

high-energy geometry. In (IV), the loss in total conformational energy might be compensated by lowering the lattice energy due to the intermolecular  $\pi$ - $\pi$  charge-transfer interaction as described above.

Comparison of the powder diffraction patterns at 298 and 403 K revealed that all the forms are transformed to the fifth form (V) at 403 K, and that the diffraction pattern of (V) is very similar to that of (II). The transition temperatures measured by differential thermal analysis are 371–391 K, 341 K, 343–383 K, and 356 K for (I), (II), (III) and (IV) respectively. (V) is transformed into (II) at 298 K, but no definite transition point can be found during the cooling process. In (V) the arrangement of dipoles oriented parallel to each other is probably zigzag as in (II) and (IV), in contrast to the straight arrangement in (I) and (III) (Fig. 2). We suppose that the transitions to (V) on heating (I) and (III) accompany rearrangement of these dipoles and, hence, occur over a wide temperature range.

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## The Structure of 2,2',4,4',6,6'-Hexa-*tert*-butylbenzil\*

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### Abstract

The structure of the title compound and a refinement of the parent compound, benzil, have been carried out. The first is  $C_{38}H_{58}O_2$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.973$  (1),  $b = 15.796$  (1),  $c = 22.006$  (2) Å,  $\beta = 90.140$  (7)° at 115 K giving  $Z = 4$  and  $D_c = 1.05$  Mg  $m^{-3}$ .  $R_F$  is 6.4% for 2905 observed reflections. The crystals were bright yellow blocks of square cross section somewhat elongated along [100]. The benzene rings are non-planar because of the crowding of the central part of the molecule. Benzil itself is  $C_{14}H_{10}O_2$ , hexagonal,  $P3_121$ ,  $a = 8.4091$  (8),  $c = 13.672$  (2) Å,

at 298 K,  $Z = 3$  and  $D_c = 1.249$  Mg  $m^{-3}$ .  $R_F$  is 3.2% for 411 observed reflections up to 125°  $2\theta$  with Cu  $K\alpha$  radiation.

### Introduction

The structure of 2,2',4,4',6,6'-hexa-*tert*-butylbenzil has been determined as part of a continuing study of hindered azobenzene derivatives and related compounds (Le Page, Gabe & Wang, 1981; Le Page, Gabe, Wang, Barclay & Holm, 1980). The structure of benzil itself (Brown & Sadanaga, 1965) has been refined from diffractometer data to allow comparisons to be made on results of similar accuracy.

\* NRC No. 18596.

