Crystal structure of the solid state photoreactive 2,2′,4,4′,6,6′-hexaisopropylbenzil †

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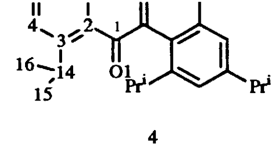
2,2′,4,4′,6,6′-Hexaisopropylbenzil undergoes an intramolecular solid state photochemical cyclization initiated by hydrogen abstraction by a carbonyl oxygen. The crystal structure of the diketone has been determined by X-ray diffraction methods and the molecular geometry was found to possess an inversion centre. There are three hydrogen atoms (and another three are related by the inversion centre) in close contact (2.68, 2.86 and 2.99 Å) with an oxygen atom, which suggests the feasibility of both γ- and δ-hydrogen abstraction. The molecular conformation and geometry at the central diketone moiety are compared with those of other diaryl diketones.

Introduction

2,2′,4,4′,6,6′-Hexaisopropylbenzil (**1**) undergoes a clean photochemical cyclization in the solid state to the 2-hydroxyindan-1-one. (**2**)[1] which further photocleaves to a keto aldehyde (**3**). The fact that the reaction proceeds in the solid state is mechanistically significant since the mechanism of the photocyclization of *o*-alkylbenzils has been controversial for two decades, especially considering the results of Hamer[2] and Ogata.[3] It is difficult to imagine how an indanol could be formed in the solid state following γ-hydrogen abstraction if the initially formed 1,4-biradical cyclizes immediately before undergoing any competing process. Consequently, the crystal structure of 2,2′,4,4′,6,6′-hexaisopropylbenzil was determined by a single crystal X-ray diffraction method in order to examine the molecular structure in relation to the geometrical possibility of a γ- and δ-hydrogen abstraction. In addition it was interesting to compare its molecular structure with those of other diaryl diketones.



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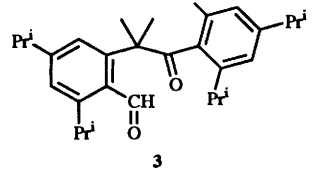

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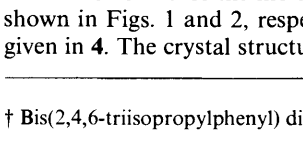

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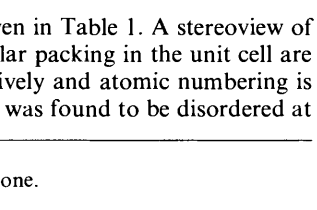

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Molecular and crystal structure

Bond lengths and angles are given in Table 1. A stereoview of the molecule and of the molecular packing in the unit cell are shown in Figs. 1 and 2, respectively and atomic numbering is given in **4**. The crystal structure was found to be disordered at the position of the *p*-isopropyl. The disorder is ascribed to the presence of two equivalent orientations defined by rotation of the isopropyl group around its bond to the aryl ring [C(5)–C(11)].

There are only two molecules in the unit cell, hence the molecule occupies a crystallographic inversion centre. Consequently, the two carbonyl groups are co-planar and adopt the s-*trans* conformation where the O=C–C=O torsional angle is constrained to 180°. Three other diketones RCOCOR with R = CHN_2,[4] R = cyclopropyl[5] and R = mesityl[6] are known to adopt this conformation. A similar gross conformation was found in other systems but the O=C–C=O torsion angle was not constrained to 180°—the value in the s-*trans* arrangement.

In the 12 years since the crystal structures of several vicinal diaryl polyketones were published by one of us,[6] several new structures of diaryl diketones have been reported. In a few of these cases the authors were unaware of previous work and the crystal structure of the same compound has been published in different journals. In order to clarify the confusion we compare in Table 2 the most important geometrical parameters at the diketone site using the latest data of structure refinement, while also citing the references to all previous works. The comparison includes the torsion angles OC–CO between the two carbonyl groups and the dihedral angles between an aryl group and its neighbouring carbonyl. The latter is defined as the angle between the normals to the two planes formed through the aromatic ring and through the carbonyl group and the aryl *ipso*-carbon atom to which it is bound. The dihedral angles were found to be highly dependent on the steric environment imposed by the *ortho* substituent at the vicinity of the aryl group. In benzil **5a** and in the series of *para*-substituted compounds **5b–f** and **5l**, where the *ortho* positions are occupied by hydrogens, the dihedral angles ranged between 2.6° and 12.2°, thus maximizing the stabilization arising by Ar–CO conjugation. Replacement of one *o*- and *m*-hydrogen by one phenyl group (**5j**) does not change the situation, whereas replacement of one *o*-hydrogen by a methoxy group (**5g**) causes a small increase of the Ar–CO dihedral angles to 11.5° and 16.2°. When both *ortho* positions are occupied by bulkier groups such as methyl (**5h**), *tert*-butyl (**5i**) as well as isopropyl (**1**) the dihedral angle is much larger, being in a range 71.0°–85.9°. The range of the bond length between the two carbonyl carbon atoms is between 1.519 and 1.585 Å. These values are higher than expected for a formal sp^2–sp^2 single bond such as in butadiene

