[x,y,z]–C(40)[$1+x, y, z$]: 3·146 Å and N(25)-[x,y,z]–C(40)[$1-x, 1-y, \bar{z}$]: 3·498 Å.

The atomic numbering, bond distances and angles are given in Fig. 1, torsion angles in Table 3. Fig. 2 is a stereoview of the molecule and Fig. 3 shows the molecular packing.

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A Stable Benzocyclobutene: 1,4-Di(*tert*-butyl)-2,3-diphenyl-5,6-bis(1-phenyl-2,2-dicyanovinyl)benzocyclobutene–Acetone

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Abstract. $C_{48}H_{38}N_4.C_3H_6O$, monoclinic, $P2_1/c$, $a = 12{\cdot}772$ (2), $b = 15{\cdot}970$ (3), $c = 22{\cdot}230$ (3) Å, $\beta = 109{\cdot}35$ (1)°, D_m (flotation) = 1·14, $D_x = 1{\cdot}13$ g cm^{-3}, $Z = 4$. The structure of the title compound has been determined by X-ray diffraction. Although the structure of the skeletal eight-membered ring is in qualitative agreement with that deduced by MO calculations, it is highly strained by the bulky substituents.

Introduction. Deep-red crystals were recrystallized from acetone solution. Weissenberg photographs showed the systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, indicating the space group $P2_1/c$. Intensities and accurate cell dimensions were measured on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The intensities were corrected for Lorentz and polarization effects. Of the 5947 independent reflections ($2\theta \leq 45°$), 2516 had intensities greater than $3\sigma(I)$. The structure was solved by the direct method (Karle & Karle, 1966).

The atomic parameters were refined by the least-squares method using a 9 × 9 block-diagonal matrix. During the isotropic refinement, thermal parameters of the acetone molecule became about three times as large as those of the other atoms. This could be attributed to the disorder and/or the low occupancy of acetone in the crystal. Therefore its parameters were fixed and the occupancy factor was assumed to be $\frac{2}{3}$. Although most of the H atoms were found by the difference synthesis, their positional parameters were fixed at values calculated geometrically. Their isotropic temperature factors were also fixed at 5 Å^2. At the final stage of the refinement, anisotropic temperature factors were introduced for non-hydrogen atoms, except for those of acetone.

The weighting scheme was $w = 1/(\sigma + a|F_o|^2)$, where σ was from counting statistics and $a = 9 \times 10^{-6}$. The final R was 0·19 for all reflexions, and 0·10 for the non-zero reflexions.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final positional parameters and the bond lengths of the non-hydrogen atoms, with the crystallographic numbering system, are listed in Tables 1 and 2 respectively.*

Discussion. The present compound is the final product of the reaction of a substituted benzodicyclobutene (I) with tetracyanoethylene (TCNE) (Toda & Dan, 1976). At first a 1:1 adduct (II) is produced; this adduct is easily isomerized into the title compound (III) by heating.† Compounds with a benzocyclobutene skeleton are very unstable. The title compound may be the first derivative to be isolated in a stable form. The

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* Lists of structure factors, anisotropic thermal parameters, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32721 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† On the basis of the resemblance to the reaction which had previously been reported by Huth, Straub & Müller (1973), Toda & Dan presumed that (III) would have the *anti* conformation with respect to the cyanovinyl groups and that (II) was its *syn* isomer.

Table 1. *Final positional parameters* ($\times 10^4$)

Standard deviations are given in parentheses.