Table 1. Atomic parameters for 2,2',4,4',6,6'-hexa-*tert*-butylbenzil
$$B_{\text{iso}} = \frac{8}{3}\pi^2 (U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )
O(1)	0.4327 (3)	0.19208 (18)	0.94319 (13)	2.72 (18)
C(1)	0.5333 (4)	0.3280 (3)	0.91297 (19)	2.0 (2)
C(2)	0.4753 (4)	0.3955 (3)	0.88213 (18)	2.1 (3)
C(3)	0.5530 (4)	0.4681 (3)	0.87300 (19)	2.2 (3)
C(4)	0.6800 (4)	0.4768 (3)	0.89516 (19)	2.1 (3)
C(5)	0.7265 (4)	0.4140 (3)	0.93410 (20)	2.4 (3)
C(6)	0.6582 (4)	0.3388 (3)	0.94475 (19)	2.3 (3)
C(7)	0.4831 (4)	0.2377 (3)	0.90486 (20)	2.3 (3)
C(8)	0.3260 (4)	0.4033 (3)	0.86225 (20)	2.4 (3)
C(9)	0.7708 (5)	0.5512 (3)	0.87968 (21)	3.2 (3)
C(10)	0.7150 (4)	0.2757 (3)	0.99342 (20)	2.3 (3)
C(81)	0.2384 (5)	0.3272 (3)	0.87785 (22)	3.3 (3)
C(82)	0.3116 (5)	0.4215 (3)	0.79468 (22)	3.3 (3)
C(83)	0.2716 (5)	0.4794 (3)	0.89954 (22)	3.2 (3)
C(91)	0.7014 (5)	0.6176 (3)	0.84044 (22)	3.8 (3)
C(92)	0.8199 (6)	0.5960 (4)	0.93698 (26)	6.4 (5)
C(93)	0.8892 (5)	0.5152 (4)	0.84142 (27)	5.8 (4)
C(101)	0.8425 (5)	0.3083 (3)	1.02203 (22)	3.2 (3)
C(102)	0.7481 (5)	0.1884 (3)	0.96707 (20)	2.6 (3)
C(103)	0.6100 (5)	0.2677 (3)	1.04583 (20)	3.0 (3)
O(1')	0.4575 (3)	0.23884 (19)	0.79573 (13)	2.77 (18)
C(1')	0.5817 (4)	0.1175 (3)	0.83589 (19)	2.0 (3)
C(2')	0.5276 (4)	0.0423 (3)	0.85878 (19)	2.1 (3)
C(3')	0.6154 (4)	-0.0240 (3)	0.87329 (19)	2.2 (3)
C(4')	0.7515 (4)	-0.0184 (3)	0.86503 (19)	2.0 (3)
C(5')	0.8007 (4)	0.0531 (3)	0.83468 (19)	2.3 (3)
C(6')	0.7197 (4)	0.1216 (3)	0.81830 (19)	2.1 (3)
C(7')	0.5039 (4)	0.2002 (3)	0.83873 (20)	2.3 (3)
C(8')	0.3759 (4)	0.0190 (3)	0.86494 (20)	2.3 (3)
C(9')	0.8486 (4)	-0.0863 (3)	0.88697 (20)	2.5 (3)
C(10')	0.7814 (5)	0.1930 (3)	0.77853 (20)	2.7 (3)
C(81')	0.2773 (4)	0.0874 (3)	0.84556 (20)	2.6 (3)
C(82')	0.3448 (5)	-0.0069 (3)	0.93039 (22)	3.1 (3)
C(83')	0.3539 (5)	-0.0589 (3)	0.82263 (22)	3.1 (3)
C(91')	0.9352 (5)	-0.1193 (3)	0.83507 (22)	4.0 (3)
C(92')	0.7750 (5)	-0.1612 (3)	0.91791 (25)	4.3 (4)
C(93')	0.9412 (5)	-0.0454 (3)	0.93567 (22)	3.6 (3)
C(101')	0.7719 (5)	0.2825 (3)	0.80526 (21)	3.0 (3)
C(102')	0.9333 (5)	0.1772 (3)	0.76850 (24)	4.7 (4)
C(103')	0.7117 (6)	0.1906 (3)	0.71632 (21)	4.1 (4)
H(3)	0.522 (3)	0.521 (2)	0.8465 (14)	1.8 (9)
H(5)	0.819 (4)	0.420 (2)	0.9522 (16)	3.8 (11)
H(811)	0.268 (3)	0.274 (2)	0.8492 (14)	2.4 (9)
H(812)	0.147 (4)	0.339 (2)	0.8763 (16)	4.2 (11)
H(813)	0.239 (4)	0.310 (2)	0.9214 (17)	4.2 (11)
H(821)	0.214 (3)	0.429 (2)	0.7850 (15)	2.5 (9)
H(822)	0.357 (3)	0.467 (2)	0.7829 (14)	2.1 (9)
H(823)	0.364 (4)	0.349 (3)	0.7773 (17)	5.3 (12)
H(831)	0.325 (4)	0.535 (2)	0.8848 (16)	3.9 (11)
H(832)	0.280 (4)	0.463 (2)	0.9514 (16)	4.7 (11)
H(833)	0.171 (5)	0.487 (3)	0.8971 (21)	10.2 (17)
H(911)	0.785 (4)	0.655 (3)	0.8204 (18)	5.6 (12)
H(912)	0.630 (4)	0.647 (2)	0.8588 (17)	4.9 (12)
H(913)	0.645 (4)	0.592 (3)	0.7958 (19)	6.5 (13)
H(921)	0.876 (4)	0.565 (2)	0.9620 (17)	5.0 (12)
H(922)	0.895 (5)	0.638 (3)	0.9175 (23)	11.0 (18)
H(923)	0.724 (6)	0.608 (4)	0.9588 (28)	17.1 (25)
H(931)	0.857 (5)	0.496 (3)	0.8014 (21)	10.0 (17)
H(932)	0.933 (4)	0.479 (3)	0.8680 (19)	7.8 (15)
H(933)	0.965 (5)	0.566 (3)	0.8397 (23)	11.6 (19)
H(1011)	0.932 (4)	0.315 (3)	0.9873 (18)	5.4 (12)
H(1012)	0.820 (4)	0.348 (2)	1.0410 (17)	4.9 (12)
H(1013)	0.902 (5)	0.265 (3)	1.0579 (23)	11.1 (18)
H(1021)	0.814 (3)	0.199 (2)	0.9337 (14)	1.9 (9)
H(1022)	0.670 (4)	0.147 (3)	0.9495 (17)	5.2 (12)
H(1023)	0.778 (3)	0.145 (2)	0.9941 (15)	3.0 (10)
H(1031)	0.648 (3)	0.232 (2)	1.0849 (14)	1.9 (9)
H(1032)	0.598 (4)	0.337 (2)	1.0632 (16)	3.8 (11)
H(1033)	0.519 (3)	0.245 (2)	1.0278 (15)	3.4 (10)
H(3')	0.580 (3)	-0.0804 (19)	0.8912 (13)	1.0 (8)
H(5')	0.906 (4)	0.053 (3)	0.8271 (18)	6.0 (13)

