For $Cu[OC(NH_2)NHNH_2]_2Cl_2$

N(1)–Cl($x-1, y, z$)	3·34 ± 0·02 Å
N(1)–Cl($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	3·36 ± 0·01
N(3)–Cl($\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$)	3·24 ± 0·01

For $Zn[OC(NH_2)NHNH_2]_2Cl_2$

N(1)–Cl($\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$)	3·35 ± 0·02 Å
N(2)–Cl($x, y-1, z$)	3·31 ± 0·01

The other packing contacts shorter than 3·5 Å are:

$Cu[OC(NH_2)NHNH_2]_2Cl_2$

Cl–O	3·43 ± 0·01 Å
Cl–O($\bar{x}, \bar{y}, \bar{z}$)	3·48 ± 0·01
Cl–N(2)($\bar{x}, \bar{y}, 1-z$)	3·18 ± 0·02
Cl–N(3)	3·37 ± 0·01
O–N(1)($x, \frac{1}{2}-y, z-\frac{1}{2}$)	3·14 ± 0·02
O–N(3)($\bar{x}, \bar{y}, \bar{z}$)	2·96 ± 0·02
O–N(3)($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	3·23 ± 0·01
N(1)–N(1)($x, \frac{1}{2}-y, \frac{1}{2}+z$)	3·48 ± 0·03

$Zn[OC(NH_2)NHNH_2]_2Cl_2$

Cl–O	3·38 ± 0·01 Å
Cl–O($\bar{x}, \bar{y}, \bar{z}$)	3·25 ± 0·01
Cl–N(1)($x, 1+y, z$)	3·38 ± 0·02
Cl–N(3)	3·34 ± 0·01
Cl–N(3)($\bar{x}, \bar{y}, \bar{z}$)	3·30 ± 0·01
Cl–N(3)($1-x, \bar{y}, \bar{z}$)	3·34 ± 0·01
O–N(1)($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	2·98 ± 0·02
O–N(3)($\bar{x}, \bar{y}, \bar{z}$)	3·17 ± 0·01

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The Crystal and Molecular Structure of *cis,cis*-1, 2, 3, 4-Tetraphenylbutadiene

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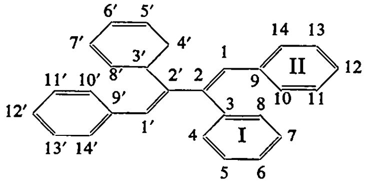
The crystal structure of *cis, cis*-1,2,3,4-tetraphenylbutadiene has been determined by application of the symbolic addition procedure. The space group is $P2_1/c$ with cell dimensions: $a=5{\cdot}87$, $b=21{\cdot}31$, $c=8{\cdot}13$ Å, and $\beta=97°\ 05'$. Since $Z=2$, the asymmetric unit is one-half the molecule. The butadiene chain is planar and the C–C distances show the typical effects of conjugation. One pair of phenyl rings forms an angle of 34° with the plane of the chain and the other pair of phenyl rings make an angle of 75°. The angle between the planes of the phenyl rings is 69°.

Introduction

Phenyl rings substituted on the same or adjacent atoms usually rotate about the connecting bonds so as to maximize the intramolecular distances between them. The present investigation on *cis, cis*-1,2,3,4-tetraphenylbutadiene,



was undertaken to determine the degree of rotation of the phenyl rings from the plane of the butadiene chain, especially the degree of rotation of the two rings at the extremes of the butadiene group where the effects of conjugation may tend to keep the rings coplanar with the chain. Since the diffraction data show that the molecule has a center of symmetry, the atoms have been numbered as shown above.

Experimental

Crystals of tetraphenylbutadiene are white needles elongated parallel to the *a* axis. Intensity data were obtained with copper radiation from multiple film, equi-inclination Weissenberg photographs with the crystal mounted on the *a* axis. All cell dimensions were determined from *hk*0 and *h*0*l* precession photographs. The space group was found to be $P2_1/c$ and the cell parameters are:

$a = 5{\cdot}87 \pm 0{\cdot}02$ Å
$b = 21{\cdot}31 \pm 0{\cdot}02$
$c = 8{\cdot}13 \pm 0{\cdot}02$
$\beta = 97°05' \pm 10'$
$Z = 2$

The calculated density based on these parameters is 1·191 g.cm^{-3}; the measured density was found to be 1·181 g.cm^{-3} by the flotation technique using a silver nitrate solution.

