

Fig. 2. Space-filling model of (I) showing the steric congestion between the *tert*-butyl groups which opened the *tert*-Bu—C=C angle.

the rings remain planar, within 0.01 Å of a common plane, and there was no pyramidalization at C(11) or C(17) (Tirado-Rives, Fronczek & Gandour, 1985). As often happens in hydrocarbons, additional strain relief was obtained by stretching the *tert*-Bu—C bonds to 1.556 (5) Å.

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## 2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one and 5,6,7,8-Tetrachloro-3a,9a-dihydro-2,3,3a,9a-tetraphenylcyclopenta[2,3-*b*][1,4]benzodioxin-1-one-toluene (2/1): Compounds of Photochemical Interest

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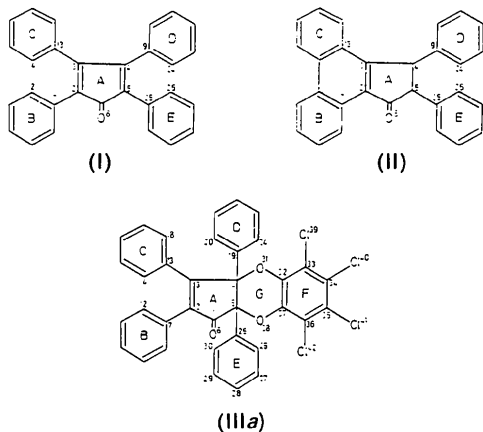
(Received 22 February 1990; accepted 23 April 1990)

**Abstract.** (I)  $C_{29}H_{20}O$ ,  $M_r = 384.45$ , monoclinic,  $C2/c$ ,  $a = 26.16$  (2),  $b = 8.38$  (1),  $c = 21.57$  (2) Å,  $\beta = 119.5$  (2)°,  $V = 4115.6$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.24$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 4.9$  cm<sup>-1</sup>,  $F(000) = 1616$ ,  $T = 293$  K,  $R = 0.063$  for 1789 reflexions. (IIIa)  $C_{35}H_{20}Cl_4O_3 \cdot 0.5C_7H_8$ ,  $M_r = 676.42$ , monoclinic,  $P2_1/a$ ,  $a = 18.26$  (2),  $b = 10.50$  (1),  $c = 17.74$  (2) Å,  $\beta = 109.6$  (1)°,  $V = 3204.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.40$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 35.2$  cm<sup>-1</sup>,  $F(000) = 1394$ ,  $T = 293$  K,  $R = 0.079$  for 2461 reflexions. The mechanisms of photolytic ring closure in tetraphenylcyclopentadienone (I) and its adduct (IIIa) with tetrachloro-*o*-benzoquinone are still in doubt. In the crystal the non-bonded C···C distances of the atoms linked during photolysis are 3.264 (6) Å

(I) and 3.208 (7) Å (IIIa). Packing-energy calculations suggest that the observed structures are stabilized by lattice forces and that the phenyl groups are further from coplanarity with the central ring in the free molecule.

**Introduction.** The photochemical behaviour of tetraphenylcyclopentadienone (I) and its derivatives is complicated by apparent hydrogen-abstraction reactions (Toshima & Moritani, 1967) as well as *cis*-stilbene-type cyclization to phenanthrocyclopentenones (II) (Moritani, Toshima, Nakagawa & Yakushiji, 1967). High yields of (II) can be obtained by the irradiation of adducts (III) of tetraaryl substituted cyclopentadienones (Horspool, 1969, 1971).

These adducts are readily prepared by the thermal reaction of the cyclopentadienones with tetrachloro-*o*-benzoquinone.



In the general molecule (III), rings *B*, *C*, *D* and *E* can be any aryl group

The first step in the photolysis of the cyclopentadienone (I) seems likely to be the reduction to the cyclopentenone followed by the *cis*-stilbene-type cyclization. Cyclopentenones with built-in leaving groups undergo the same facile cyclization but in our examples (Horspool 1969, 1971) the formation of the final product involved the elimination of a leaving group, a built-in oxidant.

The crystal structures of tetraphenylcyclopentadienone (I) and of the adduct [(IIIa); Ar = phenyl, toluene solvate] have now been investigated to see if the distance between the *ortho* positions of the phenyl groups on C2 and C3 of the ring is more favourable for bond formation in the adduct than in the parent compound.

