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References

- ADAMS, J. M. & RAMDAS, V. (1976). *Acta Cryst.* **B32**, 3224–3227.
 ADAMS, J. M. & RAMDAS, V. (1977). In preparation.
 CALVO, C. (1965). *Canad. J. Chem.* **43**, 1147–1153.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

- GUARINI, G. G. T. & SPINICCI, R. (1972). *J. Therm. Anal.* **4**, 435–450.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 LEUNG, K. Y. & CALVO, C. (1972). *Canad. J. Chem.* **50**, 2519–2526.
 SKLAR, N., SENKO, M. E. & POST, B. (1961). *Acta Cryst.* **14**, 716–720.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972, update of April 1974. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1977). **B33**, 3657–3669

Electron Density Distribution in Cumulenes: An X-ray Study of Tetraphenylbutatriene at 20°C and –160°C

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The structure of tetraphenylbutatriene (TPBT), $C_{28}H_{20}$, was investigated by X-ray ($\lambda = 0.709 \text{ \AA}$) diffraction at 20°C and –160°C. The space group is $P1$ with $Z_0 = 2$ and $a = 10.035 (3)$, $b = 10.458 (4)$, $c = 9.978 (3)$ Å, $\alpha = 105.04 (4)$, $\beta = 105.27 (3)$, $\gamma = 92.17 (3)^\circ$, at –160°C. The molecule is not planar, the rings being twisted by 27.9, 27.4, 41.8, 38.5° out of the butatriene plane. The molecular symmetry approximates to 222. The central =C=C= bond is short (1.260 Å), in contrast to the outer >C=C bonds, of length 1.348 Å. The molecular electron density distribution was determined from the low-temperature data by a least-squares procedure. The observed deformation densities in the butatriene skeleton show that the π lobes in adjacent C=C bonds are mutually perpendicular. The aromatic C=C bond shows π character, whereas the exocyclic C–C bond appears to be purely σ .

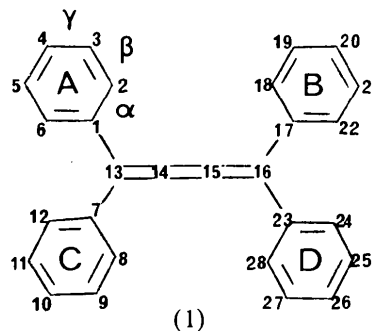
Introduction

The role of the crystal structures of substituted ethylenes in determining the stereochemistry of the cyclobutane photodimers obtained therefrom has been demonstrated (Schmidt, 1971). A separation of $4.0 \pm 0.2 \text{ \AA}$ between potentially reactive C=C double bonds is necessary for photodimerization. It has been observed (Schmidt, 1971; Lahav & Schmidt, 1967; Frank & Paul, 1973) that neighbouring C=C bonds, which fulfil the above requirement, but which are far offset, implying insufficient overlap of their π electrons, do not dimerize. A system which allows systematic analysis of the importance of the alignment of the π electrons is provided by the cumulenes in which the π lobes of adjacent C=C bonds lie in mutually perpendicular planes. This study of TPBT was primarily motivated towards the determination of the electron density distribution in the butatriene system so as to provide information on the orientation of the π lobes of adjacent C=C bonds. Photochemical studies were also undertaken (Berkovitch-Yellin, Lahav & Leiserowitz, 1974)

to correlate the electron density distribution with topochemical behaviour in the cumulenic system.

Experimental

Yellow crystals of TPBT (1) were obtained by evaporation from ethyl acetate. The structure was determined at room temperature and at –160°C. There



is no phase transition in this temperature range. The crystallographic data are given in Table 1. The cell dimensions at both temperatures were derived by a least-squares procedure from high-order reflexions ($\theta > 20^\circ$) measured on a diffractometer with Mo $K\alpha$ radiation.

The intensities were collected on a diffractometer controlled by an IBM 1800 computer. For the measurements at -160°C the crystal was cooled in a stream of cold air (van Bolhuis, 1971). The details of the data

collection and processing are given in Table 2. The intensities were corrected for absorption by the Gaussian quadrature method (Coppens, Leiserowitz & Rabinovich, 1965). The corrections were negligible (Table 2). The standard deviation for each observation was estimated to comprise a 3% error in the intensity in addition to the statistical counting error, *i.e.* $\sigma^2(I - B) = I + B + |0.03(I - B)|^2$. The statistical weight of each reflexion was taken as the sum of the calculated weights $\omega = 1/\sigma^2$, estimated by the formula above, slightly modified to reflect the match between several observations of the same reflexion.

Table 1. *Crystal data*

| | | |
|--|--|------------|
| Formula | $\text{C}_{28}\text{H}_{20}$ | |
| M_r | 356 | |
| m.p. ($^\circ\text{C}$) | 237 | |
| Crystallization | Slow evaporation from ethyl acetate solution | |
| Dominant faces | {010}, {100}, {011}, {110} | |
| Crystal shape | Yellow needles | |
| Space group | $P\bar{1}$ | |
| $\mu(\text{Mo } K\alpha)$ (cm^{-1}) | 0.7 | |
| | 20°C | -160°C |
| a (Å) | 10.070 (3) | 10.035 (3) |
| b (Å) | 10.525 (4) | 10.458 (4) |
| c (Å) | 10.077 (3) | 9.978 (3) |
| α ($^\circ$) | 105.04 (3) | 105.04 (4) |
| β ($^\circ$) | 104.65 (3) | 105.27 (3) |
| γ ($^\circ$) | 92.15 (3) | 92.17 (3) |
| $\lambda(\text{Mo } K\alpha_1)$ (Å) | 0.70926 | 0.70926 |
| V (Å ³) | 1067 | 975.2 |
| Z | 2 | 2 |
| D_c (g cm^{-3}) | 1.107 | 1.129 |

Determination of the structure and refinement of the room-temperature structure

The structure was derived from the room-temperature data by the multi-solution method (Germain & Woolfson, 1968) *via* MULTAN (Germain, Main & Woolfson, 1971). The E map of the model with the highest figure of merit revealed the molecular skeleton. The individual atomic parameters of the C atoms were refined isotropically and then anisotropically by a full-matrix least-squares program. The H atoms, inserted in chemically reasonable positions, were refined isotropically. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The seven strongest reflexions, which were suspected to suffer from extinction, were not included in the refinement. The low-temperature data were corrected for extinction (Rabinovich, Schmidt &

Table 2. *Intensity measurement and processing*

| | 20°C | -160°C |
|---|------------------------|----------------------------|
| Diffractometer | Siemens | Nonius CAD-3 |
| Monochromatization | Zr, Y balanced filters | Graphite monochromator |
| λ | Mo $K\alpha$ | Mo $K\alpha$ |
| Number of crystals measured | 1 | 4 |
| Crystal dimensions (mm) | 0.5 × 0.4 × 0.3 | 0.1 × 0.1 × 0.36 |
| Reciprocal lattice vector parallel to φ axis | [001] | (a) [115] (b) [014] |
| Maximum θ angle ($^\circ$) | 27.5 | 40.0 |
| Scanning mode | | $\theta/2\theta$ step scan |
| Scan angle ($^\circ$) (+ calculated $\alpha_1 - \alpha_2$ separation) | 0.5 | 0.5 |
| θ step for reflexion scan ($^\circ$) | 0.01 | 0.01 |
| Step scan time for intensity and background (s) | 0.5, 0.2 | 0.4, 0.2 |
| Offset for background measurements ($^\circ$) | 0.7 | 0.9 |
| Number of monitor reflexions | 4 | 4 |
| Monitor-reflexion interval | 50 | 100 |
| Number of reflexions measured | 6256 | 22241 |
| Number of unique reflexions | 4573 | 8319 |
| Number of 'unobserved' reflexions, for which $F_o^2 < 2\sigma(F_o^2)$ | 1633 | 4134 |
| The match R'^* between equivalent reflexions | 0.035 | 0.075 |
| Variation in the computed absorption factor A | 0.95-0.96 | 0.987-0.993 |

* $R' = \sum_i (F_{ij} - \bar{F}_j)^2 / \sum_i w_{ij} F_{ij}^2$ where $\bar{F}_j = \sum_i w_{ij} F_{ij} / \sum_i w_{ij}$ is the weighted average of the j th group of i symmetry-equivalent reflexions. F_{ij} is the individual value of each reflexion in the group and w_{ij} is the corresponding weight.

Ubell, 1967). Additional information on the refinement is listed in Table 3.

Refinement of the low-temperature structure

The refinement was carried out in four stages, details of which are presented in Table 3.