Intensities for the five Weissenberg layers were estimated visually by comparison with a calibrated film strip. These intensities were corrected for spot size, Lorentz and polarization factors and thermal motion, and were adjusted to an absolute scale on the IBM 7030 (STRETCH) computer using a revision of an earlier data reduction program (Norment, 1962). The normalized structure factors $|E_{\mathbf h}|$ were computed in addition to the usual structure factors $|F_{\mathbf h}|$. For the monoclinic space group $P2_1/c$, the $|E_{\mathbf h}|$ are defined by:

$$E_{\mathbf h}^2 = F_{\mathbf h}^2/\varepsilon \sum_{j=1}^{N} f_{j\mathbf h}^2 \tag{1}$$

where $\varepsilon = 2$ when $\mathbf h$ is $h0l$ or $0k0$, $\varepsilon = 1$ otherwise, $f_{j\mathbf h}$ is the atomic scattering factor for the jth atom, and N is the number of atoms in the unit cell.

Non-zero intensity data numbered 1100. The distribution of the total 1400 $|E|$ values is shown in Table 1 where the theoretical values are based on a centrosymmetric crystal with randomly distributed atoms. The averages in Table 2 confirm that the crystal is centrosymmetric.

Table 1. *Distribution of normalized structure factors*

	$\|E\| > 3$	$\|E\| > 2$	$\|E\| > 1$
Theoretical	0·3 %	5·0 %	32·0 %
Experimental	0·4	5·7	27·3

Table 2. *Statistical averages*

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle\|E\|\rangle$	0·783	0·798	0·886
$\langle\|E^2-1\|\rangle$	1·015	0·968	0·736
$\langle\|E\|^2\rangle$	1·041	1·000	1·000

Phase determination

Phases for tetraphenylbutadiene were determined by means of the symbolic addition procedure (Karle & Karle, 1963, 1964; Karle, Britts & Gum, 1964). The origin was specified by assigning positive signs to three structure factors of large magnitude having linearly independent vectors. The Σ_2 relationship

$$sE_{\mathbf h} \sim s\sum_{\mathbf k} E_{\mathbf k} E_{\mathbf{h-k}}, \tag{2}$$

where s means 'sign of', was implemented by use of the assignments specifying the origin and three other structure factors of large magnitude whose signs were specified by the symbols, a, b, and c. This starting set is shown in Table 3. It was chosen on the basis that the vectors had many interactions among themselves in the application of the Σ_2 formula. Approximately ninety phases were determined in terms of the starting signs and letters. Indications that the symbol a should be negative were numerous among the Σ_2 combinations. A moderate number of relationships suggested that $a = -b$ and a few that $c = +$. The relationships occurred when there were many different pairs of contributors to the Σ_2 formula for the determination of a single phase. When a particular relationship among the unknown symbols occurs repeatedly, then it is fairly safe to assume that such a relationship is correct.

The E map shown in Fig. 1, computed with the assignments $a = -$, $b = +$, and $c = +$, revealed the molecular structure. Since the molecule possesses a center of symmetry, only one-half of the molecule is illustrated. The map contains approximately 280 terms, the additional 190 phases having been determined on a computer using the initial 90 phases as a basis for the continued application of Σ_2. The map contains approximately 20 terms per atom and has no extraneous peaks of density greater than one-half that of the 14 carbon atoms.

Table 3. *Starting set for the application of* Σ_2

Phase	h	k	l	$\|E\|$
+	4	2	3	3·505
+	3	1	5	3·183
+	3	12	1	2·774
a	0	18	2	2·335
b	1	4	3	2·676
c	1	5	3	2·610

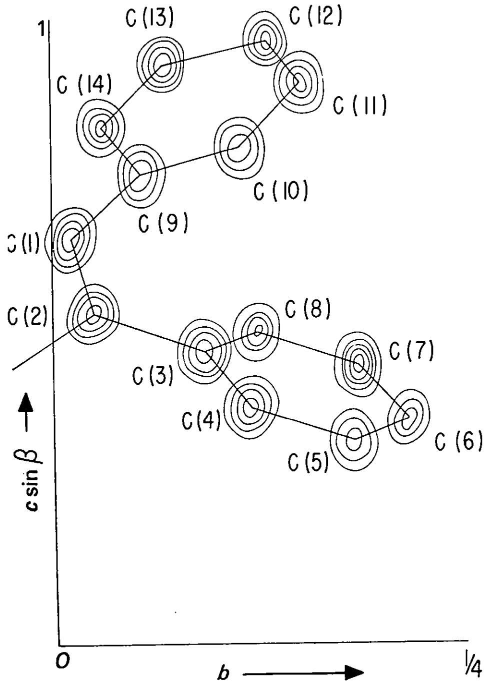


Fig. 1. A three-dimensional E map, where E values rather than F values are used as the Fourier coefficients, computed from 280 terms for which phases had been directly determined by the symbolic addition procedure. The contours are equally spaced on an arbitrary scale. Since the molecule possesses a center of symmetry, only one-half of the molecule is illustrated.