Table 1 (cont.)

	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )
H(811')	0.187 (4)	0.065 (2)	0.8516 (16)	3.6 (10)
H(812')	0.277 (3)	0.144 (2)	0.8817 (14)	1.7 (9)
H(813')	0.302 (3)	0.114 (2)	0.8053 (14)	1.5 (8)
H(821')	0.367 (5)	0.036 (3)	0.9581 (20)	8.2 (15)
H(822')	0.269 (3)	-0.023 (2)	0.9343 (15)	3.4 (10)
H(823')	0.414 (4)	-0.057 (3)	0.9512 (17)	5.6 (12)
H(831')	0.419 (4)	-0.126 (3)	0.8402 (19)	6.7 (14)
H(832')	0.255 (4)	-0.076 (2)	0.8219 (17)	4.7 (11)
H(833')	0.353 (5)	-0.043 (3)	0.7760 (21)	9.1 (16)
H(911')	0.995 (4)	-0.071 (3)	0.8055 (19)	6.7 (14)
H(912')	0.865 (4)	-0.144 (2)	0.8034 (17)	4.4 (11)
H(913')	1.018 (5)	-0.156 (3)	0.8561 (21)	9.5 (17)
H(921')	0.863 (4)	-0.204 (3)	0.9370 (20)	7.8 (15)
H(922')	0.732 (4)	-0.190 (3)	0.8780 (19)	7.6 (14)
H(923')	0.721 (4)	-0.136 (3)	0.9560 (19)	6.7 (14)
H(931')	1.009 (4)	-0.103 (2)	0.9512 (16)	4.3 (11)
H(932')	1.006 (4)	-0.006 (3)	0.9134 (18)	6.7 (14)
H(933')	0.874 (5)	-0.026 (3)	0.9641 (22)	10.7 (18)
H(1011')	0.818 (3)	0.320 (2)	0.7760 (14)	2.3 (9)
H(1012')	0.665 (4)	0.308 (3)	0.8158 (18)	5.3 (12)
H(1013')	0.820 (4)	0.292 (2)	0.8502 (17)	4.9 (12)
H(1021')	0.993 (4)	0.175 (3)	0.8124 (18)	5.8 (12)
H(1022')	0.960 (4)	0.225 (3)	0.7394 (17)	5.1 (12)
H(1023')	0.948 (5)	0.122 (4)	0.7484 (25)	13.6 (21)
H(1031')	0.601 (4)	0.214 (3)	0.7226 (20)	8.2 (15)
H(1032')	0.761 (4)	0.241 (3)	0.6917 (19)	6.5 (13)
H(1033')	0.718 (4)	0.134 (2)	0.6971 (16)	4.0 (11)