In the first stage (a), standard free-atom scattering factors were used, with atomic parameters obtained

from the room-temperature structure. Anisotropic vibration tensors were assigned to the C atoms; the H atoms were assigned isotropic thermal parameters. In an alternative refinement (stage b) the number of thermal parameters was reduced on the assumption that the thermal motion of each phenyl ring can be described as that of a rigid body (Schomaker & Trueblood, 1968). In the next stage (c) the spherical atomic charge distributions were modified by the

Table 3. *Crystal structure refinement*

| | 20°C | -160°C | | | |
|--|-------|-----------------------|---------|---------|---------|
| | | Four-stage refinement | | | |
| | (a) | (b) | (c) | (d) | |
| Total number of parameters | 333 | 333 | 249 | 349 | 413 |
| Positional parameters | 144 | 144 | 144 | 144 | 144 |
| Thermal parameters | 188 | 188 | 104 | 104 | 168 |
| Deformation parameters | — | — | — | 100 | 100 |
| Number of reflexions used in the refinement | 2798 | 8319 | 8319 | 8320 | 8320 |
| Number of strong reflexions given zero weight believed to suffer extinction errors | 7 | — | — | — | — |
| R_1 (omitting unobserved reflexions) | 0.066 | 0.08751 | 0.08837 | 0.06901 | 0.06902 |
| R_2 (including unobserved reflexions) | 0.066 | 0.09443 | 0.09528 | 0.07604 | 0.07608 |
| r^* | 0.095 | 0.11482 | 0.1199 | 0.07919 | 0.07859 |
| Goodness of fit† | 1.98 | 2.34 | 2.48 | 1.572 | 1.558 |

$$*r = \left[\frac{\sum w(F_o^2 - K^2 F_c^2)}{\sum w F_o^4} \right]^{1/2}$$

$$\dagger \text{g.o.f.} = \left[\frac{\sum w(F_o^2 - K^2 F_c^2)}{n - p} \right]^{1/2}, \quad n = \text{number of observations, } p = \text{number of parameters.}$$

Table 4. *Fractional atomic coordinates and their e.s.d.'s ($\times 10^4$ for C and $\times 10^3$ for H) at 20°C*

| | x | y | z | | x | y | z |
|-------|----------|----------|----------|-------|----------|----------|----------|
| C(1) | 2781 (2) | 5564 (2) | 8856 (2) | C(2) | 1396 (2) | 5392 (2) | 8833 (2) |
| C(3) | 724 (2) | 6456 (2) | 9328 (3) | C(4) | 1406 (3) | 7716 (2) | 9855 (3) |
| C(5) | 2784 (3) | 7908 (2) | 9893 (3) | C(6) | 3467 (2) | 6846 (2) | 9403 (2) |
| C(7) | 3022 (2) | 3061 (2) | 8152 (2) | C(8) | 2615 (2) | 2737 (2) | 9265 (2) |
| C(9) | 2195 (3) | 1433 (2) | 9145 (3) | C(10) | 2148 (3) | 445 (2) | 7925 (3) |
| C(11) | 2542 (3) | 759 (2) | 6823 (3) | C(12) | 2991 (2) | 2052 (2) | 6940 (3) |
| C(13) | 3496 (2) | 4446 (2) | 8257 (2) | C(14) | 4554 (2) | 4692 (2) | 7738 (2) |
| C(15) | 5505 (2) | 4987 (2) | 7248 (2) | C(16) | 6511 (2) | 5386 (2) | 6738 (2) |
| C(17) | 6664 (2) | 6794 (2) | 6734 (2) | C(18) | 7938 (2) | 7458 (2) | 6881 (2) |
| C(19) | 8061 (3) | 8787 (2) | 6943 (3) | C(20) | 6934 (3) | 9481 (2) | 6847 (3) |
| C(21) | 5664 (3) | 8840 (2) | 6693 (3) | C(22) | 5527 (2) | 7513 (2) | 6640 (3) |
| C(23) | 7454 (2) | 4440 (2) | 6250 (2) | C(24) | 7954 (2) | 4492 (2) | 5082 (2) |
| C(25) | 8804 (2) | 3578 (3) | 4618 (3) | C(26) | 9209 (2) | 2635 (2) | 5323 (3) |
| C(27) | 8731 (2) | 2584 (2) | 6478 (3) | C(28) | 7850 (2) | 3471 (2) | 6934 (3) |
| H(2) | 91 (2) | 451 (2) | 847 (2) | H(3) | -27 (2) | 628 (2) | 924 (2) |
| H(4) | 94 (2) | 847 (2) | 1019 (2) | H(5) | 326 (2) | 883 (2) | 1025 (3) |
| H(6) | 448 (2) | 696 (2) | 947 (2) | H(8) | 261 (2) | 346 (2) | 1009 (2) |
| H(9) | 194 (2) | 119 (2) | 996 (3) | H(10) | 182 (2) | -54 (2) | 782 (2) |
| H(11) | 247 (2) | 1 (2) | 590 (2) | H(12) | 330 (2) | 230 (2) | 623 (2) |
| H(18) | 873 (2) | 694 (2) | 697 (2) | H(19) | 896 (2) | 922 (2) | 709 (2) |
| H(20) | 702 (2) | 1043 (2) | 688 (3) | H(21) | 482 (2) | 932 (2) | 666 (3) |
| H(22) | 462 (2) | 704 (2) | 651 (3) | H(24) | 767 (2) | 517 (2) | 460 (2) |
| H(25) | 913 (2) | 361 (2) | 375 (3) | H(26) | 985 (2) | 202 (2) | 503 (2) |
| H(27) | 900 (2) | 189 (2) | 700 (3) | H(28) | 749 (2) | 342 (2) | 775 (3) |

Table 5. Fractional atomic coordinates and their *e.s.d.*'s ($\times 10^4$ for C and $\times 10^3$ for H) at -160°C

| | <i>x</i> | <i>y</i> | <i>z</i> | | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|-------|----------|----------|----------|
| C(1) | 2778 (1) | 5554 (1) | 8867 (1) | C(2) | 1374 (1) | 5366 (1) | 8837 (1) |
| C(3) | 687 (1) | 6447 (1) | 9327 (1) | C(4) | 1382 (1) | 7733 (1) | 9852 (1) |
| C(5) | 2782 (1) | 7931 (1) | 9893 (1) | C(6) | 3471 (1) | 6854 (1) | 9407 (1) |
| C(7) | 3014 (1) | 3042 (1) | 8158 (1) | C(8) | 2597 (1) | 2709 (1) | 9280 (1) |
| C(9) | 2163 (1) | 1392 (1) | 9159 (1) | C(10) | 2102 (1) | 390 (1) | 7900 (1) |
| C(11) | 2509 (1) | 714 (1) | 6775 (1) | C(12) | 2976 (1) | 2026 (1) | 6908 (1) |
| C(13) | 3493 (1) | 4429 (1) | 8271 (1) | C(14) | 4554 (1) | 4676 (1) | 7748 (1) |
| C(15) | 5514 (1) | 4980 (1) | 7251 (1) | C(16) | 6520 (1) | 5393 (1) | 6739 (1) |
| C(17) | 6660 (1) | 6802 (1) | 6728 (1) | C(18) | 7954 (1) | 7473 (1) | 6879 (1) |
| C(19) | 8083 (1) | 8825 (1) | 6951 (1) | C(20) | 6923 (1) | 9526 (1) | 6851 (1) |
| C(21) | 5632 (1) | 8863 (1) | 6691 (1) | C(22) | 5503 (1) | 7521 (1) | 6638 (1) |
| C(23) | 7467 (1) | 4449 (1) | 6245 (1) | C(24) | 7971 (1) | 4508 (1) | 5072 (1) |
| C(25) | 8835 (1) | 3586 (1) | 4594 (1) | C(26) | 9248 (1) | 2622 (1) | 5314 (1) |
| C(27) | 8756 (1) | 2558 (1) | 6491 (1) | C(28) | 7861 (1) | 3452 (1) | 6942 (1) |
| H(2) | 88 (2) | 448 (3) | 845 (1) | H(3) | -29 (3) | 631 (1) | 929 (1) |
| H(4) | 90 (2) | 848 (2) | 1018 (1) | H(5) | 328 (2) | 883 (3) | 1029 (1) |
| H(6) | 445 (3) | 698 (1) | 946 (1) | H(8) | 265 (1) | 341 (2) | 1016 (3) |
| H(9) | 190 (1) | 116 (1) | 995 (3) | H(10) | 180 (1) | -53 (3) | 782 (1) |
| H(11) | 244 (1) | 1 (2) | 588 (3) | H(12) | 326 (1) | 224 (1) | 612 (3) |
| H(18) | 877 (3) | 699 (2) | 696 (1) | H(19) | 900 (3) | 928 (2) | 706 (1) |
| H(20) | 700 (1) | 1047 (3) | 690 (1) | H(21) | 481 (3) | 934 (2) | 659 (1) |
| H(22) | 460 (3) | 707 (2) | 650 (1) | H(24) | 769 (1) | 518 (2) | 456 (2) |
| H(25) | 917 (1) | 363 (1) | 376 (3) | H(26) | 987 (1) | 200 (2) | 501 (1) |
| H(27) | 906 (1) | 188 (2) | 701 (2) | H(28) | 751 (1) | 340 (1) | 776 (3) |

introduction of deformation coefficients as additional least-squares parameters (Hirshfeld, 1971; Harel & Hirshfeld, 1975).