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† Bis(2,4,6-triisopropylphenyl) diketone.

Table 1 Bond lengths (Å) and angles (°)

Atom	Atom	Distance
O(1)	C(1)	1.203(3)
C(1)	C(1)	1.534(6)
C(1)	C(2)	1.516(3)
C(2)	C(3)	1.367(5)
C(2)	C(7)	1.414(3)
C(3)	C(4)	1.402(4)
C(3)	C(14)	1.533(4)
C(4)	C(5)	1.392(5)
C(5)	C(6)	1.344(6)
C(5)	C(11)	1.531(4)
C(6)	C(7)	1.410(4)
C(7)	C(8)	1.506(5)
C(8)	C(9)	1.498(9)
C(8)	C(10)	1.527(5)
C(11)	C(121)	1.41(3)
C(11)	C(131)	1.49(1)
C(11)	C(122)	1.37(1)
C(11)	C(132)	1.41(2)
C(14)	C(15)	1.471(5)
C(14)	C(16)	1.513(8)

Atom	Atom	Atom	Angle
O(1)	C(1)	C(1)	119.0(3)
O(1)	C(1)	C(2)	122.8(3)
C(1)	C(1)	C(2)	118.2(3)
C(1)	C(2)	C(3)	119.6(2)
C(1)	C(2)	C(7)	118.3(3)
C(3)	C(2)	C(7)	122.1(2)
C(2)	C(3)	C(4)	119.2(3)
C(2)	C(3)	C(14)	122.8(3)
C(4)	C(3)	C(14)	118.0(4)
C(3)	C(4)	C(5)	120.4(3)
C(4)	C(5)	C(6)	118.9(3)
C(4)	C(5)	C(11)	119.0(5)
C(6)	C(5)	C(11)	122.0(4)
C(5)	C(6)	C(7)	123.8(3)
C(2)	C(7)	C(6)	115.5(3)
C(2)	C(7)	C(8)	123.8(2)
C(6)	C(7)	C(8)	120.6(3)
C(7)	C(8)	C(9)	112.3(3)
C(7)	C(8)	C(10)	111.5(4)
C(9)	C(8)	C(10)	112.1(4)
C(5)	C(11)	C(121)	112.2(7)
C(5)	C(11)	C(131)	115.3(6)
C(5)	C(11)	C(122)	117.4(7)
C(5)	C(11)	C(132)	111.7(9)
C(121)	C(11)	C(131)	110(1)
C(122)	C(11)	C(132)	114.2(8)
C(3)	C(14)	C(15)	113.6(3)
C(3)	C(14)	C(16)	110.4(3)
C(15)	C(14)	C(16)	112.9(5)

and we believe that the bond lengthening reflects one of the ways of decreasing the unfavourable interaction between the positive ends of vicinal CO dipoles. It is interesting to note that 9,9′-anthril (**5k**) crystallizes in two modifications having significantly different conformations. In the triclinic α-form the diketone moiety is in a *cis*, whereas in the orthorhombic β-form it is in a *trans* conformation.