	x	*y*	*z*
C(1)	3907 (6)	2560 (5)	831 (3)
C(2)	4946 (6)	2259 (5)	923 (3)
C(3)	5469 (5)	1923 (4)	1554 (3)
C(4)	4912 (6)	1855 (5)	2013 (3)
C(5)	3802 (6)	2193 (5)	1893 (3)
C(6)	3367 (6)	2515 (5)	1293 (3)
C(7)	2341 (6)	2943 (5)	808 (3)
C(8)	2871 (5)	3006 (5)	376 (3)
C(9)	5467 (6)	2298 (5)	380 (4)
C(10)	4554 (8)	2078 (8)	−251 (4)
C(11)	5914 (10)	3178 (8)	350 (6)
C(12)	6390 (8)	1673 (8)	434 (4)
C(13)	3149 (6)	2276 (6)	2360 (3)
C(14)	3682 (7)	2009 (9)	3052 (4)
C(15)	2059 (8)	1800 (8)	2104 (5)
C(16)	2883 (8)	3211 (7)	2387 (5)
C(17)	6651 (6)	1688 (5)	1777 (3)
C(18)	6947 (7)	854 (6)	1838 (4)
C(19)	6134 (8)	211 (6)	1562 (5)
C(20)	8042 (9)	513 (6)	2170 (5)
C(21)	7476 (6)	2371 (5)	1969 (3)
C(22)	7139 (7)	3163 (6)	2075 (4)
C(23)	7892 (9)	3829 (6)	2256 (5)
C(24)	8976 (9)	3710 (7)	2307 (5)
C(25)	9312 (8)	2944 (8)	2173 (6)
C(26)	8609 (8)	2260 (7)	2007 (5)
C(27)	5489 (6)	1387 (4)	2600 (3)
C(28)	5083 (9)	626 (6)	2680 (4)
C(29)	4162 (10)	247 (6)	2202 (5)
C(30)	5460 (10)	128 (7)	3273 (6)
C(31)	6446 (7)	1778 (5)	3101 (3)
C(32)	6418 (8)	2622 (5)	3229 (4)
C(33)	7309 (10)	2992 (6)	3700 (4)
C(34)	8208 (10)	2519 (9)	4018 (5)
C(35)	8275 (8)	1683 (8)	3891 (5)
C(36)	7382 (7)	1287 (7)	3443 (4)
C(37)	1237 (6)	3251 (6)	775 (4)
C(38)	1052 (9)	4098 (6)	791 (6)
C(39)	−17 (9)	4386 (7)	719 (7)
C(40)	−870 (8)	3852 (8)	626 (6)
C(41)	−698 (7)	3004 (7)	604 (5)
C(42)	340 (7)	2692 (6)	660 (4)
C(43)	2494 (7)	3406 (5)	−250 (4)
C(44)	1527 (7)	3121 (7)	−715 (4)
C(45)	1120 (7)	3537 (8)	−1297 (4)
C(46)	1668 (9)	4219 (7)	−1414 (5)
C(47)	2613 (9)	4505 (7)	−975 (4)
C(48)	3012 (8)	4101 (6)	−400 (4)
N(1)	5528 (11)	−304 (6)	1337 (6)
N(2)	8855 (10)	192 (7)	2422 (6)
N(3)	3414 (11)	−53 (7)	1838 (6)
N(4)	5720 (12)	−266 (8)	3718 (6)

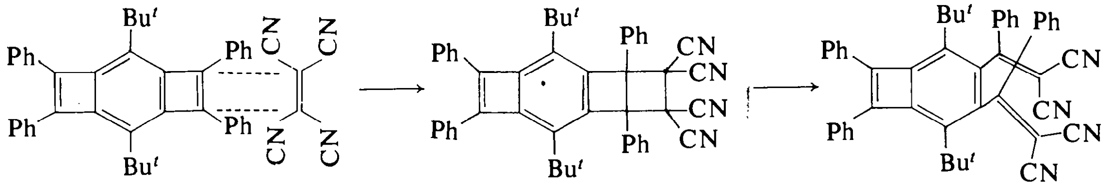
Table 2. *Bond lengths* (Å) *with their e.s.d.'s in parentheses*