**Experimental.** All calculations were performed on the Dundee University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). The atomic scattering parameters stored in *SHELX76* were used.

Compound (I) was prepared by the method of Allen & Van Allan (1950) and recrystallized from ethyl acetate as dark-purple plates (0.42 × 0.30 × 0.07 mm). After preliminary oscillation and Weissenberg photographs, data were collected by equi-inclination Weissenberg photographs ( $2\theta_{\max} = 155^\circ$ ) for layers 0–18 *kl* and *h* 0–1 *l* of the diagonal cell in space group *I2/a* and reindexed to the standard setting, *C2/c* ( $-29 \leq h \leq 24$ ;  $0 \leq k \leq 9$ ;  $0 \leq l \leq 24$ ). Unit-cell parameters were refined during intensity measurement by the SERC Microdensitometer Service at Daresbury Laboratory, using a least-squares

procedure based on all observed reflexions. Data were corrected for the Lorentz and polarization terms but not for absorption. The 4209 measured reflexions gave 1789 unique reflexions above background, with  $R_{\text{int}} 0.082$ . Almost all of these reflexions were measured more than once. Visual estimation of nine very strong planes and addition of 141 unobserved reflexions [set at  $0.5(F_o)_{\min}$ ] gave 1939 unique reflexions used in the solution of the structure by the direct-methods routine *TANG* (part of *SHELX76*). The best *E* maps showed all non-H atoms. Refinement proceeded by conventional least-squares analysis and difference synthesis using only the 1789 measured reflexions. In the final cycles anisotropic thermal parameters were used for all non-H atoms. The H atoms were placed in calculated positions with a single refinable isotropic thermal parameter for the hydrogens of each phenyl group.

Final refinement (minimizing  $\sum w||F_o - |F_c||^2$ ): 282 refined parameters,  $R = 0.063$ ,  $wR = 0.090$ ,  $w = 1.00/(1.00 + 0.020835F^2)$ , mean shift/e.s.d. = 0.006, max. shift/e.s.d. = 0.029, max. difference map features 0.33,  $-0.28 \text{ e } \text{Å}^{-3}$ .

Compound (IIIa) was prepared by the method of Horspool (1971) and recrystallized from a mixture of ethanol and toluene to give pale-yellow plates (0.55 × 0.37 × 0.17 mm). Data were collected as described for compound (I) for layers 0–10 *kl* and *h* 0–9 *l* to give 6715 measured reflexions ( $2\theta_{\max} = 155^\circ$ ) reducing to 2461 unique reflexions with  $R_{\text{int}} 0.056$  ( $-20 \leq h \leq 19$ ;  $0 \leq k \leq 12$ ;  $0 \leq l \leq 21$ ). Almost all of these reflexions were measured more than once. The structure was solved without data enhancement using the direct methods routine *EEES* (part of *SHELX76*). The best *E* maps showed peaks for 21 atoms. The structure was extended by conventional least-squares refinement and difference synthesis to show all non-H atoms ( $R = 0.37$ ). Refinement continued with anisotropic thermal parameters for all non-H atoms and the H atoms in calculated positions to  $R = 0.12$  when inspection of the difference map revealed features close to the centre of inversion at 0.5, 0.5, 0.5. Comparison of these features with NMR data indicated the presence of a toluene molecule. Attempts to refine this both unconstrained and as a rigid group indicated that it is disordered over several closely adjacent positions as well as the end-for-end disorder required by the centre of inversion (see below). Since the main interest centred on the larger molecule the toluene was included in the final cycle of refinement with fixed, compromise, atomic coordinates and isotropic thermal parameters.

Final refinement (minimizing  $\sum w||F_o - |F_c||^2$ ): 474 refined parameters,  $R = 0.079$ ,  $wR = 0.099$ ,  $w = 1.00/(1.00 + 0.013885F^2)$ , mean shift/e.s.d. = 0.062, max. shift/e.s.d. = 0.228, max. features on difference map 1.14 (near toluene),  $-0.51 \text{ e } \text{Å}^{-3}$ .