The structure

A least-squares refinement of the coordinates obtained from the initial E map illustrated in Fig. 1 was performed with a modification of the ORFLS program (Busing, Martin & Levy, 1962). Two cycles varying coordinates and scale factors were followed by two cycles in which the isotropic temperature factors also were varied. Finally, two cycles in which anisotropic temperature factors were refined resulted in the coordinates and parameters listed in Table 4. The final R index was 12·1%*. No hydrogen atoms were included in the refinement. The electron density map illustrated in Fig. 2 was computed with phases calculated from the final least-squares coordinates. All of the data were used.

The two phenyl rings are planar. The least-squares equation for ring I, consisting of the six atoms C(3) to C(8), is

$$2{\cdot}457x+6{\cdot}541y+6{\cdot}477z=3{\cdot}786\,, \qquad (3)$$

referred to the monoclinic axes and where the value on the right-hand side of the equation is equal to the origin-to-plane distance in Å (Schomaker, Waser, Marsh & Bergman, 1959). The equation for ring II, composed of C(9) to C(14), is

$$-2{\cdot}879x-7{\cdot}955y+6{\cdot}844z=3{\cdot}740\,. \qquad (4)$$

The butadiene chain and four carbon atoms attached to it also lie in a plane, whose equation is

$$4{\cdot}473x-2{\cdot}695y-5{\cdot}886z=-2{\cdot}943\,. \qquad (5)$$

Deviations of the individual atoms from these planes are shown in Table 5. The dihedral angle between the two phenyl rings is 69°. The angle between ring I and the chain group is 75°; between ring II and the chain, 34°.

Bond distances and angles were computed using the coordinates in Table 4. The results are shown in Fig. 3. Average bond distances of 1·403 and 1·406 Å were found for ring I and ring II, respectively. The mean angle for both rings is 120·0°. Significant intramolecular distances between the phenyl rings are shown in Table 6. The closest intermolecular approach found was 3·31 Å, occurring across a center of symmetry between C(14) and C(14″). All intermolecular distances less than 3·8 Å are listed in Table 7. These shorter distances indicate close packing in the **a** and **c** directions; however, no distances less than 4 Å were found in the **b** direction.

In general, the orientation, packing, and distances are in accord with those found for similar molecules. Phenyl rings substituted on the same or near neighbor atoms usually twist to maximize intramolecular distances, as, for example, in 1,2,3,4-tetraphenylcyclobutane (Dunitz, 1949) and 1,3,5-triphenylbenzene (Farag, 1954). The 75° and 34° inclinations of the phenyl rings to the butadiene chain of the present study are closely analogous to the 92° and 39° inclinations of adjacent phenyl rings to the central ring in the cyclobutane compound. Moreover, the intramolecular distances involving the phenyl rings are comparable in

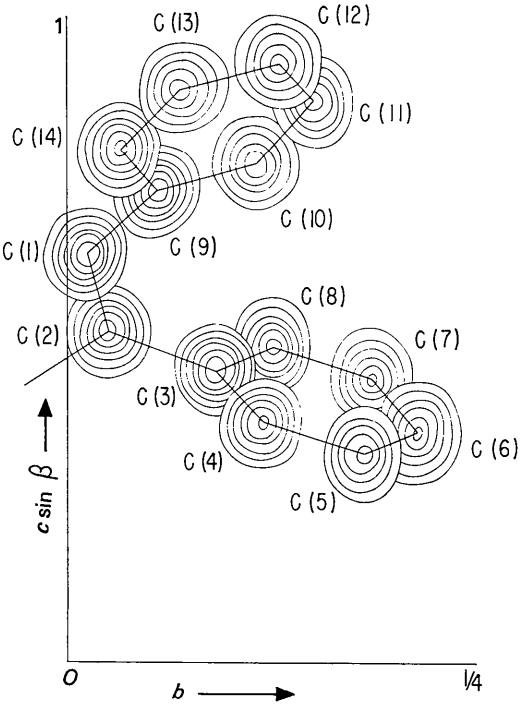


Fig. 2. Sections of the final three-dimensional electron density map projected on the (100) plane. Contours are at intervals of 1 e.Å^{-3}, beginning in the 1 e.Å^{-3} contour.

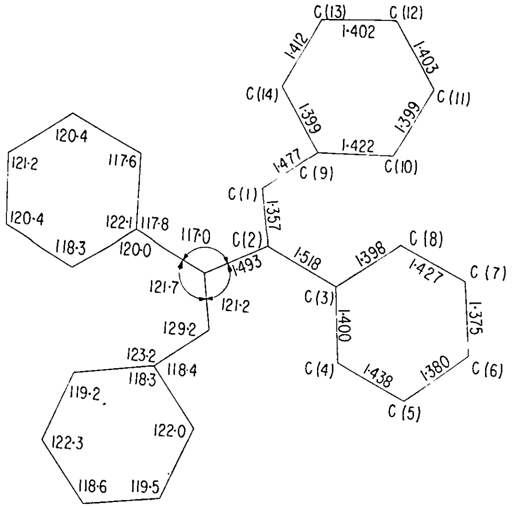


Fig. 3. Bond distances and angles. The standard deviation for the bond lengths ranges between 0·009 and 0·012 Å. The standard error for the angles is approximately 0·5°.