In defining the deformation model the molecule was supposed to comprise four identical phenyl rings; each phenyl ring was taken to be symmetric with respect to a local mirror plane lying perpendicular to the ring and passing through atoms 1 and 4, 7 and 10, 17 and 20, 23 and 26 (scheme 1) for rings *A*, *C*, *B* and *D* respectively. The butatriene system was assumed to be symmetric with respect to a mirror plane perpendicular to it at its centre. In addition, all the H atoms were assumed to be identical. These constraints were not applied to the atomic coordinates but only to the deformation density around the atoms. These assumptions led to the reduction of the deformation parameters by the inclusion of all the 'symmetry-related' atoms in the same deformation type, assuming that the same linear combination of deformation functions can describe the electron density distributions around those atoms which belong to the same type. According to the assumptions stated above, all the atoms in the molecule were distributed between seven 'deformation types'. The number of parameters was further reduced by assuming that the deformation density at each phenyl C atom is symmetric with respect to two mirror planes; one plane coincides with the phenyl ring and the other is perpendicular to this plane and passes through that atom and the atom opposite to it in the ring. The C atoms along the butatriene chain were assumed to be symmetric with

respect to a mirror plane which lies in the butatriene system. For the H atoms we assumed axial symmetry about the C-H direction.

Two additional deformation parameters were refined: the exponential factors γ , which govern the width of the deformation functions, one for each atomic type, C and H.

At this stage of refinement we used modified scattering factors for C atoms (Hirshfeld, 1971); the H atoms were contracted by an effective nuclear charge ($\zeta = 1.3$, Harel, 1974). In order to maintain electric neutrality of the entire crystal, $F(000)$ was treated as an observed quantity with a standard deviation of $F(000)/100$.

In the next stage (*d*) we removed the rigid-body constraint and continued the refinement with independent atomic vibration components U^{ij} for the C atoms. The thermal parameters of the H atoms were fixed at their rigid-body values.

By means of the *R* factor test (Hamilton, 1965), we compared the two methods of refinement (*c*) and (*d*) to establish whether constraining the thermal motion of the phenyl C atoms resulted in a significant worsening of the structure determination. We found that the constrained model can be accepted as genuine at a 5% significance level and that constraining the number of refined thermal parameters, and so considerably reducing the number of refined atomic parameters to allow the construction of a more general deformation model, did not worsen the match between the observed and calculated structure factors significantly.

Results

The final atomic coordinates for the room- and low-temperature structures are listed in Tables 4 and 5. The bond lengths and angles are in Tables 6 and 7. (The interatomic distances and angles and e.s.d.'s of the low-temperature structure were calculated from the final positional parameters of stage *d* of the refinement.) Table 8 lists T_{ij} , L_{ij} and S_{ij} — the components of the tensors of translation, libration and screw axis for the four phenyl rings, the thermal motions of which were treated as those of rigid bodies (Schomaker & Trueblood, 1968). Some short intermolecular contacts are given in Table 9. The deviations from best planes of various parts of the molecule are presented in Table 10.*

Discussion

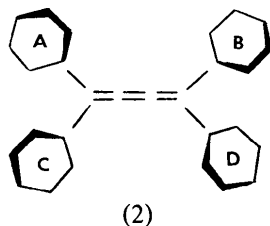
Throughout the discussion only numerical results from the low-temperature structure will be given, unless otherwise stated.

Molecular shape

TPBT consists of a butatriene chain substituted by four phenyl rings. As the butatriene is symmetrically substituted we would expect the molecule to have either point symmetry 222 or a centre of inversion, $\bar{1}$. The molecule does not possess the latter symmetry nor complete 222 symmetry.

Steric interactions preclude a planar molecule. The deviations from planarity can be described by the angles between the planes of each of the phenyl rings and that of the butatriene system >C=C=C=C< ; the angles are 27.9, 27.4, 41.8 and 38.5° for rings *A*, *B*, *C* and *D* respectively with relative senses of rotation shown in (2).

In tetraphenylethylene (Hoekstra & Vos, 1975) the analogous angles of 43, 46, 57 and 45° are significantly larger, presumably because the molecule is more overcrowded. The question of whether the preferred molecular symmetry is 222 or $\bar{1}$ may be



* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32752 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

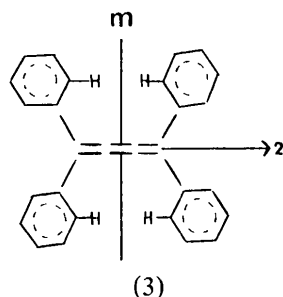
analysed as follows: Let us assume that the molecule lies on a centre of symmetry, the butatriene chain lies on a molecular twofold axis, the phenyl rings are twisted out of the plane of the butatriene system by 34°, the average observed angle of twist. This

Table 6. Final bond lengths (Å) for the room-temperature and the low-temperature structures (standard deviations in parentheses)

d_0 is the uncorrected and d is the corrected value (Busing & Levy, 1964).

| | 20°C | | -160°C | |
|-------------|-----------|-----------|-----------|-----|
| | d_0 | d_0 | d_0 | d |
| C(1)—C(13) | 1.477 (3) | 1.477 (2) | 1.473 (2) | |
| C(1)—C(2) | 1.393 (3) | 1.406 (1) | 1.413 (1) | |
| C(1)—C(6) | 1.398 (3) | 1.404 (1) | 1.411 (2) | |
| C(2)—C(3) | 1.378 (3) | 1.394 (1) | 1.400 (2) | |
| C(3)—C(4) | 1.377 (3) | 1.393 (1) | 1.400 (2) | |
| C(4)—C(5) | 1.384 (4) | 1.401 (1) | 1.407 (1) | |
| C(5)—C(6) | 1.382 (3) | 1.391 (1) | 1.397 (2) | |
| C(7)—C(13) | 1.486 (3) | 1.477 (2) | 1.473 (2) | |
| C(7)—C(8) | 1.401 (4) | 1.410 (2) | 1.417 (3) | |
| C(7)—C(12) | 1.388 (3) | 1.404 (1) | 1.411 (2) | |
| C(8)—C(9) | 1.386 (4) | 1.394 (1) | 1.399 (3) | |
| C(9)—C(10) | 1.378 (4) | 1.397 (1) | 1.404 (1) | |
| C(10)—C(11) | 1.380 (5) | 1.404 (2) | 1.411 (2) | |
| C(11)—C(12) | 1.383 (4) | 1.394 (1) | 1.394 (2) | |
| C(13)—C(14) | 1.344 (3) | 1.346 (2) | 1.346 (3) | |
| C(14)—C(15) | 1.246 (3) | 1.260 (2) | 1.260 (2) | |
| C(15)—C(16) | 1.345 (3) | 1.349 (2) | 1.349 (2) | |
| C(16)—C(23) | 1.480 (3) | 1.478 (1) | 1.474 (4) | |
| C(16)—C(17) | 1.485 (3) | 1.478 (2) | 1.475 (2) | |
| C(17)—C(18) | 1.393 (3) | 1.405 (1) | 1.412 (1) | |
| C(17)—C(22) | 1.393 (3) | 1.403 (1) | 1.411 (4) | |
| C(18)—C(19) | 1.383 (3) | 1.396 (1) | 1.401 (2) | |
| C(19)—C(20) | 1.370 (4) | 1.394 (2) | 1.402 (2) | |
| C(20)—C(21) | 1.377 (4) | 1.396 (2) | 1.403 (3) | |
| C(21)—C(22) | 1.384 (4) | 1.390 (1) | 1.395 (3) | |
| C(23)—C(28) | 1.390 (3) | 1.411 (1) | 1.417 (2) | |
| C(23)—C(24) | 1.404 (4) | 1.407 (1) | 1.413 (2) | |
| C(24)—C(25) | 1.382 (3) | 1.397 (1) | 1.402 (2) | |
| C(25)—C(26) | 1.380 (4) | 1.398 (2) | 1.404 (2) | |
| C(26)—C(27) | 1.379 (4) | 1.404 (2) | 1.410 (2) | |
| C(27)—C(28) | 1.383 (3) | 1.394 (1) | 1.399 (2) | |
| C(2)—H(2) | 0.97 (2) | 0.97 (3) | 0.97 (5) | |
| C(3)—H(3) | 0.99 (2) | 0.97 (3) | 0.97 (7) | |
| C(4)—H(4) | 0.97 (2) | 0.97 (2) | 0.97 (7) | |
| C(5)—H(5) | 1.00 (2) | 0.98 (3) | 0.98 (8) | |
| C(6)—H(6) | 1.00 (2) | 0.97 (3) | 0.97 (7) | |
| C(8)—H(8) | 0.97 (2) | 0.98 (2) | 0.98 (7) | |
| C(9)—H(9) | 1.01 (3) | 0.97 (3) | 0.97 (7) | |
| C(10)—H(10) | 1.04 (2) | 0.98 (3) | 0.98 (6) | |
| C(11)—H(11) | 1.04 (5) | 0.98 (2) | 0.98 (6) | |
| C(12)—H(12) | 0.94 (3) | 0.98 (3) | 0.98 (5) | |
| C(18)—H(18) | 0.97 (2) | 0.98 (2) | 0.98 (5) | |
| C(19)—H(19) | 0.95 (2) | 0.98 (3) | 0.98 (6) | |
| C(20)—H(20) | 0.99 (2) | 0.97 (3) | 0.97 (6) | |
| C(21)—H(21) | 1.00 (2) | 0.98 (2) | 0.98 (8) | |
| C(22)—H(22) | 0.98 (2) | 0.96 (3) | 0.96 (7) | |
| C(24)—H(24) | 0.97 (2) | 0.98 (2) | 0.98 (5) | |
| C(25)—H(25) | 1.02 (3) | 0.99 (3) | 0.99 (6) | |
| C(26)—H(26) | 0.97 (2) | 0.96 (2) | 0.96 (5) | |
| C(27)—H(27) | 1.01 (2) | 0.99 (2) | 0.99 (7) | |
| C(28)—H(28) | 0.99 (3) | 0.98 (3) | 0.98 (5) | |

hypothetical molecule would exhibit $2/m$ symmetry where the mirror is perpendicular to the butatriene chain and passes through its centre, as depicted in (3).