C(1)–C(2)	1·36 (1)	C(17)–C(21)	1·48 (1)
C(2)–C(3)	1·44 (1)	C(21)–C(22)	1·38 (1)
C(3)–C(4)	1·43 (1)	C(22)–C(23)	1·40 (1)
C(4)–C(5)	1·46 (1)	C(23)–C(24)	1·37 (2)
C(5)–C(6)	1·36 (1)	C(24)–C(25)	1·36 (2)
C(6)–C(7)	1·55 (1)	C(25)–C(26)	1·39 (2)
C(7)–C(8)	1·35 (1)	C(26)–C(21)	1·43 (1)
C(8)–C(1)	1·55 (1)	C(27)–C(31)	1·49 (1)
C(1)–C(6)	1·42 (1)	C(31)–C(32)	1·38 (1)
C(2)–C(9)	1·56 (1)	C(32)–C(33)	1·40 (1)
C(9)–C(10)	1·54 (1)	C(33)–C(34)	1·36 (2)
C(9)–C(11)	1·53 (2)	C(34)–C(35)	1·37 (2)
C(9)–C(12)	1·52 (1)	C(35)–C(36)	1·39 (2)
C(5)–C(13)	1·54 (1)	C(36)–C(31)	1·42 (1)
C(13)–C(14)	1·52 (1)	C(7)–C(37)	1·47 (1)
C(13)–C(15)	1·52 (1)	C(37)–C(38)	1·38 (1)
C(13)–C(16)	1·54 (1)	C(38)–C(39)	1·40 (2)
C(3)–C(17)	1·47 (1)	C(39)–C(40)	1·35 (2)
C(17)–C(18)	1·38 (1)	C(40)–C(41)	1·38 (2)
C(18)–C(19)	1·44 (1)	C(41)–C(42)	1·38 (1)
C(18)–C(20)	1·45 (1)	C(42)–C(37)	1·41 (1)
C(19)–N(1)	1·13 (2)	C(8)–C(43)	1·46 (1)
C(20)–N(2)	1·13 (2)	C(43)–C(44)	1·40 (1)
C(4)–C(27)	1·47 (1)	C(44)–C(45)	1·39 (1)
C(27)–C(28)	1·36 (1)	C(45)–C(46)	1·37 (2)
C(28)–C(29)	1·43 (2)	C(46)–C(47)	1·36 (2)
C(28)–C(30)	1·48 (2)	C(47)–C(48)	1·37 (1)
C(29)–N(3)	1·13 (2)	C(48)–C(43)	1·39 (1)
C(30)–N(4)	1·13 (2)		

structural analysis has been undertaken as part of a study of the π-electron character of this ring system and the steric effects of the bulky substituents. The reaction route, which was ambiguous from the results of chemical and spectral work, has been established by the present analysis.

Two perspective views are shown in Fig. 1. The eight-membered ring is almost planar, but all the phenyl and cyanovinyl groups are rotated at least 61° around the connecting bonds. Therefore the conjugation effect between the skeleton and the substituents may be negligible.

A comparison was made between the observed structure and that calculated by the CNDO/2 method, as shown in Fig. 2. The calculation indicates the π-electron localization in the six-membered ring which is due to the annelation of the four-membered ring.



(I) (II) (III)