Tetraketones **6a–d** represent another type of diaryl diketones. Two diaryl diketone moieties share one aryl group whereas the other terminal aryl group is phenyl. The dihedral angles of the terminal phenyl groups range between 3.1° and 19.9° and those of the central aryl groups for **6a–c** range between 2.4° and 7.8° as found for **5a–f** and **5l** and discussed above. However, the dihedral angle of the *ortho*-substituted aryl group in **6d** is 68.8° and is therefore comparable to the observed dihedral angles found in **1** and **5h–i** and **5k**. The conjugation effect between the aryl and the carbonyl groups is very well observed by the strong correlation between the Ar–CO dihedral angles and the Ar–CO

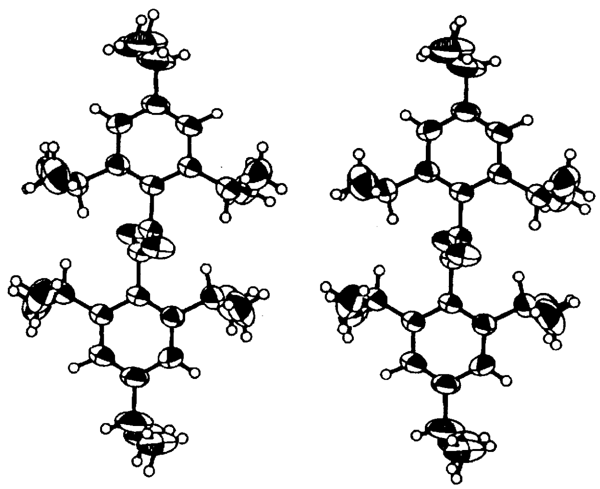


Fig. 1 Stereoscopic view of **1** (a single orientation of the disordered isopropyl group is shown)

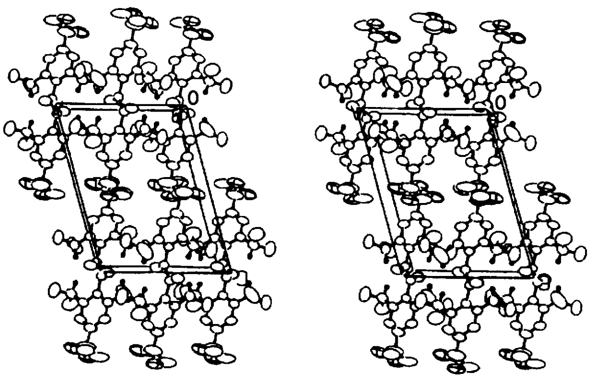


Fig. 2 Stereoscopic view of the packing of **1** in the unit cell (the disorder is shown by the two possible orientations of the *p*-isopropyl group), only relevant hydrogen atoms are shown

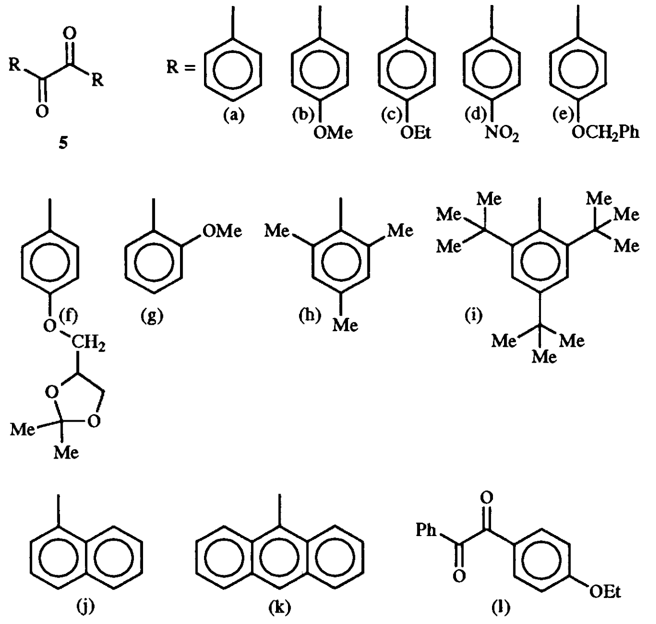
bond lengths. The dihedral angles scatter in two main groups: averaged at 6.3° (ranged between 1.4° and 19.9°) and at 73.9° (ranged between 52.3° and 85.9°) and the average bond lengths within each range are 1.47(1) Å (ranged between 1.413 and 1.491 Å) and 1.50(1) Å (ranged between 1.481 and 1.522 Å), respectively.