This structure would contain rather short $H\cdots H$ contacts of ~ 2.3 Å between $C-H$ bonds which are almost directed at each other across the mirror plane.

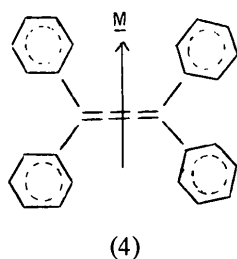
Intermolecular $H\cdots H$ contacts as short as 2.3 Å are rarely observed in the solid state. The observed $H\cdots H$ distance is 3.0 Å. Consequently 222 molecular symmetry is probably preferred on steric grounds. There is another point to be considered: whether the observed crystal structure of TPBT is a more stable arrangement than a hypothetical crystal in which the molecules would exhibit $2/m$ symmetry. This question is answerable in part since the cell constants of tetra-*p*-anisylbutatriene (Berkovitch-Yellin, Lahav & Leiserowitz, 1974) are similar to those of tetraphenylbutatriene which implies that their molecular structures are similar. Since the intermolecular contacts in the two crystals must differ appreciably, because the H atom is replaced by OCH_3 , it is reasonable to deduce that the preferred molecular symmetry is 222 .

The magnitudes of the angles between the plane of the butatriene system and each of the phenyl rings (see

Table 7. *Uncorrected bond angles and their e.s.d.'s (°)*

| | -160°C | 20°C | | -160°C | 20°C |
|-------------------|------------|------------|-------------------|------------|------------|
| C(2)-C(1)-C(6) | 118.5 (1) | 118.0 (2) | C(15)-C(16)-C(17) | 118.3 (1) | 118.1 (2) |
| C(2)-C(1)-C(13) | 121.1 (1) | 121.6 (2) | C(15)-C(16)-C(23) | 119.7 (1) | 119.8 (2) |
| C(6)-C(1)-C(13) | 120.3 (1) | 120.4 (2) | C(17)-C(16)-C(23) | 122.0 (1) | 122.0 (2) |
| C(1)-C(2)-C(3) | 120.6 (1) | 120.9 (2) | C(16)-C(17)-C(18) | 121.4 (1) | 122.1 (2) |
| C(1)-C(2)-H(2) | 119.5 (12) | 119.3 (12) | C(16)-C(17)-C(22) | 120.2 (1) | 120.3 (2) |
| C(3)-C(2)-H(2) | 119.8 (12) | 119.8 (12) | C(18)-C(17)-C(22) | 118.3 (1) | 117.6 (2) |
| C(2)-C(3)-C(4) | 120.4 (1) | 120.7 (2) | C(17)-C(18)-C(19) | 120.7 (1) | 120.8 (2) |
| C(2)-C(3)-H(3) | 120.3 (5) | 117.4 (10) | C(17)-C(18)-H(18) | 119.1 (12) | 116.3 (12) |
| C(4)-C(3)-H(3) | 119.3 (5) | 121.8 (11) | C(19)-C(18)-H(18) | 120.2 (12) | 122.9 (12) |
| C(3)-C(4)-C(5) | 119.5 (1) | 119.3 (2) | C(18)-C(19)-C(20) | 120.4 (1) | 121.0 (2) |
| C(3)-C(4)-H(4) | 120.2 (12) | 121.4 (12) | C(18)-C(19)-H(19) | 119.6 (12) | 118.6 (12) |
| C(5)-C(4)-H(4) | 120.3 (12) | 119.3 (12) | C(20)-C(19)-H(19) | 119.9 (12) | 120.4 (12) |
| C(4)-C(5)-C(6) | 120.2 (1) | 120.3 (2) | C(19)-C(20)-C(21) | 119.2 (1) | 119.1 (2) |
| C(4)-C(5)-H(5) | 119.8 (12) | 118.5 (14) | C(19)-C(20)-H(20) | 121.0 (5) | 121.0 (13) |
| C(6)-C(5)-H(5) | 119.9 (12) | 121.1 (14) | C(21)-C(20)-H(20) | 119.7 (5) | 119.9 (13) |
| C(1)-C(6)-C(5) | 120.8 (1) | 120.8 (2) | C(20)-C(21)-C(22) | 120.5 (1) | 120.6 (2) |
| C(1)-C(6)-H(6) | 118.7 (5) | 117.7 (10) | C(20)-C(21)-H(21) | 119.8 (12) | 121.8 (13) |
| C(5)-C(6)-H(6) | 120.5 (5) | 121.4 (10) | C(22)-C(21)-H(21) | 119.7 (12) | 117.6 (14) |
| C(8)-C(7)-C(12) | 118.9 (1) | 118.5 (2) | C(17)-C(22)-C(21) | 120.9 (1) | 121.0 (2) |
| C(8)-C(7)-C(13) | 121.6 (1) | 121.4 (2) | C(17)-C(22)-H(22) | 119.3 (12) | 117.8 (13) |
| C(12)-C(7)-C(13) | 119.5 (1) | 120.1 (2) | C(21)-C(22)-H(22) | 119.8 (12) | 121.2 (13) |
| C(7)-C(8)-C(9) | 120.7 (1) | 120.2 (2) | C(16)-C(23)-C(24) | 121.3 (1) | 120.9 (2) |
| C(7)-C(8)-H(8) | 119.1 (16) | 117.4 (14) | C(16)-C(23)-C(28) | 119.8 (1) | 120.4 (2) |
| C(9)-C(8)-H(8) | 120.1 (17) | 122.4 (14) | C(24)-C(23)-C(28) | 118.9 (1) | 118.7 (2) |
| C(8)-C(9)-C(10) | 120.0 (1) | 120.6 (3) | C(23)-C(24)-C(25) | 120.6 (1) | 120.1 (2) |
| C(8)-C(9)-H(9) | 120.5 (6) | 120.5 (11) | C(23)-C(24)-H(24) | 119.9 (10) | 118.7 (14) |
| C(10)-C(9)-H(9) | 119.5 (6) | 118.8 (11) | C(25)-C(24)-H(24) | 119.5 (10) | 121.3 (14) |
| C(9)-C(10)-C(11) | 119.6 (1) | 119.4 (2) | C(24)-C(25)-C(26) | 120.1 (1) | 120.5 (3) |
| C(9)-C(10)-H(10) | 119.5 (5) | 121.2 (14) | C(24)-C(25)-H(25) | 119.7 (6) | 119.2 (14) |
| C(11)-C(10)-H(10) | 120.8 (5) | 119.4 (14) | C(26)-C(25)-H(25) | 120.1 (6) | 120.2 (14) |
| C(10)-C(11)-C(12) | 120.5 (1) | 120.5 (2) | C(25)-C(26)-C(27) | 119.7 (1) | 119.7 (2) |
| C(10)-C(11)-H(11) | 119.2 (16) | 118.3 (14) | C(25)-C(26)-H(26) | 120.7 (11) | 120.6 (15) |
| C(12)-C(11)-H(11) | 120.3 (16) | 121.2 (13) | C(27)-C(26)-H(26) | 119.6 (11) | 119.6 (15) |
| C(7)-C(12)-C(11) | 120.2 (1) | 120.7 (3) | C(26)-C(27)-C(28) | 120.2 (1) | 120.5 (3) |
| C(7)-C(12)-H(12) | 119.8 (6) | 116.2 (11) | C(26)-C(27)-H(27) | 120.0 (10) | 121.1 (15) |
| C(11)-C(12)-H(12) | 119.9 (6) | 123.1 (11) | C(28)-C(27)-H(27) | 119.8 (10) | 118.4 (15) |
| C(1)-C(13)-C(7) | 121.4 (1) | 121.3 (2) | C(23)-C(28)-C(27) | 120.4 (1) | 120.5 (3) |
| C(1)-C(13)-C(14) | 118.7 (1) | 118.8 (2) | C(23)-C(28)-H(28) | 119.3 (6) | 118.9 (13) |
| C(7)-C(13)-C(14) | 119.8 (1) | 119.8 (2) | C(27)-C(28)-H(28) | 120.2 (6) | 120.6 (13) |
| C(13)-C(14)-C(15) | 176.1 (1) | 176.3 (2) | | | |
| C(14)-C(15)-C(16) | 176.0 (1) | 176.3 (2) | | | |

above) indicate that the molecule does not possess exact 222 symmetry but has almost exact twofold symmetry about an axis M perpendicular to the butatriene chain in the plane of the butatriene system (4). This twofold symmetry is further substantiated by an examination of the coordinates of the 'symmetry-related' atoms in a coordinate system whose axes are parallel to the three principal axes of inertia of the molecule. These coordinates may be derived from the transformation matrix given in Table 11.



