C(1) | -C(11) | -C(46) | 108.8( 2) | C(40) | -C(39) | -C(44) | 117.7( 3) |
| C(12) | -C(11) | -C(45) | 109.8( 2) | C(39) | -C(40) | -C(41) | 120.9( 3) |
| C(12) | -C(11) | -C(46) | 111.4( 2) | C(40) | -C(41) | -C(42) | 120.4( 3) |
| C(45) | -C(11) | -C(46) | 107.8( 2) | C(41) | -C(42) | -C(43) | 119.7( 3) |
| C(6) | -C(12) | -C(11) | 106.8( 2) | C(42) | -C(43) | -C(44) | 119.9( 3) |
| C(6) | -C(12) | -C(47) | 109.1( 2) | C(39) | -C(44) | -C(43) | 121.4( 3) |
| C(6) | -C(12) | -C(48) | 112.9( 2) | C(11) | -C(45) | -N(1) | 178.9( 3) |
| C(11) | -C(12) | -C(47) | 110.9( 2) | C(11) | -C(46) | -N(2) | 179.0( 4) |
| C(11) | -C(12) | -C(48) | 110.1( 2) | C(12) | -C(47) | -N(3) | 176.9( 4) |
| C(47) | -C(12) | -C(48) | 107.1( 3) | C(12) | -C(48) | -N(4) | 178.9( 4) |

Standard deviations are given in parentheses.

*Electronic Interaction in the Intermediate State.*
Benzodicyclobutene is a molecule with a conjugate planar skeleton. Therefore, the electronic interaction between this molecule, R, and a dienophile, S, can be calculated by using the equation presented by Fueno;[13]

$$\Delta E = 2(\sum_{i}^{occ}\sum_{j}^{un}-\sum_{i}^{un}\sum_{j}^{occ})(a_{ir}b_{js}\gamma_{rs}+a_{it}b_{ju}\gamma_{tu})^2/(E_i-E_j),$$

where $E_i$ and $E_j$ indicate the energy levels of the two molecules, where $a_{ir}$ and $b_{js}$ are the coefficients of the MO's and where $\gamma$ is the resonance integral between the overlapping atoms. All these values were obtained by CNDO/2 calculation.[14] The distance between the two molecules is assumed to be 3.4 Å. The calculated energy corresponds to the stabilization of the intermediate state of the reacting molecules. The results are summarized in Table 6.

The sites of the molecule, R, (1,6), (3,4), and (4,5),

Table 6. Electronic interaction energy (eV)

| Site of R | Ethylene | TCNE |
|---|---|---|
| (1, 3) | −0.101 | −0.106 |
| (1, 6) | −0.144 | −0.143 |
| (1, 7) | −0.097 | −0.099 |
| (1, 8) | −0.035 | −0.044 |
| (2, 7) | −0.123 | −0.121 |
| (4, 5) | −0.003 | −0.016 |
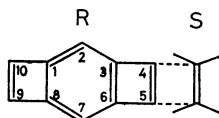
indicate the "cross," "angular," and "linear" positions respectively. The stabilization is greatest in the cross addition. Although the electron-withdrawing effect of the cyano groups lowered the energy of the linear addition mode, it is less preferable than the cross addition mode. The result is not, however, consistent with the reactivity of the molecule 1 or the substituted R, with TCNE, since the main product is the linear adduct. Therefore, it is necessary to take account of the non-bonded interaction between the bulky substituents.

*Non-bonded Interaction Energy.* In the previous paper, we calculated the non-bonded interaction energy between the molecule 1 and the approaching TCNE. It was found that the energy is at its minimum when they have a slight torsion angle along the axis of the approaching direction and that the torsion angle is in qualitative agreement with that of the cyclobutane ring of 2. Therefore, this kind of calculation, which has been used mainly for conformational or packing analysis, can be applied to the intermolecular interaction between the approaching reactants. In the present study, we shall extend this method to the discussion of what approaching mode is most to be preferred.