Table 1. *Tetraphenylcyclopentadienone*: coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\times 10^3$ ) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|     | x        | y        | z        | $U_{eq}(\text{\AA}^2)$ |
|-----|----------|----------|----------|------------------------|
| C1  | 2189 (1) | 5000 (5) | 4548 (2) | 41 (1)                 |
| C2  | 1834 (1) | 4967 (4) | 4921 (2) | 39 (1)                 |
| C3  | 2227 (1) | 4951 (4) | 5629 (1) | 35 (1)                 |
| C4  | 2847 (1) | 5066 (4) | 5737 (2) | 35 (1)                 |
| C5  | 2825 (1) | 5102 (5) | 5105 (2) | 39 (1)                 |
| O6  | 1998 (1) | 4897 (4) | 3913 (1) | 65 (1)                 |
| C7  | 1194 (1) | 5031 (5) | 4542 (2) | 41 (1)                 |
| C8  | 864 (2)  | 4281 (6) | 3878 (2) | 54 (1)                 |
| C9  | 256 (2)  | 4333 (7) | 3526 (2) | 73 (1)                 |
| C10 | -31 (2)  | 5145 (7) | 3807 (3) | 77 (1)                 |
| C11 | 281 (2)  | 5915 (6) | 4453 (2) | 70 (1)                 |
| C12 | 889 (1)  | 5866 (5) | 4814 (2) | 51 (1)                 |
| C13 | 2101 (1) | 4794 (4) | 6218 (2) | 35 (1)                 |
| C14 | 1711 (1) | 3628 (5) | 6189 (2) | 40 (1)                 |
| C15 | 1560 (1) | 3495 (5) | 6712 (2) | 48 (1)                 |
| C16 | 1807 (2) | 4511 (5) | 7294 (2) | 48 (1)                 |
| C17 | 2203 (2) | 5650 (5) | 7340 (2) | 47 (1)                 |
| C18 | 2354 (1) | 5789 (5) | 6814 (2) | 41 (1)                 |
| C19 | 3371 (1) | 5138 (5) | 6453 (2) | 39 (1)                 |
| C20 | 3506 (2) | 3897 (5) | 6933 (2) | 49 (1)                 |
| C21 | 4015 (2) | 3974 (7) | 7597 (2) | 70 (1)                 |
| C22 | 4377 (2) | 5278 (9) | 7773 (2) | 80 (2)                 |
| C23 | 4243 (2) | 6506 (8) | 7312 (2) | 71 (1)                 |
| C24 | 3743 (1) | 6442 (6) | 6641 (2) | 52 (1)                 |
| C25 | 3302 (1) | 5074 (5) | 4919 (2) | 41 (1)                 |
| C26 | 3846 (1) | 4406 (5) | 5373 (2) | 48 (1)                 |
| C27 | 4273 (2) | 4326 (6) | 5169 (2) | 58 (1)                 |
| C28 | 4165 (2) | 4908 (6) | 4520 (2) | 58 (1)                 |
| C29 | 3624 (2) | 5588 (6) | 4063 (2) | 57 (1)                 |
| C30 | 3194 (2) | 5684 (5) | 4261 (2) | 48 (1)                 |