These deviations from 222 point symmetry, namely the differences in the torsion angles involving rings A , B , C and D , may be ascribed to intermolecular interactions since the molecule lies in a general position and so the environments of the four phenyl rings are different. In a similar manner the deviations from molecular 222 point symmetry found in tetraphenylethylene (Hoekstra & Vos, 1975) were assumed to be due to intermolecular interactions since the molecule appears in space group $P2_1$. That intermolecular forces may induce changes in the torsion angles $\varphi-C=C$ is substantiated by the observation that biphenyl is planar in the crystal (Trotter, 1961) but in the gas phase the angle of twist between two phenyl rings is $45 \pm 10^\circ$ (Bastiansen, 1949). The forced planarity of biphenyl in the crystal was ascribed to crystal forces. The observation that TPBT maintains almost complete twofold molecular symmetry may also be explained in terms of intermolecular forces and will be discussed below.

The butatriene system itself is not completely planar (Table 10); the magnitudes and signs of the atomic deviations from planarity of the four substituted atoms [C(1), 0.079; C(7), -0.117; C(17), -0.100; C(23), 0.086 Å] indicate that the distortion from planarity is primarily due to a twist about the cumulenic axis. The

angle of twist between the $C=C\begin{matrix} C \\ C \end{matrix}$ groups at the two

ends of the chain is 8.8° . The chain is not completely linear (Table 7), the $C=C=C$ angles being 176.0 and 176.1° . This type of distortion is also found in other cumulenic crystal structures (Leiserowitz & Nader, 1973; Berkovitch-Yellin, Lahav & Leiserowitz, 1974; Berkovitch-Yellin, Leiserowitz & Nader, 1977).

The four phenyl rings A , B , C , D are planar with maximum deviations of 0.01 Å (Table 10). The

Table 8. *Rigid-body tensors of the four phenyl rings*

Phenyl ring A

$$\mathbf{T} (\text{Å}^2) = \begin{pmatrix} 0.0146 (2) & 0.0033 (1) & 0.0037 (5) \\ & 0.0176 (2) & 0.0060 (3) \\ & & 0.0102 (2) \end{pmatrix}$$

$$\mathbf{L} (\text{rad}^2) = \begin{pmatrix} 0.0080 (11) & -0.0011 (1) & -0.0032 (4) \\ & 0.0076 (10) & 0.0004 (2) \\ & & 0.0029 (2) \end{pmatrix}$$

$$\mathbf{S} (\text{rad Å}) = \begin{pmatrix} -0.0013 (2) & 0.0004 (2) & -0.0015 (4) \\ 0.0007 (1) & 0.0011 (1) & -0.0010 (2) \\ -0.0013 (1) & -0.0015 (1) & 0.0002 \end{pmatrix}$$

Origin of the coordinate system is at $(x,y,z) = (0.2257, 0.6175, 0.9152)$.

Phenyl ring B

$$\mathbf{T} = \begin{pmatrix} 0.0083 (1) & 0.0031 (3) & 0.0028 (7) \\ & 0.0166 (2) & 0.0053 (2) \\ & & 0.0157 (4) \end{pmatrix}$$

$$\mathbf{L} = \begin{pmatrix} 0.0028 (3) & 0.0017 (3) & -0.0032 (5) \\ & 0.0091 (10) & -0.0018 (2) \\ & & 0.0073 (11) \end{pmatrix}$$

$$\mathbf{S} = \begin{pmatrix} 0.0012 (2) & -0.0008 (1) & -0.0010 (1) \\ -0.0003 (1) & -0.0001 (1) & 0.0009 (1) \\ -0.0015 (4) & 0.0007 (1) & -0.0011 \end{pmatrix}$$

Origin is at $(x,y,z) = (0.2662, 0.2276, 0.8079)$.

Phenyl ring C

$$\mathbf{T} = \begin{pmatrix} 0.0150 (2) & 0.0004 (1) & 0.0048 (4) \\ & 0.0170 (2) & 0.0016 (5) \\ & & 0.0110 (8) \end{pmatrix}$$

$$\mathbf{L} = \begin{pmatrix} 0.0066 (11) & 0.0008 (1) & -0.0021 (3) \\ & 0.0118 (12) & -0.0027 (3) \\ & & 0.0021 (2) \end{pmatrix}$$

$$\mathbf{S} = \begin{pmatrix} 0.0007 (2) & -0.0014 (2) & -0.0018 (6) \\ -0.0010 (2) & -0.0013 (1) & 0.0000 (2) \\ -0.0016 (1) & 0.0007 (1) & 0.0005 \end{pmatrix}$$

Origin is at $(x,y,z) = (0.7024, 0.7494, 0.6714)$.

Phenyl ring D

$$\mathbf{T} = \begin{pmatrix} 0.0102 (12) & -0.0030 (9) & 0.0021 (9) \\ & 0.0131 (8) & 0.0000 (8) \\ & & 0.0143 (8) \end{pmatrix}$$

$$\mathbf{L} = \begin{pmatrix} 0.0064 (7) & -0.0028 (4) & -0.0037 (5) \\ & 0.0063 (9) & -0.0018 (4) \\ & & 0.0066 (11) \end{pmatrix}$$

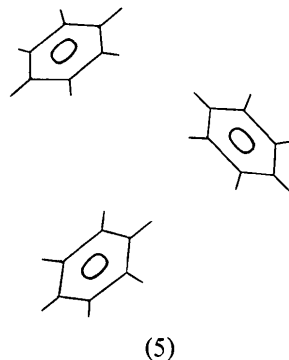
$$\mathbf{S} = \begin{pmatrix} 0.0006 (1) & 0.0013 (1) & -0.0004 (1) \\ 0.0012 (2) & 0.0006 (1) & -0.0006 (1) \\ -0.0014 (3) & -0.0015 (2) & -0.0012 \end{pmatrix}$$

Origin is at $(x,y,z) = (0.8109, 0.3963, 0.6005)$.

Table 9. Intermolecular contacts (Å)

Intermolecular distances between C atoms <3.6 Å, between C and H atoms <3.2 Å and between H atoms <2.8 Å are shown. The five-digit code attached to the second atom indicates that its x, y, z coordinates are derived from those of the corresponding atom in the asymmetric unit. The first three digits a, b, c specify a lattice translation ($a - 5$), ($b - 5$), ($c - 5$); the last two digits specify one of the symmetry operations 01, 02. Symmetry operations: 01 x, y, z ; 02 $-x, -y, -z$.

| | |
|--------------------------|--------------------------|
| C(1)···H(25) 66602 3.17 | C(2)···H(25) 66602 2.98 |
| C(2)···H(28) 66702 3.18 | C(3)···H(18) 45501 2.83 |
| C(3)···H(28) 66702 2.96 | C(3)···H(25) 66602 3.11 |
| C(3)···C(18) 45501 3.56 | C(3)···C(12) 66702 3.59 |
| C(4)···H(28) 66702 2.92 | C(4)···H(10) 56501 3.14 |
| C(5)···H(28) 66702 3.10 | C(5)···H(20) 67702 3.15 |
| C(5)···C(20) 67702 3.15 | C(7)···H(6) 66702 3.00 |
| C(8)···H(6) 66702 2.87 | C(8)···H(3) 56702 3.11 |
| C(10)···H(19) 44501 3.11 | C(11)···H(21) 54501 2.79 |
| C(12)···H(26) 45501 3.19 | C(12)···C(19) 66602 3.57 |
| C(13)···H(24) 66602 2.91 | C(14)···H(24) 66602 2.81 |
| C(15)···H(8) 66702 2.81 | C(16)···H(8) 66702 2.90 |
| C(17)···H(8) 66702 3.07 | C(18)···H(12) 66602 3.02 |
| C(18)···H(9) 66702 3.09 | C(18)···H(3) 65501 3.14 |
| C(19)···H(12) 66602 2.90 | C(19)···H(9) 66702 3.10 |
| C(19)···H(26) 76602 3.19 | C(20)···H(5) 67702 2.99 |
| C(20)···H(12) 66602 3.02 | C(20)···H(11) 66602 3.11 |
| C(20)···H(27) 56502 3.15 | C(23)···H(22) 66602 2.98 |
| C(24)···H(22) 66602 2.84 | C(24)···H(25) 76602 3.17 |
| C(24)···C(25) 76602 3.60 | C(25)···H(18) 76602 3.18 |
| C(26)···C(25) 76602 3.48 | C(26)···H(11) 65602 2.96 |
| C(26)···H(2) 65501 3.19 | C(27)···H(2) 65501 2.80 |
| C(27)···H(20) 54501 2.94 | C(27)···H(11) 65602 3.04 |
| C(28)···H(2) 65501 3.02 | C(28)···H(20) 54501 3.20 |
| H(2)···H(3) 56702 2.79 | H(3)···H(8) 56702 2.59 |
| H(3)···H(18) 45501 2.56 | H(5)···H(10) 56501 2.78 |
| H(10)···H(19) 44501 2.71 | H(11)···H(21) 54501 2.48 |
| H(18)···H(25) 76602 2.43 | H(19)···H(26) 76602 2.70 |
| H(19)···H(27) 56501 2.74 | H(20)···H(27) 56501 2.45 |



contacts between phenyl rings, but rather contacts between the C—H groups and neighbouring rings. This type of contact (5) is common in aromatic structures, e.g. benzene (Cox, Cruickshank & Smith, 1958), naphthalene (Abrahams, Robertson & White, 1949) and anthracene (Sinclair, Robertson & Mathieson, 1950).