Hexa-*tert*-butylbenzil

The diffraction intensities of an approximately 0.3 × 0.3 × 0.3 mm crystal of the title compound were collected twice with graphite-monochromatized Cu  $K\alpha$  radiation. The  $\theta/2\theta$  scan technique was used and the data were subjected to profile analysis (Grant & Gabe, 1978). The first data set was collected at room temperature first to  $2\theta_{\text{max}} = 80^\circ$  and then to  $100^\circ$ . In the  $80^\circ$  set 2180 reflections were measured, of which 1806 were observed at the  $2\sigma(I)$  level. In the  $100^\circ$  set, the numbers were 3663 and 2548 respectively. The data were also collected at 115 K to  $2\theta_{\text{max}} = 100^\circ$  and in this set 2905 reflections out of 3567 were observed. No absorption correction was performed ( $\mu = 0.441 \text{ mm}^{-1}$ ).

Attempts to solve the structure with the limited ( $2\theta_{\text{max}} = 80^\circ$ ) room-temperature data set were unsuccessful, but when the supplementary data to  $100^\circ$  were added, the structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) on the first attempt. It may be worth mentioning that in the  $80^\circ$  set, 26 of the first 50  $E$  values occurred in the range 70 to  $80^\circ$  which represents 29% of the data, whereas in the  $100^\circ$  set, only 24 of the first 50  $E$  values occurred in the range 80 to  $100^\circ$  which represents 41% of the data. Thus an inadequate data set (*i.e.* one from which the structure could not be solved) produced a distribution with a preponderance of the high  $|E|$  values in the highest  $2\theta$  range. It may thus be worthwhile to include the calculation of such distributions in the normalization step of data reduction and possibly prevent subsequent problems.

Refinement of the non-hydrogen atoms stalled at 17% and a difference-Fourier map showed that both *tert*-butyl groups in the *para* positions were disordered.

The data were then recollected at 115 K and further refinement showed that the *tert*-butyl groups had become ordered. The positions of 54 hydrogen atoms were located from a difference-Fourier map at  $R_F = 13\%$  and the positions for the remaining four were calculated. Final refinement of positional and thermal parameters (anisotropic for the C and O atoms) yielded values of  $R_F = 6.35$  and  $wR_F = 5.16\%$ . The atomic positional parameters and equivalent isotropic  $B$ 's are listed in Table 1. All calculations were performed using the NRC system of programs for the PDP-8e (Larson & Gabe, 1978). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

### Benzil

The diffraction intensities of a  $0.15 \times 0.15 \times 0.25$  mm crystal of benzil were measured, using the same conditions as for the former study up to  $2\theta = 125^\circ$ . 748 measurements were made leading to 546 valid unique intensities of which 411 were larger than  $3\sigma(I)$  and were considered to be observed. The 20 measurements of the systematic absences were below the observation level. The agreement between the symmetry-related intensities  $\langle \Delta I \rangle / \langle I \rangle$  was 0.8%. No absorption correction was performed ( $\mu = 0.634 \text{ mm}^{-1}$ ). The intensities were corrected for measured direct-beam polarization (0.90) (Le Page, Gabe & Calvert, 1979).