Table 2. *5,6,7,8-Tetrachloro-3a,9a-dihydro-2,3,3a,9a-tetraphenylcyclopenta[2,3-b][1,4]benzodioxin-1-one-toluene (2/1)*: coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\times 10^3$ ) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|      | x         | y         | z         | $U_{eq}(\text{\AA}^2)$ |
|------|-----------|-----------|-----------|------------------------|
| C1   | 7064 (4)  | 2122 (5)  | 3443 (4)  | 37 (2)                 |
| C2   | 7496 (4)  | 2879 (5)  | 3013 (4)  | 36 (2)                 |
| C3   | 7317 (3)  | 2455 (5)  | 2262 (3)  | 28 (1)                 |
| C4   | 6834 (3)  | 1218 (5)  | 2144 (3)  | 29 (1)                 |
| C5   | 6442 (4)  | 1320 (5)  | 2795 (4)  | 30 (1)                 |
| O6   | 7149 (3)  | 2160 (4)  | 4130 (3)  | 55 (2)                 |
| C7   | 8059 (4)  | 3847 (6)  | 3432 (4)  | 34 (2)                 |
| C8   | 7847 (5)  | 4800 (7)  | 3876 (5)  | 59 (3)                 |
| C9   | 8415 (7)  | 5715 (7)  | 4283 (5)  | 68 (3)                 |
| C10  | 9174 (6)  | 5689 (7)  | 4274 (5)  | 65 (3)                 |
| C11  | 9373 (5)  | 4749 (8)  | 3839 (5)  | 59 (3)                 |
| C12  | 8835 (4)  | 3846 (6)  | 3434 (5)  | 46 (2)                 |
| C13  | 7566 (4)  | 2983 (5)  | 1612 (4)  | 31 (2)                 |
| C14  | 7741 (4)  | 4308 (5)  | 1617 (4)  | 38 (2)                 |
| C15  | 8009 (5)  | 4797 (6)  | 1035 (5)  | 52 (3)                 |
| C16  | 8086 (4)  | 4052 (6)  | 429 (5)   | 46 (2)                 |
| C17  | 7868 (4)  | 2739 (6)  | 410 (4)   | 41 (2)                 |
| C18  | 7641 (4)  | 2233 (6)  | 1002 (4)  | 35 (2)                 |
| C19  | 7340 (4)  | 30 (5)    | 2251 (4)  | 28 (1)                 |
| C20  | 8054 (4)  | -41 (6)   | 2874 (4)  | 39 (2)                 |
| C21  | 8487 (4)  | -1155 (6) | 3019 (4)  | 39 (2)                 |
| C22  | 8220 (4)  | -2243 (6) | 2568 (4)  | 43 (2)                 |
| C23  | 7510 (5)  | -2163 (6) | 1955 (5)  | 54 (3)                 |
| C24  | 7067 (4)  | -1049 (6) | 1801 (4)  | 36 (2)                 |
| C25  | 6170 (4)  | 59 (6)    | 3023 (4)  | 37 (2)                 |
| C26  | 6593 (5)  | -578 (7)  | 3708 (5)  | 54 (2)                 |
| C27  | 6338 (6)  | -1790 (9) | 3858 (6)  | 71 (3)                 |
| C28  | 5696 (6)  | -2336 (9) | 3334 (6)  | 73 (1)                 |
| C29  | 5279 (5)  | -1722 (8) | 2647 (6)  | 62 (3)                 |
| C30  | 5499 (5)  | -494 (7)  | 2493 (5)  | 54 (3)                 |
| O31  | 6248 (3)  | 1112 (4)  | 1361 (3)  | 33 (1)                 |
| C32  | 5683 (4)  | 2032 (5)  | 1189 (4)  | 35 (2)                 |
| C33  | 5288 (4)  | 2344 (6)  | 397 (4)   | 38 (2)                 |
| C34  | 4710 (4)  | 3313 (6)  | 223 (5)   | 42 (2)                 |
| C35  | 4541 (4)  | 3928 (6)  | 828 (5)   | 48 (2)                 |
| C36  | 4925 (4)  | 3583 (6)  | 1613 (5)  | 47 (2)                 |
| C37  | 5488 (4)  | 2595 (6)  | 1800 (4)  | 38 (2)                 |
| O38  | 5789 (3)  | 2220 (4)  | 2568 (3)  | 46 (1)                 |
| C139 | 5514 (1)  | 1532 (2)  | -331 (1)  | 53 (1)                 |
| C140 | 4222 (1)  | 3683 (2)  | -764 (1)  | 65 (1)                 |
| C141 | 3875 (1)  | 5156 (2)  | 611 (2)   | 72 (1)                 |
| C142 | 4708 (1)  | 4288 (2)  | 2387 (2)  | 72 (1)                 |
| C51  | 5508 (13) | 4979 (21) | 4884 (13) | 172 (7)                |
| C52  | 5302 (6)  | 6005 (9)  | 5260 (6)  | 72 (3)                 |
| C53  | 4730 (12) | 6290 (18) | 5448 (13) | 163 (7)                |
| C54* | 6094 (11) | 4647 (17) | 4742 (11) | 67 (5)                 |

\* This atom has site-occupancy factor 0.50.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters for (I) and (IIIa) are given in Tables 1 and 2.\* Tables 3 and 4 contain interatomic distances and angles. The molecules are shown in Figs. 1 and 2.