The molecule makes very close contacts (~ 4 Å) with its neighbours about the centres of inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 1)$. This array of molecules, which are in contact along c , forms a pseudo $P2/c$ symmetry set, since the molecular centre (at $x = 0.496$, $y = 0.499$, $z = 0.749$) lies very close to $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ and the molecular twofold axis M , shown in (4) is almost perpendicular to c (88.6°). The goodness of fit to the pseudo $P2/c$ symmetry of the array of molecules along c may be seen from a comparison of pseudosymmetry-related

exocyclic substituents of B and D lie well within their corresponding ring planes while those of A and C show significant deviations (A , 0.08; B , 0.004; C , 0.007; D , 0.01 Å).

Packing arrangement

The packing is shown in Fig. 1. The intermolecular contacts are dominated by those involving the phenyl rings. The structure does not contain plane-to-plane

Table 11. The transformation matrix between x, y, z and l, m, n — the atomic coordinates in the inertial frame

$$\begin{pmatrix} -8.685313 & -3.401107 & 6.473059 \\ 3.003198 & -9.842128 & -0.244185 \\ 4.027445 & -0.984171 & 7.593224 \end{pmatrix} \begin{pmatrix} x - x_0 \\ y - y_0 \\ z - z_0 \end{pmatrix} = \begin{pmatrix} l \\ m \\ n \end{pmatrix}$$

The origin of the L, M, N system is at $(x_0, y_0, z_0) = (0.499995, 0.491559, 0.750088)$.

Table 10. Deviations from best planes

| Plane | The equation of the plane | $\left(\frac{\sum A^2}{n-1}\right)^{1/2*}$ |
|----------|--|--|
| Ring A | $0.32564x - 4.07677y + 9.47316z - 6.2290 = 0$ | 0.002 |
| Ring B | $-8.72440x + 3.21272y - 2.24970z + 3.4901 = 0$ | 0.008 |
| Ring C | $-0.98165x - 0.34179y + 9.54943z - 5.5376 = 0$ | 0.007 |
| Ring D | $6.27246x + 4.63340y + 2.88131z - 8.5411 = 0$ | 0.010 |
| > = = < | $4.02744x - 0.98418y + 7.59323z - 7.2255 = 0$ | 0.060 |

* $\sum A^2$ is the sum of the squares of the deviations (Å) from the best plane of the n atoms forming the plane.

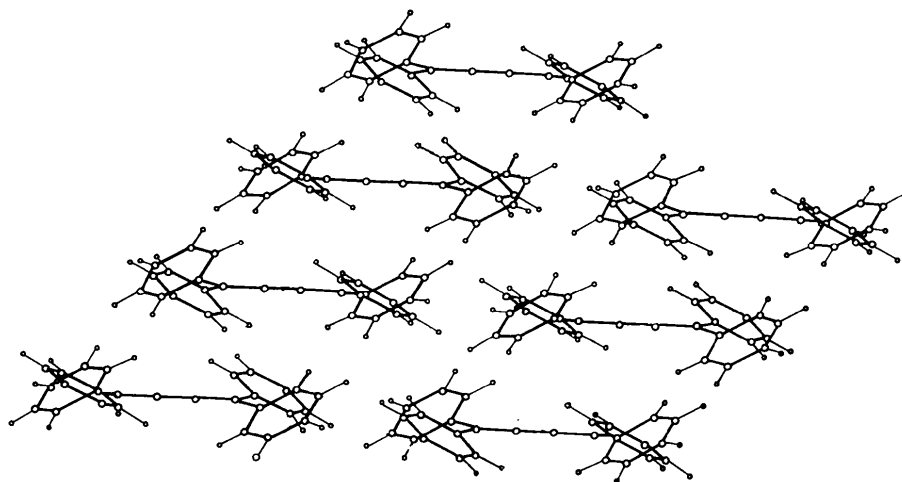


Fig. 1. Packing arrangement viewed along the pseudo twofold molecular axis M .

intermolecular contacts between the molecule at (x, y, z) to its neighbours at $(1-x, 1-y, 1-z)$ and $(1-x, 1-y, 2-z)$. The average deviation from the mean of these contacts is 0.04 \AA . A hypothetical $P2/c$ crystal structure would require that the molecular twofold axis M be parallel to \mathbf{b} and perpendicular to \mathbf{a} and \mathbf{c} . The vector M makes angles of 20° and 60° with \mathbf{b} and \mathbf{a} respectively, so the overall structure is far removed from $P2/c$ symmetry. According to a model it is obvious that a more favourable packing is achieved by translation along \mathbf{b} (20° off the molecular twofold axis M), than by translation along M (as would be required by $P2/c$ symmetry). The structure obtained is more close-packed and the orientation of phenyl rings permits formation of the 'herring-bone' structure. The overall effect is the formation of a $P\bar{1}$ structure rather than $P2/c$. In fact close packing cannot generally be obtained in $P2/c$ as demonstrated by Kitaigorodskii (1955).

Both terminal $>C=C$ bonds [$C(15)=C(16)$, $C(14)=C(15)$] make contacts of 3.91 and 3.86 \AA about the inversion centres at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 1)$ respectively (Fig. 1). This arrangement allows for the formation of dimers and probably also of polymers upon irradiation. A photodimer was isolated (Berkovitch-Yellin, Lahav & Leiserowitz, 1974), but polymeric products were not obtained upon irradiation of powder of TPBT in the absence of air (Berkovitch-Yellin, 1976).

Molecular dimensions

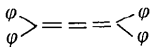
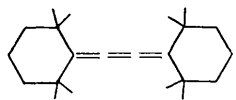
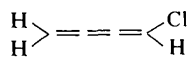
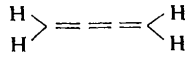
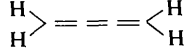
The scatter in bond lengths and angles calculated from a comparison between chemically equivalent bonds [from $\sigma = [\sum (b - \bar{b})^2 / (n - 1)]^{1/2}$ where b is bond length or angle, \bar{b} is the mean value and n is the number of equivalent bonds] is 0.002 \AA and 0.2° . (Room-temperature results are 0.003 \AA and 0.4° .)

There is a marked difference in length of the three chemically different C—C aromatic bonds [designated α , β , γ in scheme 1]; α is the longest (1.413 ± 2), β (1.398 ± 2) is the shortest, and γ has an intermediate value of $1.405 \pm 3 \text{ \AA}$. The uncorrected bond lengths exhibit the same trend (Table 6).

The C=C lengths in the butatriene chain show a striking difference between the 'inner' [$C(14)=C(15)$] and 'outer' [$C(13)=C(14)$, $C(15)=C(16)$] bonds (1.260 vs. 1.348 \AA), the inner bond being much shorter than a C=C double bond. These differences will be discussed below.