Using the positional and thermal parameters of Brown & Sadanaga (1965) as starting values in space group  $P3_121$ , the atoms were refined anisotropically except for the hydrogens which were refined isotropically. An extinction correction was included. The final residuals are  $R_F = 3.2$ ,  $wR_F = 2.0\%$ . The atomic positional parameters and equivalent isotropic  $B$ 's are given in Table 2.\* We could not observe the optical activity in the crystals because they were not clear enough. The effect of anomalous scattering on most reflections was so small that we did not attempt to determine the absolute space group.

### Discussion

The distances and angles involving the heavier atoms of the hexa-*tert*-butyl derivative (HTB) are shown in Fig.

\* Lists of structure factors and anisotropic thermal parameters for both molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35509 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic parameters for benzil

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}} (\text{\AA}^2)$
C(0)	0.2264 (3)	0.1901 (3)	0.05296 (12)	6.59 (16)
C(1)	0.2310 (3)	0.0230 (3)	0.07643 (13)	5.77 (14)
C(2)	0.2848 (3)	0.0000 (3)	0.16878 (14)	7.65 (17)
C(3)	0.2852 (4)	-0.1591 (3)	0.19152 (15)	9.6 (2)
C(4)	0.2330 (4)	-0.2943 (3)	0.12316 (15)	10.3 (2)
C(5)	0.1815 (4)	-0.2744 (3)	0.03197 (14)	8.4 (2)
C(6)	0.1798 (3)	-0.1153 (3)	0.00817 (14)	6.68 (16)
O	0.2578 (2)	0.3106 (2)	0.11172 (10)	9.73 (15)
H(2)	0.330 (2)	0.099 (2)	0.2133 (9)	6.8 (5)
H(3)	0.334 (3)	-0.162 (3)	0.2576 (11)	10.8 (6)
H(4)	0.248 (2)	-0.401 (3)	0.1401 (10)	11.1 (7)
H(5)	0.147 (3)	-0.369 (3)	-0.0168 (11)	9.6 (6)
H(6)	0.147 (2)	-0.097 (2)	-0.0564 (9)	7.7 (5)

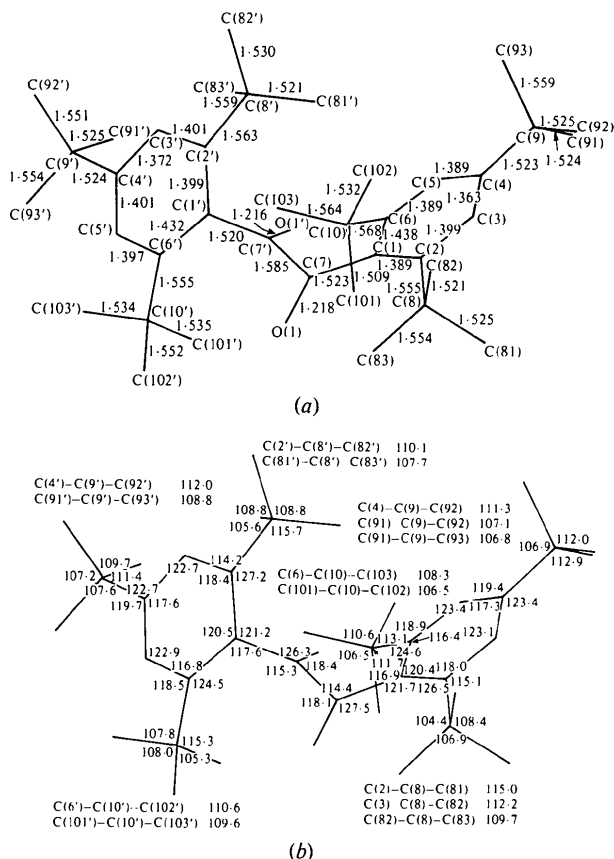


Fig. 1. (a), (b) Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) between C and O atoms in hexa-*tert*-butylbenzil. E.s.d.'s are 0.006  $\text{\AA}$  and 0.4 $^\circ$ .