An isolated tetraphenylcyclopentadienone molecule has a possible C<sub>2</sub> axis through C1 and O6. Fig. 1 shows that this idealized conformation is not approached in the crystal. Ring *A* is planar to within 0.02 Å. The angles between the normal to this plane and the normal to planes *B*, *C*, *D* and *E* are 35.3 (2), 132.7 (4), 61.1 (3) and 28.0 (2)°, respectively, to give a four-bladed propeller with the blades alternately above and below ring *A*. Rings *B* and *E* have C10 and C28 0.369 and -0.359 Å from plane *A*, whereas ring *C* has C16 0.253 Å from plane *A* and ring *D* has C22 only 0.066 Å from this plane.

*cis*-Stilbene-type photocyclization could occur at two structurally different sites in this molecule, between C12 and C14 or between C24 and C26. In the crystal the distances between these pairs of C atoms are 3.264 (6) and 3.346 (6) Å, respectively. In each case the rings are well placed for conrotatory cyclization in which the protons to be lost are

arranged *trans* across the incipient bond. However, there is no evidence for the formation of any product with more than one ring closure.

In (IIIa) ring *A* is less planar than in (I). The atoms lie within 0.18 Å of the best plane. Phenyl groups *D* and *E* are forced away from plane *A* and can take no part in cyclization reactions. C22 is 4.348 (6) Å from plane *A* and C28 1.672 (5) Å. Ring *G* adopts a twist-boat configuration with O31, C32, C37 and O38 close to planar. The normal to the mean plane of ring *F* makes an angle of 88.9 (4)° to the normal to plane *A* but the projection of C32—C37 onto plane *A* lies at 34° to C4—C5. The torsion angle C5—O38—C37—C32 is 9.5 (4)° whereas the corresponding angle C4—O31—C32—C37 is -28.7 (5)°. The four Cl atoms lie within 0.09 Å of plane *F*. As in (I), cyclization can occur by a conrotatory motion of rings *B* and *C*. In

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53214 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Tetraphenylcyclopentadienone: interatomic distances (Å) and angles (°)*

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| C2—C1       | 1.500 (6) | C5—C1       | 1.500 (4) |
| O6—C1       | 1.208 (4) | C3—C2       | 1.358 (4) |
| C7—C2       | 1.458 (4) | C4—C3       | 1.524 (5) |
| C13—C3      | 1.466 (6) | C5—C4       | 1.338 (5) |
| C19—C4      | 1.478 (4) | C25—C5      | 1.484 (6) |
| C8—C7       | 1.406 (5) | C12—C7      | 1.389 (6) |
| C9—C8       | 1.385 (5) | C10—C9      | 1.359 (9) |
| C11—C10     | 1.380 (7) | C12—C11     | 1.383 (5) |
| C14—C13     | 1.392 (5) | C18—C13     | 1.397 (5) |
| C15—C14     | 1.370 (6) | C16—C15     | 1.386 (6) |
| C17—C16     | 1.375 (6) | C18—C17     | 1.377 (7) |
| C20—C19     | 1.385 (6) | C24—C19     | 1.383 (6) |
| C21—C20     | 1.397 (4) | C22—C21     | 1.371 (9) |
| C23—C22     | 1.352 (9) | C24—C23     | 1.394 (5) |
| C26—C25     | 1.387 (5) | C30—C25     | 1.400 (6) |
| C27—C26     | 1.389 (7) | C28—C27     | 1.374 (7) |
| C29—C28     | 1.388 (5) | C30—C29     | 1.388 (8) |
|             |           |             |           |
| C5—C1—C2    | 108.0 (3) | O6—C1—C2    | 125.9 (3) |
| O6—C1—C5    | 126.0 (4) | C3—C2—C1    | 106.1 (3) |
| C7—C2—C1    | 122.9 (3) | C7—C2—C3    | 130.9 (4) |
| C4—C3—C2    | 109.3 (3) | C13—C3—C2   | 127.3 (3) |
| C13—C3—C4   | 123.3 (2) | C5—C4—C3    | 109.8 (2) |
| C19—C4—C3   | 122.2 (3) | C19—C4—C5   | 128.0 (3) |
| C4—C5—C1    | 106.7 (3) | C25—C5—C1   | 122.1 (3) |
| C25—C5—C4   | 130.9 (3) | C8—C7—C2    | 120.9 (4) |
| C12—C7—C2   | 121.4 (3) | C12—C7—C8   | 117.7 (3) |
| C9—C8—C7    | 120.4 (4) | C10—C9—C8   | 120.7 (4) |
| C11—C10—C9  | 120.1 (4) | C12—C11—C10 | 120.0 (5) |
| C11—C12—C7  | 121.1 (4) | C14—C13—C3  | 119.8 (3) |
| C18—C13—C3  | 122.5 (3) | C18—C13—C14 | 117.7 (4) |
| C15—C14—C13 | 121.4 (3) | C16—C15—C14 | 120.1 (4) |
| C17—C16—C15 | 119.4 (5) | C18—C17—C16 | 120.7 (4) |
| C17—C18—C13 | 120.7 (4) | C20—C19—C4  | 120.9 (3) |
| C24—C19—C4  | 119.7 (3) | C24—C19—C20 | 119.4 (3) |
| C21—C20—C19 | 119.6 (4) | C22—C21—C20 | 120.1 (5) |
| C23—C22—C21 | 120.6 (4) | C24—C23—C22 | 120.3 (5) |
| C23—C24—C19 | 120.0 (4) | C26—C25—C5  | 121.5 (4) |
| C30—C25—C5  | 119.4 (3) | C30—C25—C26 | 119.1 (4) |
| C27—C26—C25 | 120.2 (4) | C28—C27—C26 | 120.7 (4) |
| C29—C28—C27 | 119.8 (5) | C30—C29—C28 | 120.1 (5) |
| C29—C30—C25 | 120.1 (3) |             |           |