The most interesting parameters in **1** are those connected with the solid state hydrogen abstraction. We emphasize that although the structure was disordered and therefore some of the hydrogen positions had to be calculated and could not be well refined, the two most relevant hydrogen atoms [H(8) and H(14)] were detected in the difference Fourier maps and had been refined to very satisfactory positions and isotropic atomic displacement parameters. The ideal geometry for a γ- and δ-hydrogen abstraction in the solid state has been a subject of many investigations and was reviewed by Ramamurthy and Venkatesan.[15] The hydrogen to oxygen atom distance in these cases was found to range between 2.4 and 2.7 Å. In the present work, however, there are three short distances between hydrogen atoms [H(8) and H(14)] and the carbonyl oxygens: H(8)–O(1) 2.684, H(14)–O(1) 2.992 and H(14)–O(1)* 2.860 Å. Although the first distance is short enough to lead to hydrogen abstraction this will generate in this case the four-membered ring product, which was not observed, rather than the observed five-membered ring when H(14) is abstracted and a bond formed with O(1)*. However, this conclusion is based on the cyclization of the initially formed 1,4-biradical. If rearrangement of the latter to give a 1,5-biradical which gives five-

Table 2 Comparison of geometrical parameters of the diketone moiety

	Torsion angle (°)[a]		Bond length (Å)			
Compound	CO-CO	Ar-CO	CO-CO	Ar-CO	Symmetry	Ref.
5a[b]	108.8	5.1	1.521	1.450	Two-fold	7(*a*)[f]
5a[c] A	107.8	5.5; 5.2	1.548	1.475; 1.478	No symmetry	7(*a*)
5a[c] B	113.8	6.2; 5.2	1.526	1.469; 1.479	No symmetry	7(*a*)
5a[c] C	103.1	5.5; 4.5	1.532	1.484; 1.474	No symmetry	7(*a*)
5b	122.5	2.6	1.534	1.467	Two-fold	8(*a*)
5c	97.8	4.4	1.544	1.459	Two-fold	8(*a*)
5d	111.5	1.4; 2.2	1.532	1.491; 1.490	No symmetry	9
5e	126.3	1.6; 12.2	1.528	1.477; 1.477	No symmetry	8(*a*)
5f *meso*	89.1	3.4; 3.4	1.527	1.475; 1.475	No symmetry	8(*b*)
5f (*S*,*S*)	94.2	2.2; 8.4	1.562	1.446; 1.413	No symmetry	8(*b*)
5g	103.5	16.2; 11.5	1.519	1.462; 1.482	No symmetry	8(*a*)
5h mon.A	180.0	85.7	1.520	1.500	Inversion	6
5h mon.B	180.0	79.3	1.535	1.488	Inversion	6
5h orth.	177.6	77.6; 73.9	1.533	1.481; 1.494	No symmetry	10(*a*, *b*)
1	180.0	76.5	1.534	1.516	Inversion	Present work
5i	125.8	71.0; 74.9	1.585	1.522; 1.521	No symmetry	7(*c*)
5j	89.9	7.6; 5.8	1.541	1.470; 1.476	No symmetry	11(*a*, *b*)
5k tric.	43.3	52.3; 54.8	1.564	1.491; 1.500	No symmetry	12
5k orth.	179.3	85.9; 85.5	1.555	1.510; 1.513	Pseudo invers.	12
5l	98.2	1.7; 5.6	1.528	1.469; 1.465	No symmetry	8(*b*)
6a	111.6	3.1;[d] 7.8[e]	1.530	1.473; 1.477	Inversion[g]	13
6a	109.5	3.1;[d] 3.1[e]	1.526	1.467; 1.483	Inversion[g]	13
6b	137.8	19.9;[d] 2.4[e]	1.524	1.476; 1.483	No symmetry	13
6b	96.1	3.3;[d] 3.8[e]	1.535	1.460; 1.476	No symmetry	13
6c	121.9	14.9;[d] 4.3[e]	1.534	1.478; 1.473	No symmetry	14
6c	106.4	12.6;[d] 3.1[e]	1.520	1.480; 1.476	No symmetry	14
6d	144.6	17.4;[d] 68.8[e]	1.542	1.486; 1.509	Inversion[g]	14

[a] The Ar-CO dihedral angle is defined as the angle between the mean plane of the aryl moiety and the plane formed by the CCO moiety. [b] High temperature phase (hexagonal). [c] Low temperature phase (monoclinic). [d] Ph-CO dihedral angle. [e] Ar-CO torsion angle. [f] Earlier works are described in refs. 7(*b*) and (*c*). [g] The inversion centre is at the central aryl group and not at the centre of the diketone.