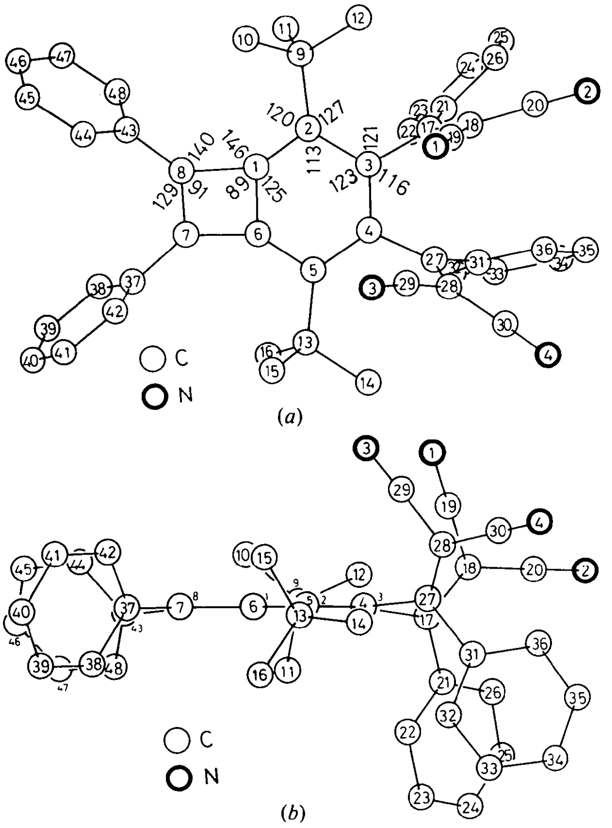


Fig. 1. (a) Projection on the plane of the eight-membered ring with some average bond angles. (b) Projection along C(1)—C(6). Small numbers indicate the rear atoms.

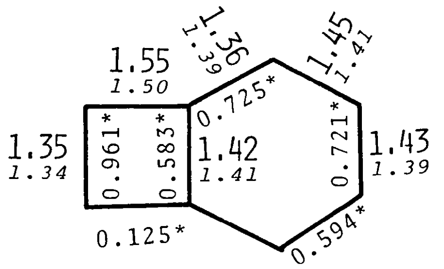


Fig. 2. Observed and calculated (*italic*) bond lengths (Å) and π-bond orders (*). Observed bond lengths are averaged for the chemically equivalent bonds.

Table 3. *Deviations* (Å) *from the least-squares plane through the eight atoms of the skeleton*

An asterisk indicates an atom used to define the plane.

C(1)*	0·00	C(8)*	0·02
C(2)*	−0·02	C(9)	−0·08
C(3)*	0·02	C(13)	0·16
C(4)*	−0·02	C(17)	0·22
C(5)*	0·02	C(27)	−0·16
C(6)*	0·00	C(37)	0·02
C(7)*	−0·02	C(43)	0·12

Observed bond lengths are in qualitative agreement with those predicted from the bond order–bond length correlation (l = 1·520 − 0·186p). However, some bonds were stretched by the repulsion between the bulky substituents. For example, C(2)—C(3) (1·44 Å) is about 0·03 Å longer than the calculated value, and may be the longest in the benzenoid compound. This elongation effect is almost the same as that for 1,2,4,5-tetra(*tert*-butyl)benzene (Stam, 1972). The bond between the *tert*-butyl group and the skeleton is also elongated. The average value (1·55 Å) is closer to a C(sp^3)—C(sp^3) rather than a C(sp^2)—C(sp^3) length. Such a repulsion also greatly distorts the bond angles. *tert*-Butyl groups are bent towards the four-membered ring. The difference between the angles C(3)—C(2)—C(9) and C(1)—C(2)—C(9) is 7° (Fig. 1). The contraction of the angle C(1)—C(2)—C(3) from the sp^2 angle may also reduce this repulsion.

The cyanovinyl groups are rotated so as to minimize repulsions with each other and with the *tert*-butyl groups. Since the angle C(4)—C(3)—C(17) is smaller than C(2)—C(3)—C(17), it can be seen that the *tert*-butyl groups are more bulky than the planar cyanovinyl groups.

The side view of this molecule shows some characteristic features. Most of the atoms directly attached to the eight-membered ring deviate from the plane. All the *tert*-butyl and cyanovinyl groups, which are neighbours to each other, are 'up' and 'down' alternately from the plane (Table 3). Such a trend is also observed in the six-membered ring of the skeleton. This suggests that the planarity of the conjugated system is slightly affected by the repulsive force of the bulky substituents.

The cyanovinyl groups have the *syn* conformation with respect to each other. Both *tert*-butyl groups are so oriented that one of the methyl groups is jammed by the phenyl and cyano groups onto the skeletal plane, whereas the other two methyl groups stick out on both sides of the plane. These out-of-plane methyl groups may play the role of the most effective protective group in the reaction shown above. The remaining unsaturated cyclobutene ring may be protected from the addition of one or more TCNE molecules by these methyl groups and the phenyl groups attached to the four-membered ring.

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