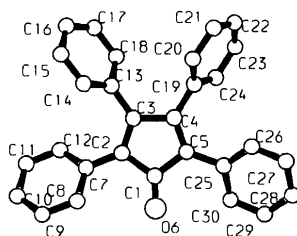
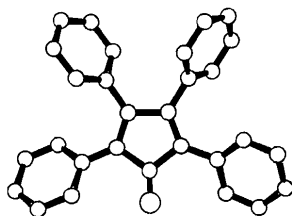


Fig. 1. Stereopair showing tetraphenylcyclopentadienone (I), viewed normal to the five-membered ring.

Fig. 2. Stereopair showing packing of structure (IIIa), including the disordered toluene, viewed down *b*.Table 4. *5,6,7,8-Tetrachloro-3a,9a-dihydro-2,3,3a,9a-tetraphenylcyclopenta[2,3-*b*][1,4]benzodioxin-1-one-toluene (2/1): interatomic distances (Å) and angles (°)*

|             |            |              |            |
|-------------|------------|--------------|------------|
| C2—C1       | 1.496 (10) | C21—C20      | 1.387 (9)  |
| C5—C1       | 1.563 (8)  | C22—C21      | 1.386 (9)  |
| O6—C1       | 1.178 (9)  | C23—C22      | 1.387 (10) |
| C3—C2       | 1.338 (9)  | C24—C23      | 1.396 (10) |
| C7—C2       | 1.459 (8)  | C26—C25      | 1.376 (10) |
| C4—C3       | 1.545 (7)  | C30—C25      | 1.396 (10) |
| C13—C3      | 1.480 (10) | C27—C26      | 1.410 (13) |
| C5—C4       | 1.552 (10) | C28—C27      | 1.356 (13) |
| C19—C4      | 1.526 (8)  | C29—C28      | 1.363 (13) |
| O31—C4      | 1.445 (6)  | C30—C29      | 1.405 (12) |
| C25—C5      | 1.515 (9)  | C32—O31      | 1.371 (7)  |
| O38—C5      | 1.468 (8)  | C33—C32      | 1.386 (9)  |
| C8—C7       | 1.405 (11) | C37—C32      | 1.382 (11) |
| C12—C7      | 1.417 (11) | C34—C33      | 1.424 (9)  |
| C9—C8       | 1.421 (12) | C139—C33     | 1.709 (8)  |
| C10—C9      | 1.391 (17) | C35—C34      | 1.371 (13) |
| C11—C10     | 1.374 (13) | C140—C34     | 1.722 (7)  |
| C12—C11     | 1.381 (10) | C126—C35     | 1.381 (11) |
| C14—C13     | 1.428 (8)  | C141—C35     | 1.725 (7)  |
| C18—C13     | 1.382 (10) | C37—C36      | 1.419 (9)  |
| C15—C14     | 1.382 (12) | C142—C36     | 1.719 (10) |
| C16—C15     | 1.374 (12) | O38—C37      | 1.345 (9)  |
| C17—C16     | 1.432 (9)  | C52—C51      | 1.383 (26) |
| C18—C17     | 1.360 (11) | C54—C51      | 1.230 (34) |
| C20—C19     | 1.401 (8)  | C53—C52      | 1.235 (28) |
| C24—C19     | 1.379 (8)  |              |            |
|             |            |              |            |
| C5—C1—C2    | 106.8 (5)  | C24—C19—C4   | 120.9 (5)  |
| O6—C1—C2    | 126.9 (6)  | C24—C19—C20  | 118.2 (5)  |
| O6—C1—C5    | 126.2 (7)  | C21—C20—C19  | 120.9 (6)  |