The potential function:

$$V(r) = Ae^{-Br}/r^D - C/r^6$$

and the parameters used were taken from Giglio.[3] Two parameters were used for the orientation of the approaching molecules, the distance, $d$, between the molecular planes, and the relative rotational angle, $\theta$. (Fig. 4) The former was varied from 4.0 Å to 3.0 Å
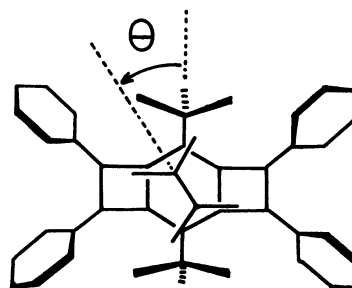


Fig. 4. Relative orientation $\theta$ in the cross approaching mode.

with 0.1 Å steps, and the latter, from 0° to 180° with 10° steps. In the two-dimensional energy map of $d$ and $\theta$ (Fig. 5), there are three potential grooves along the former. The relative rotational angles for these approaches are 0°, 50°, and 130° (or −50°). The first one implies the addition of TCNE to the C(2)–C(7) of the molecule 1, while the latter two will give the "cross" adduct. Since the two-dimensional energy map is inconvenient for a detailed comparison of the three approaching modes in the calculation or between the "linear" and "cross" addition, the cross section at the distance of 3.4 Å is shown in Fig. 6. The distance of 3.4 Å is chosen because it is the so-called van der Waals contact at which the $\pi$ electron system of two molecules may, to some extent, interact with each other. Although the conformations of the substituents were varied in
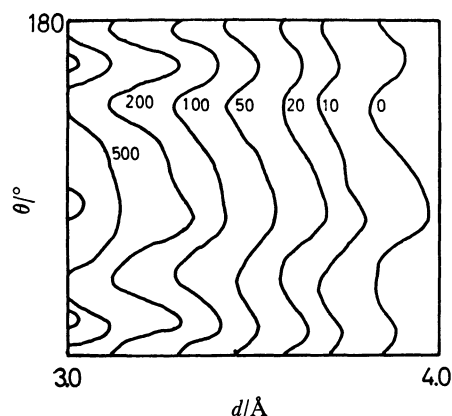
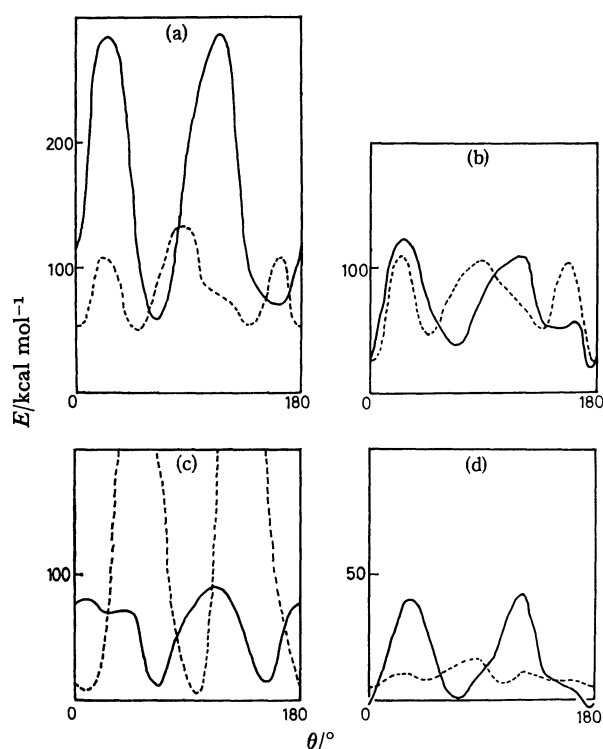Fig. 5. Two-dimensional map of the non-bonded interaction energy (kcal mol⁻¹).



Fig. 7. Conformation model of the $t$-butyl groups.