Values of $=C=C=$ ($sp-sp$) and $>C=C=$ (sp^2-sp) lengths obtained by spectroscopy and by X-ray diffraction are listed in Table 12. The bond lengths obtained by Raman spectroscopy (Stoicheff, 1957) and the earlier electron diffraction study of unsubstituted butatriene (Almenningen, Bastiansen & Trætterberg, 1961) are considerably different from the values obtained by X-rays and the recent electron diffraction study of Almenningen, Gundersen, Borg, Granberg & Karlsson (1975) of butatriene derivatives. These discrepancies may arise from two main sources: (a) The values obtained for the bond lengths of butatriene by Almenningen *et al.* (1961) were not correct because of improper theoretical treatment, according to Almenningen *et al.* (1975). (b) Substituent effects; the study by Raman spectroscopy and the earlier study by electron diffraction were carried out on unsubstituted butatriene in the gas phase, whereas the other results were obtained on substituted butatrienes. We have computed the lengths of the ($>C=C$) $sp-sp^2$ and ($=C=C=$) $sp-sp$ bonds in butatriene by *ab initio* molecular orbital calculations with an STO-31G extended basis set, employing the GAUSSIAN 70 program (Hehre, Lathan, Ditchfield, Newton & Pople, 1970). These bond lengths were varied keeping the C chain linear and the C—H lengths and H—C=C angles

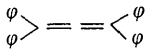
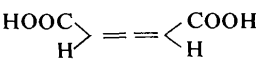
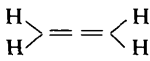
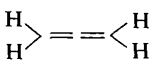
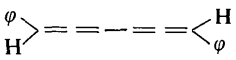
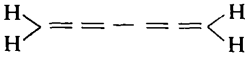
Table 12. =C=C= (*sp-sp*) and >C=C (*sp-sp²*) bond lengths in butatrienes

| Molecule | Bond lengths (Å) | | Technique | Reference |
|---|------------------|--------------------------|---------------------------------|----------------------------------|
| | <i>sp-sp</i> | <i>sp-sp²</i> | | |
|  | 1.259 | 1.348 | X-ray | This work |
|  | 1.261 | 1.332 | X-ray | Iringtinger & Jäger (1976) |
|  | 1.257 | 1.327 | Electron diffraction, gas phase | Almenningen <i>et al.</i> (1975) |
|  | 1.283 | 1.318 | Electron diffraction, gas phase | Almenningen <i>et al.</i> (1961) |
|  | 1.284 | 1.309 | Raman, gas phase | Stoicheff (1957) |

fixed at the observed values of 1.07 Å and 121.5° respectively (Almenningen *et al.*, 1961). The stable molecule contained >C=C and =C=C= bond lengths of 1.301 and 1.261 Å respectively. An analogous computation for chlorobutatriene incorporating the molecular geometry obtained by electron diffraction (C-Cl 1.733, C-H 1.08 Å; Cl-C-C 122.2, H-C-H 115.0°) (Almenningen *et al.*, 1975) resulted in $\text{Cl}-\text{C}=\text{C}$, $\text{H}-\text{C}=\text{C}$ and =C=C= lengths of 1.298, 1.294 and 1.259 Å respectively. Only the length of the central C=C bond compares favourably with the

electron diffraction results (Table 12). On the basis of the data available on substituted butatrienes (Table 12) and the results of the molecular orbital calculations it appears that the length of the central (=C=C=) *sp-sp* bond is not influenced by the nature of the substituents at the two ends of the butatriene system, which are fairly far removed from the central *sp-sp* bond. On the other hand, the length of the (>C=C) *sp-sp²* bond which is adjacent to the end substituents seems to be influenced by them (differences of $\sim \pm 0.01$ Å from the mean are observed). However, more information on such bonds is needed before any definite conclusions may be drawn.

Table 13. C=C (*sp-sp²*) bond lengths in allenes

| Molecule | Bond length (Å) | Technique | Reference |
|---|-----------------|--------------------------|---|
|  | 1.312* | X-ray | Iringtinger (1975) |
|  | 1.298* | X-ray | Leiserowitz & Nader (1973) |
| Allene dicarboxylic acid-acetamide (1:1 complex) | 1.307 | X-ray (low temperature) | Berkovitch-Yellin, Leiserowitz & Nader (1977) |
|  | 1.311 | Electron diffraction | Almenningen, Bastiansen & Trættestad (1959) |
|  | 1.309 | Raman spectrum | Stoicheff (1955) |
| Allene dicarboxylic acid-acetamide (1:1 complex) | 1.308 | X-ray (room temperature) | Nader (1976) |
|  | 1.308* | X-ray (room temperature) | Groth (1973) |
|  | 1.314* | Electron diffraction | Trættestad, Paulen & Hope (1973) |

* Average value.

The $sp-sp^2$ C=C< bonds in the butatrienes studied are all longer than the corresponding bond in allene and its derivatives (1.308–1.315 Å, Tables 12 and 13). In the allene derivatives the length of the $sp-sp^2$ C=C< bond (1.310 ± 0.005 Å) seems to be independent of the type of substituents attached.

A comparison between bond lengths derived at both temperatures (Table 6) shows that those obtained from the room-temperature structure analysis are all consistently shorter than those obtained at -160°C. This type of shortening has been explained in terms of libration and bonding (O'Connell, Rae & Maslen, 1966). In order to provide a quantitative measure of these effects we refined the atomic parameters (x, y, z, u) and scale factor of the room-temperature structure incorporating fixed deformation parameters obtained from the low-temperature analysis. Table 14 lists the averaged bond lengths of chemically equivalent bonds resulting from this analysis, as well as the bond lengths of the refined low-temperature structure before inclusion of the deformation parameters (stage b of refinement). The contribution of the asymmetric electron density to bond shortening appears to be negligible at both temperatures for all the C–C bond types, since the difference in averaged bond lengths with and without the deformation model are of the order of 0.003 Å. Thus the shortening of the bonds appears to be mainly a consequence of libration. This is further substantiated by the fact that the shortening of the lengths reduces systematically from 0.02 Å for

bonds on the periphery of the molecule, where the libration is most pronounced, to 0.00 Å for bonds close to the centre of the molecule where the libration is minimal. The only anomaly lies in the lengths of the central C=C bond (RT 1.248, LT 1.260 Å) for which the difference is 0.012 Å and which cannot be due to libration and also cannot be accounted for by the bonding charge in the C=C bonds.

Charge deformation maps

Electron density difference maps ($\delta\rho$) were obtained by plotting the sum of the deformation functions around each atom with coefficients determined by the least-squares refinement. No inner contours have been drawn within about 0.3 Å of the atomic centres since the calculated values of $\delta\rho$ in these regions are almost entirely without experimental significance. This agrees with the general conclusion of Stewart (1968) about the effect of uncertainty in the vibration amplitudes on the difference density near a first-row nucleus. In most other positions the standard deviations, derived from the least-squares covariance matrix, are well below 0.1 e Å⁻³, the interval between adjacent contours. Accordingly all bond peaks and troughs in the figures may be regarded as experimentally significant in their general appearance. The deformation maps show accumulation of charge between bonded atoms, and the atomic centres are placed in troughs of negative density, indicating migration of charge from the close vicinity of the atoms to the bonds, owing to the formation of a molecule.

In the butatriene plane (Fig. 2) the peak heights (in e Å⁻³) at the bond centres are: 0.89 (±0.06), 0.75 (±0.06) and 0.47 (±0.03) for the 'inner' (=C=C=) and 'outer' (>C=C=) double bonds, and for the single (φ -C=) bond respectively. The density sections perpendicular to the former two bonds through their centres (Fig. 3) are elliptic in shape with their long axes mutually perpendicular; the charge in the outer C=C bond is elongated along the normal to the butatriene plane while that in the inner C=C bond is elongated in the plane. These charge distributions are in agreement with classical theory of π electrons in cumulenic systems.

Table 14. Comparison between average bond lengths (Å) obtained at 20°C and -160°C with and without the deformation model

| Bond† | Room temperature | | Low temperature | | Δ^* |
|-------|-------------------|----------------|-------------------|----------------|------------|
| | Without the model | With the model | Without the model | With the model | |
| | 1.378 | 1.381 | 1.391 | 1.398 | 0.017 |
| | 1.383 | 1.378 | 1.389 | 1.393 | 0.015 |
| | 1.395 | 1.396 | 1.404 | 1.406 | 0.01 |
| | 1.482 | 1.478 | 1.482 | 1.478 | 0.00 |
| | 1.345 | 1.346 | 1.346 | 1.348 | 0.002 |
| | 1.246 | 1.248 | 1.258 | 1.260 | 0.012 |

* The difference between bond lengths obtained at low temperature and room temperature, with the deformation model.

† The bold lines indicate the bonds which were averaged.

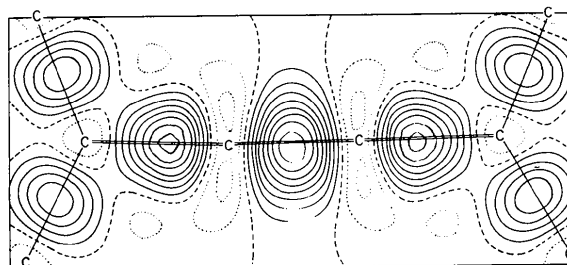


Fig. 2. Deformation density in the butatriene system ($>=C=C<$) of tetraphenylbutatriene. Contour interval 0.1 e Å⁻³. Zero contour broken, negative contours dotted.