| C3—C2—C1    | 109.7 (5)  | C22—C21—C20  | 121.4 (6)  |
| C7—C2—C1    | 120.8 (6)  | C23—C22—C21  | 117.2 (6)  |
| C7—C2—C3    | 129.3 (7)  | C24—C23—C22  | 122.1 (6)  |
| C4—C3—C2    | 110.6 (6)  | C23—C24—C19  | 120.1 (6)  |
| C13—C3—C2   | 127.9 (5)  | C26—C25—C5   | 121.6 (6)  |
| C13—C3—C4   | 121.3 (5)  | C30—C25—C5   | 118.4 (6)  |
| C5—C4—C3    | 103.1 (5)  | C30—C25—C26  | 119.9 (7)  |
| C19—C4—C3   | 112.0 (5)  | C27—C26—C25  | 118.8 (7)  |
| C19—C4—C5   | 112.0 (5)  | C28—C27—C26  | 121.1 (8)  |
| O31—C4—C3   | 113.6 (4)  | C29—C28—C27  | 120.5 (9)  |
| O31—C4—C5   | 110.1 (5)  | C30—C29—C28  | 119.8 (8)  |
| O31—C4—C19  | 106.2 (4)  | C29—C30—C25  | 119.7 (7)  |
| C4—C5—C1    | 100.5 (5)  | C32—O31—C4   | 114.8 (5)  |
| C25—C5—C1   | 119.8 (5)  | C33—C32—O31  | 119.3 (7)  |
| C25—C5—C4   | 114.3 (5)  | C37—C32—O31  | 120.0 (6)  |
| O38—C5—C1   | 100.3 (4)  | C37—C32—C33  | 120.7 (6)  |
| O38—C5—C4   | 112.0 (5)  | C34—C33—C32  | 119.0 (7)  |
| O38—C5—C25  | 109.0 (5)  | C139—C33—C32 | 118.2 (5)  |
| C8—C7—C2    | 120.2 (7)  | C139—C33—C34 | 122.8 (5)  |
| C12—C7—C2   | 122.2 (6)  | C35—C34—C33  | 120.8 (7)  |
| C12—C7—C8   | 117.6 (6)  | C140—C34—C33 | 118.3 (6)  |
| C9—C8—C7    | 118.3 (9)  | C140—C34—C35 | 120.9 (5)  |
| C10—C9—C8   | 122.8 (9)  | C36—C35—C34  | 119.6 (7)  |
| C11—C10—C9  | 118.2 (8)  | C141—C35—C34 | 120.3 (6)  |
| C12—C11—C10 | 120.7 (9)  | C141—C35—C36 | 120.1 (7)  |
| C11—C12—C7  | 122.5 (7)  | C37—C36—C35  | 120.7 (8)  |
| C14—C13—C3  | 119.1 (6)  | C142—C36—C35 | 121.2 (6)  |
| C18—C13—C3  | 122.2 (5)  | C142—C36—C37 | 118.1 (6)  |
| C18—C13—C14 | 118.7 (7)  | C36—C37—C32  | 119.1 (7)  |
| C15—C14—C13 | 119.5 (7)  | O38—C37—C32  | 122.9 (6)  |
| C16—C15—C14 | 121.9 (6)  | O38—C37—C36  | 117.9 (7)  |
| C17—C16—C15 | 117.7 (8)  | C37—O38—C5   | 119.0 (6)  |
| C18—C17—C16 | 120.9 (7)  | C54—C51—C52  | 135.7 (20) |
| C17—C18—C13 | 121.1 (6)  | C53—C52—C51  | 135.2 (15) |
| C20—C19—C4  | 120.4 (5)  |              |            |

(IIIa) C12...C14 is 3.208 (7) Å. The stereochemical relationships of rings *A*, *D*, *E* and *G* are very similar to those found in a product obtained from 2,3-diphenylindanone by electrochemical acetoxylation (Delaunay, Simonet & Toupet, 1986).