1 and a stereoview of the molecule in Fig. 2. Comparable information for benzil itself is shown in Figs. 3 and 4.

There is considerable distortion in the benzene rings of HTB (*cf.* hexa-*tert*-butylazobenzene; Le Page, Gabe, Wang, Barclay & Holm, 1980), although the bonds and angles are reasonably normal. The distortion shows in a displacement of the atoms C(1) and C(1') by 0.152 (8) and 0.137 (8)  $\text{\AA}$  out of the planes of the other five atoms in their respective rings, while the bridging atoms C(7) and C(7') are 0.714 (8) and 0.642 (8)  $\text{\AA}$

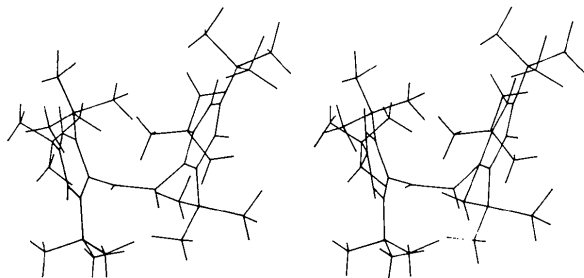


Fig. 2. A stereoview of the HTB molecule.

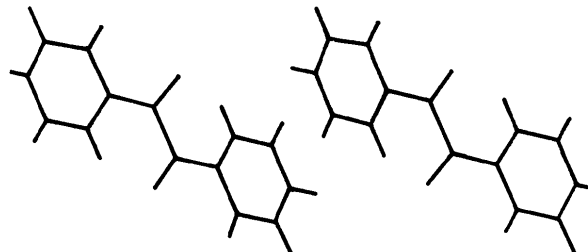


Fig. 4. A stereoview of the benzil molecule.

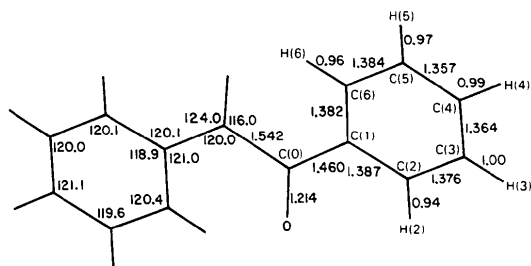


Fig. 3. Bond lengths (Å) and angles (°) in benzil. E.s.d.'s for C—C and C—O bonds and angles are 0.003 Å and 0.2°, and for bonds and angles involving H atoms they are 0.02 Å and 1.0° respectively.

out of these planes. The comparable distances in benzil itself are 0.003 (5) and 0.033 (5) Å. The dihedral angle between the five-atom planes of the rings is 31.8 (8)° in HTB and 103.6 (6)° in benzil, while the torsion angles between the C=O bonds are 125.8 (4) and 108.4 (2)° respectively. This represents a rotation of the HTB rings about the C(1)⋯C(4) [C(1')⋯C(4')] ring diagonal, so that viewed down the bond between the keto C atoms the rings are almost edge-on in benzil but almost flat in HTB. This can be seen in Figs. 2 and 4. Also the dihedral angles between the two planes C(7')C(7)O(1)C(1) and C(7)C(7')O(1')C(1') and their respective five-member 'benzene' planes are 107.5 (9) and 104.9 (8)°, while the comparable angle in benzil is 6.5 (6)°. Thus there seems to have been

little rotation around the C(7)—C(7') bond and the strain caused by the packing of the bulky *tert*-butyl groups has been taken up by rotation and deformation of the benzene rings. The four *tert*-butyl C atoms C(8), C(10), C(8') and C(10') are 0.299 (9), 0.185 (9), 0.229 (9) and 0.217 (9) Å out of the five-member 'benzene' planes in the opposite direction to C(7) and C(7').

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