The electron density peak in the inner C=C bond (Fig. 3) appears more circular in shape than that in the outer C=C bond, suggesting a measure of out-of-plane π density in this bond, in addition to the π density in the plane of the butatriene system. Moreover, as mentioned above, this inner C=C bond is decidedly shorter (1.260 vs 1.348 Å), and contains more electrons (0.3 vs 0.22 e) than the outer C=C bond (Berkovitch-Yellin & Leiserowitz, 1975) implying some C \equiv C triple-bond character for this bond. If the density sections of the two adjacent C=C double bonds are treated as formally consisting of both a σ component, with cylindrical symmetry about the C=C bond, and a π component, the ' π -bonding density' may be extracted. The π components of the density sections perpendicular to the two C=C bonds through their centres are shown in Fig. 4. The peaks of the π components lie 0.55 Å above and below the butatriene system in the outer bonds and 0.45 Å from the C=C bond axis in the plane of the butatriene system for the inner bond. The peak values are 0.19 and 0.28 e Å⁻³ for the outer and inner bonds respectively. The deformation density section through the plane of one of the phenyl rings is shown in Fig. 5. The average difference densities in the ring plane display features which have been predicted by Dawson (1965) from symmetry considerations, and which have been observed in studies of benzene derivatives

(O'Connell, Rae & Maslen, 1966), such as excess density between bonded atoms, shallow troughs of negative difference density at the atomic centres and a trough of negative charge density in the centre of the ring. The peak heights close to the centres of the C—C bonds are 0.66 for the aromatic bonds and 0.47 e Å⁻³ for the exocyclic bond. The H atoms show pronounced contraction of charge density, a feature which was described by Ruedenberg (1962) and by Hirshfeld & Rztokiewicz (1974). Density sections perpendicular to one of the aromatic C—C bonds and one of the exocyclic C—C bonds are shown in Fig. 6. The density peak in the aromatic bond is elongated in the direction perpendicular to the phenyl-ring plane. This charge distribution is in accordance with the well-known picture of π density above and below the phenyl plane. The density section through the exocyclic bond appears to be completely circular and thus this bond is purely σ .

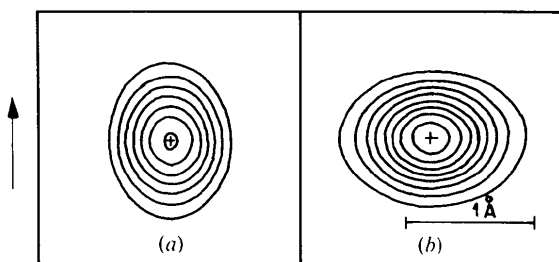


Fig. 3. Deformation density sections perpendicular to (a) the 'outer' bond and (b) the 'inner' bond of the butatriene chain through their centres. Contours as in Fig. 2. The arrow indicates the direction perpendicular to the butatriene plane.

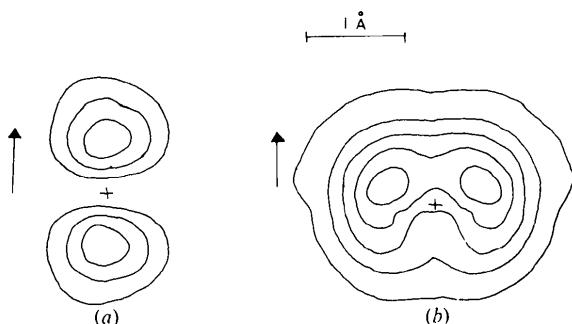


Fig. 4. π -Density diagrams in the sections perpendicular to (a) the 'outer' bond and (b) the 'inner' bond of the butatriene chain through their centres. Contours as in Fig. 2. The arrow indicates the direction perpendicular to the butatriene plane.

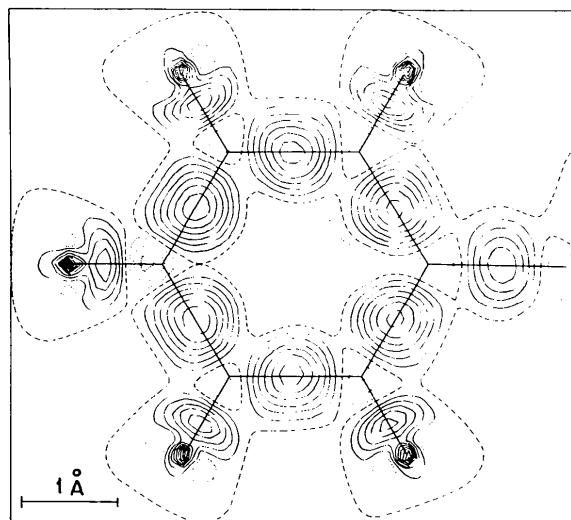


Fig. 5. Deformation density section through the plane of a phenyl ring. Contours as in Fig. 2.

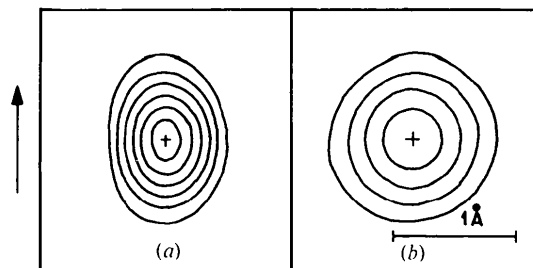


Fig. 6. Deformation density sections perpendicular to (a) an aromatic bond and (b) an exocyclic bond of a phenyl ring through their centres. The arrow indicates the direction perpendicular to the phenyl plane.

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References

- ABRAHAMS, S. C., ROBERTSON, J. M. & WHITE, J. G. (1949). *Acta Cryst.* **2**, 233–244.
- ALMENNINGEN, A., BASTIANSEN, O. & TRÆTTEBERG, M. (1959). *Acta Chem. Scand.* **13**, 1699–1702.
- ALMENNINGEN, A., BASTIANSEN, O. & TRÆTTEBERG, M. (1961). *Acta Chem. Scand.* **15**, 1557–1562.
- ALMENNINGEN, A., GUNDERSEN, G., BORG, A., GRANBERG, M. & KARLSSON, F. (1975). *Acta Chem. Scand.* **A29**, 395–403.
- BASTIANSEN, O. (1949). *Acta Chem. Scand.* **3**, 408–414.
- BERKOVITCH-YELLIN, Z. (1976). PhD Thesis, Weizmann Institute of Science, Rehovot, Israel.
- BERKOVITCH-YELLIN, Z., LAHAV, M. & LEISEROWITZ, L. (1974). *J. Amer. Chem. Soc.* **96**, 918–920.
- BERKOVITCH-YELLIN, Z. & LEISEROWITZ, L. (1975). *J. Amer. Chem. Soc.* **97**, 5627–5628.
- BERKOVITCH-YELLIN, Z., LEISEROWITZ, L. & NADER, F. (1977). *Acta Cryst.* **B33**, 3670–3677.
- BOLHUIS, F. VAN (1971). *J. Appl. Cryst.* **4**, 263–264.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc.* **A247**, 1–21.
- DAWSON, B. (1965). *Aust. J. Chem.* **18**, 595–603.
- FRANK, J. K. & PAUL, I. C. (1973). *J. Amer. Chem. Soc.* **95**, 2324–2332.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–375.
- GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
- GROTH, P. (1973). *Acta Chem. Scand.* **27**, 3302–3306.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HAREL, M. (1974). PhD Thesis, Weizmann Institute of Science, Rehovot, Israel.
- HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* **B31**, 162–172.
- HEHRE, W. J., LATHAN, W. A., DITCHFIELD, R., NEWTON, M. W. & POPLE, J. A. (1970). Quantum Chemistry Program Exchange, Indiana Univ., Bloomington, Indiana, Program No. 236.
- HIRSHFELD, F. L. (1971). *Acta Cryst.* **B27**, 769–781.
- HIRSHFELD, F. L. & RZOTKIEWICZ, S. (1974). *Mol. Phys.* **27**, 1319–1343.
- HOEKSTRA, A. & VOS, A. (1975). *Acta Cryst.* **B31**, 1722–1729.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- IRNGARTINGER, H. (1975). Private communication.
- IRNGARTINGER, H. & JÄGER, H. U. (1976). *Angew. Chem. Int. Ed.* **9**, 562–563.
- KITAIGORODSKII, A. I. (1955). *Organic Chemical Crystallography*, p. 96. New York: Consultants Bureau.
- LAHAV, M. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. (B)*, pp. 312–321.
- LEISEROWITZ, L. & NADER, F. (1973). *Angew. Chem. Int. Ed.* **12**, 158–159.
- NADER, F. (1976). *Liebigs Ann.* Submitted for publication.
- O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208–219.
- RABINOVICH, D., SCHMIDT, G. M. J. & UBELL, E. (1967). *J. Chem. Soc. (B)*, pp. 131–139.
- RUEDENBERG, K. (1962). *Rev. Mod. Phys.* **34**, 326–376.
- SCHMIDT, G. M. J. (1971). *Pure Appl. Chem.* **27**, 647–678.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SINCLAIR, V. C., ROBERTSON, J. M. & MATHIESON, A. McL. (1950). *Acta Cryst.* **3**, 251–256.
- STEWART, R. F. (1968). *Acta Cryst.* **A24**, 497–505.
- STOICHEFF, B. P. (1955). *Canad. J. Phys.* **33**, 811–818.
- STOICHEFF, B. P. (1957). *Canad. J. Phys.* **35**, 837–841.
- TRÆTTEBERG, M., PAULEN, G. & HOPE, H. (1973). *Acta Chem. Scand.* **27**, 2225–2229.
- TROTTER, J. (1961). *Acta Cryst.* **14**, 1135–1140.