Fig. 6. Variations of the non-bonded interaction energy with the relative orientation $\theta$ at a constant distance (3.4 Å). (a) Dihedral angle of the phenyl ring from the four-membered ring being 60°, and (b) 50°. (c) The conformation of the $t$-butyl groups being fixed like Fig. 7. (d) All the substituents bent down 10° opposite to the approaching TCNE.

the subsequent calculation, the approaching direction was restricted as in Fig. 4 so as to reduce the number of total parameters. In all the energy maps hereafter, the value of the linear addition will be shown by a solid curve, and that of the cross addition, by a dashed curve.

In the conformer **a**, four phenyl groups are rotated by 60° from the four-membered ring in a propeller-like manner, and the $t$-butyl groups are fixed as in the figure. The conformer **b** has a relatively smaller rotational angle of the phenyl groups (50°), so as to make it possible to estimate the variation in the total
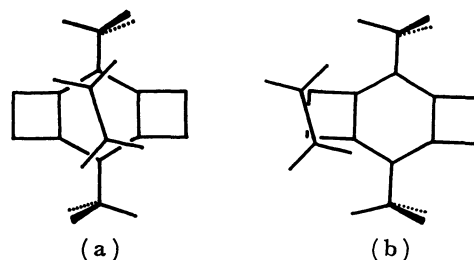
energy with respect to the conformational change. The conformations of the $t$-butyl groups were varied for the same purpose; their conformations were assumed to be as in Fig. 7(a) and Fig. 7(b) in the linear and cross approaching modes respectively.

In the case of the 60° rotation of the phenyl groups (Fig. 6(a)), the potential groove of the cross approach is somewhat lower than that of the linear approach. Moreover, the width of the groove is narrower in the latter. Both these trends suggest that the cross addition is preferable. However, once the conformation of the terminal phenyl groups is varied in the calculation, the energy change in the linear addition is serious (Fig. 6(b)). This is attributable to the decrease in the repulsive contacts of TCNE with ortho hydrogen atoms of the phenyl groups. On the contrary, the energy of the cross approaching mode is not lowered so much as that of the linear one. In this energy map, the solid curve around 0° (or 180°) is lower by 30 kcal mol⁻¹† than the dashed curve around 60°. The former corresponds to the linear approach, and the latter, to the cross approach.

The results of the calculation in which the $t$-butyl groups are so arranged as to have the smallest repulsive contacts with the approaching TCNE indicate a more characteristic feature (Fig. 6 (c)). The minimum energy is greatly lowered in both of the approaching modes. The shape of the groove of the cross approach is, however, very narrow, whereas the shape of the solid curve shows no such drastic change. Although the difference between the minimum energies of the two modes is very small, the high energy potential barrier in the dashed curve prevents TCNE from approaching and so producing the cross adduct.

This discussion is based on the assumption that the substituent atoms directly attached to the skeleton of the molecule **1** are exactly on this plane. In order to check the effect of breaking this assumption, another calculation was carried out for the mode in which all the bonds connecting the substituents with the skeletal plane are bent by 10° from the plane toward the opposite side of the approaching TCNE. The results are shown in Fig. 6(d). The energy curves for both the cross and the linear addition are greatly lowered compared to those in Fig. 6(b), and the minimum around 0°(180°) suggests the linear addition; there is no substantial change as far as the preference of the reaction modes is concerned.

The results of calculation may be summarized as

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† 1 kcal mol⁻¹=4.184 kJ mol⁻¹.

follows:

(1) The calculation of the stabilization energy of the reaction intermediates indicates that the skeletal molecule, without bulky substituents, would produce the "cross" adduct rather than the "linear" one. However, this is not the case in the observed reaction.

(2) Taking the non-bonded interaction energy into account, we can see that the linear approaching mode is preferable in terms of both the minimum value and the shape of the potential groove.

(3) The preference of the linear addition is, however, dependent on the conformation of the substituents of the molecule 1. This is consistent with the fact that the cross adduct is obtained as a by-product.

Since any estimate of the relative weights of the electronic and steric energies must be quite ambiguous at present, it cannot be concluded which type of addition reaction will really take place. However, the qualitative agreement between our calculation and the observation indicates that the contribution of the non-bonded interaction energy should be included in any theoretical approaches to the chemical reaction.

Studies of related compounds are now in progress.

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