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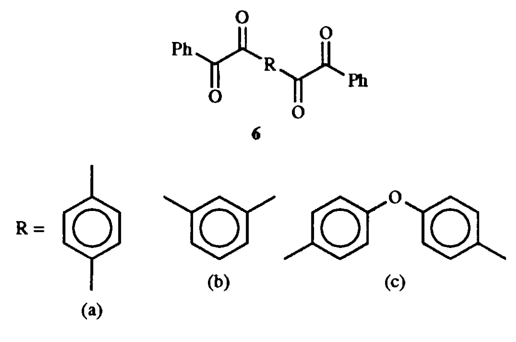

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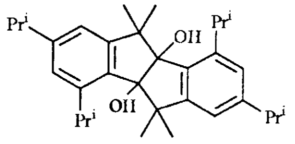
membered indanol occurs before cyclization, as discussed by Wagner *et al.*[1] then there is no geometrical obstacle to an initial γ-hydrogen abstraction.

The angle C(14)-H(14)···O(1)* is 117.0° and C(1)*-O(1)*···H(14) is 66.7° compared with the 'ideal' angles for abstraction of 90° and 180°. Since the molecule has an inversion centre, the same geometry is also found at the symmetry related part of the molecule, so that although overall there are four possible hydrogen atoms that may undergo abstraction only two can lead to a five membered ring. One may speculate that if only one of the hydrogens is in the correct geometry for abstraction, due to the presence of the symmetry related atom, a photoproduct such as **7** could be formed. The fact that this was not observed could mean that immediately after the hydrogen atom abstraction, the geometry of the molecule at the transition state changes in such a way that the second hydrogen atom cannot undergo a similar abstraction. This conclusion too depends on the absence of a faster reaction of the initially formed 1,4-biradical.



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Experimental

The IR spectrum was recorded on a Perkin-Elmer 457 spectrometer and the NMR spectra on a Bruker AMX 400 spectrometer.

Synthesis

The yellow 2,2′,4,4′,6,6′-hexaisopropylbenzil (**1**), mp 155–156 °C was obtained by the method of Fuson and Horning[16] in a mixture with the colourless enediol (*trans*-2,4,6,2′,4′,6′-hexaisopropylstilbenediol)‡ and was separated by dissolving the mixture in light petroleum (where **1** is much more soluble) and recrystallization of **1** from MeOH; ν_{max}(Nujol)/cm^{-1} 1700 (C=O); δ_H(CDCl$_3$) 1.28 (24 H, *J* 6.9 Hz, d, *o*-Me), 1.17 (12 H, *J* 6.7 Hz, d, *p*-Me), 2.63 (4 H, *J* 6.7, Hz, h, *o*-C–H), 2.91 (2 H, *J* 6.9 Hz, h, *p*-C–H) and 7.04 (4 H, s, Ar-H); δ_C(CDCl$_3$) 24.0, 32.0, 34.4, (Pr^i–C), 121.2, 132.2, 145.8, 150.9 (Ar–C) and 200.8 (C=O).

Crystal data

Compound 1. $C_{32}H_{46}O_2$, $M = 462.71$, monoclinic space group $P2_1/a$, $a = 9.926(1)$, $b = 11.970(1)$, $c = 13.366(2)$ Å, $\beta = 105.86(1)°$, $V = 1527.6(6)$ Å^3, $Z = 2$, $D_c = 1.006$ g cm^{-1}, Cu-Kα radiation, $\lambda = 1.541\,78$ Å, $T = 294$ K. The structure was solved by direct methods and refined by full-matrix least-squares against F_o^2 of 1138 reflections having $I > 3\sigma(I)$ (out of 2046 unique reflections) and $2\theta < 155.3°$, with $w = 4F_o^2/\sigma^2(F_o^2)$ weights using TEXSAN-TEXRAY (1985)[17] software. All non-hydrogen atoms were refined with anisotropic displacement parameters (including four disordered atoms) and all hydrogen atoms in isotropic approximation (fixed isotropic displacement parameters were given to all methyl hydrogens according to that of the methyl carbon atom parameters), total of 188 parameters, converging at $R = 0.054$, $R_w = 0.066$ and goodness-of-fit 2.54, $\Delta\rho_{max} = 0.08$ e Å^{-3}, $(\Delta/\sigma)_{max} = 0.21$. Atomic coordinates of the hydrogen atoms and anisotropic displacement parameters for the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.§

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‡ (*E*)-1,2-Bis(2,4,6-triisopropylphenyl)ethene-1,2-diol.

§ For details of the CCDC scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

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