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* A table of observed and calculated structure factors has been submitted with the manuscript and has been deposited as Document number 8207 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting $ 3·75 for photoprints, or $ 1·75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 4. *Fractional coordinates for cis,cis-*1,2,3,4-*tetraphenylbutadiene*

The thermal parameters are of the form $T=\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$. Each thermal parameter is multiplied by 10^4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·2372	0·0117	0·6706	444	12	144	−3	−37	−1
C(2)	0·0725	0·0252	0·5434	432	11	155	−2	−15	−3
C(3)	0·0309	0·0918	0·4804	416	10	126	−3	−5	−2
C(4)	0·1955	0·1188	0·3914	488	16	176	−18	1	−2
C(5)	0·1603	0·1828	0·3379	632	16	202	−31	−12	7
C(6)	−0·0276	0·2160	0·3769	522	15	211	−8	−63	4
C(7)	−0·1864	0·1889	0·4657	568	14	228	13	−56	0
C(8)	−0·1614	0·1251	0·5181	486	14	178	9	−31	0
C(9)	0·3908	0·0547	0·7746	419	14	146	−5	−20	1
C(10)	0·3254	0·1164	0·8168	598	14	185	4	−48	−12
C(11)	0·4766	0·1522	0·9254	574	18	216	−4	−91	−16
C(12)	0·6947	0·1304	0·9906	622	19	211	−33	−43	−1
C(13)	0·7616	0·0701	0·9465	510	24	187	−9	−46	4
C(14)	0·6071	0·0328	0·8416	425	18	175	−1	−27	−1
Standard error	0·0013	0·0003	0·0009	69	1	13	5	15	3

Table 5. *Deviations from least-squares planes*

Ring I		Ring II	
Atom	Δ	Atom	Δ
C(3)	0·0019 Å	C(9)	0·0011 Å
C(4)	0·0067	C(10)	−0·0119
C(5)	−0·0081	C(11)	0·0139
C(6)	0·0007	C(12)	0·0021
C(7)	0·0080	C(13)	−0·0130
C(8)	−0·0092	C(14)	0·0113
r.m.s.	0·0066	r.m.s.	0·0096

Butadiene chain and attached atoms

Atom	Δ
C(1)	0·0251 Å
C(2)	0·0006
C(2′)	−0·0006
C(1′)	−0·0251
C(3′)	−0·0058
C(9′)	0·0155
C(9)	−0·0155
C(3)	0·0055
r.m.s.	0·0151

Table 6. *Closest intramolecular distances between phenyl rings*

Atom	Distance
C(3) · · · C(10)	3·09 Å
C(3) · · · C(9)	3·09
C(8) · · · C(9)	3·47
C(8) · · · C(10)	3·51

Table 7. *Intermolecular distances less than* 3·8 Å

Double-primed atoms are obtained from the original coordinates, x, y, z, by performing the operation $1-x$, $-y$, $2-z$ (reflection through the center at $\frac{1}{2}$, 0, 1) and the triple-primed atoms are obtained by the operation $1+x$, y, z.

Atom	Distance
C(14) · · · C(14″)	3·31 Å
C(13) · · · C(1″)	3·57
C(14) · · · C(9″)	3·63
C(13) · · · C(14″)	3·66
C(13) · · · C(9″)	3·68
C(13) · · · C(8‴)	3·75
C(13) · · · C(10‴)	3·72
C(14 · · · C(8‴)	3·68

both examples. Distances from 2·93 to 3·42 and 3·61 Å were found by Dunitz (1949) and Farag (1954), whereas intramolecular distances of 3·09 to 3·51 Å occurred in this investigation. Intermolecular distances involving centers of symmetry of the same order of magnitude as the present 3·3 Å were found for 1,1,6,6-tetraphenylhexapentaene (Woolfson, 1953). The coplanarity and bond distances in the butadiene chain are typical of conjugated systems (see *e.g.* Robertson & Woodward, 1937). The double bond between C(1) and C(2) changed little from the normal 1·34 Å; however, the single bond distances are appreciably shorter than the usual 1·54 Å.

It is interesting to note that ring II, which is bonded to the end of the butadiene chain, where C(1)–C(9) is 1·48 Å, is not coplanar with the conjugated chain; however, it is rotated only 34° out of the plane as compared with 75° for ring I, which is attached to the chain by C(2)–C(3) whose bond length, 1·52 Å, is nearly a single bond value.

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