In a further investigation of the photocyclization reaction, packing-energy calculations have been carried out using the program *OPEC* (Gavezzotti, 1985) on (I) and (IIIa) which cyclize under non-oxidative conditions, on *o*-diphenylbenzene where the distance

in the crystal between the two C atoms which become bonded on cyclization is 3.369 Å (Brown & Levy, 1979) and the reaction occurs only under oxidative conditions (Sato, Goto & Hata, 1967), and on 6,6-dichloro-1-methyl-3,4,5-triphenylbicyclo-[3.1.0]hex-3-en-2-one (IV) (Barnes, Horspool & Mackie, 1990) where C12...C14 is 3.560 (5) Å and no cyclization is observed. [The last-named compound has been numbered like (I) up to C25.] In every calculation each phenyl group in turn has been rotated about its bond to ring A. The effect of these rotations on the lattice energy of the crystal (neglecting dipole terms) and on the interaction packing energy between the chosen phenyl group and the rest of the molecule have been evaluated.

The lattice-energy calculation showed that in every case the observed structure had the minimum energy and that rotation of any phenyl group by  $\pm 15^\circ$  increased the energy by 5–10 kJ mol<sup>-1</sup>. However the local-energy calculation showed that the energy minima usually occurred with the phenyl group rotated 15–30° further away from coplanarity with ring A than the observed structure. For (I) this minimum energy was in the range 4–10 kJ mol<sup>-1</sup> lower than the observed energy. Twisting a phenyl group towards coplanarity with ring A gives a rapid increase in local energy for rings B and C ranging from 49 kJ mol<sup>-1</sup> [ring B, (IV)] to 226 kJ mol<sup>-1</sup> [ring C, (I)] for a 45° rotation. Rotation of ring B of *o*-diphenylbenzene shows an unusually steep well of 35 kJ mol<sup>-1</sup> at 45° and 90 kJ mol<sup>-1</sup> at 30°. The photocyclization process must involve simultaneous rotation of phenyl groups B and C with distortion of ring A to allow the formation of the new C—C bond. These rotations are too complex to be examined with the present program.

The disordered toluene molecule in (IIIa) has been studied by comparing the site of approximately 8.8 × 5.3 × 4.4 Å revealed by a packing calculation (Gavezzotti, 1987) with the observed interatomic

distances, thermal parameters and the final difference map. The only symmetry constraint is that equal numbers of methyl groups must point in opposite directions to satisfy the centre of inversion. There is no requirement for each benzene ring to be symmetrical about the centre of inversion or for all the benzene rings to be coplanar (Jewess, 1982).

This study suggests an 'average molecule' in which the methyl group C54 is displaced towards the centre of inversion and the molecule tilted about C52...C52' to optimize the fit to the cavity. The displacements from the centrosymmetric positions used in the refinement are of the order of 0.2 Å. There are no channels by which the molecule could enter or leave the site so that the toluene must have been included during crystal growth.

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### Structure of Ammonium *p*-Toluenesulfonate

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**Abstract.** NH<sub>4</sub><sup>+</sup>.C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S<sup>-</sup>, *M*<sub>r</sub> = 189.24, orthorhombic, *Pn*2<sub>1</sub>*a* (an alternate setting of *Pna*2<sub>1</sub>, No.

33), *a* = 20.411 (4), *b* = 7.066 (2), *c* = 6.272 (4) Å, *V* = 904.6 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.39 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 3.22 cm<sup>-1</sup>, *F*(000) = 400, *T* = 293 K, final *R* = 0.045 for 596 observed [*F*<sub>o</sub> ≥ 5σ(*F*<sub>o</sub>)] reflex-

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