

C108	0.6447 (1)	0.3589 (1)	-0.0047 (2)	0.0551 (6)
C109	0.6674 (1)	0.3690 (1)	-0.1516 (1)	0.0489 (5)
C110	0.7387 (1)	0.3844 (1)	-0.1735 (1)	0.0514 (5)
C111	0.7843 (1)	0.3872 (1)	-0.0574 (1)	0.0498 (5)
N112	0.6236 (1)	0.3655 (1)	-0.2690 (2)	0.0689 (7)
C113	0.6490 (1)	0.3745 (1)	-0.4193 (2)	0.0682 (8)
C114	0.5496 (1)	0.3673 (2)	-0.2515 (3)	0.0821 (12)
N115	0.9111 (1)	0.2435 (1)	0.0530 (1)	0.0478 (4)
C116	0.9418 (1)	0.1961 (1)	-0.0674 (1)	0.0475 (5)
C117	0.9715 (1)	0.2429 (1)	-0.1869 (1)	0.0611 (7)
C118	0.9985 (1)	0.1886 (2)	-0.3027 (2)	0.0792 (9)
C119	0.9971 (1)	0.0908 (2)	-0.2998 (2)	0.0806 (9)
C120	0.9680 (1)	0.0439 (1)	-0.1811 (2)	0.0756 (9)
C121	0.9400 (1)	0.0966 (1)	-0.0650 (2)	0.0597 (6)
O122	0.9474 (1)	0.3989 (1)	0.0225 (1)	0.0571 (4)
O123	0.9673 (1)	0.3572 (1)	0.3683 (1)	0.0775 (7)
C201	0.7964 (1)	-0.1173 (1)	0.2268 (1)	0.0482 (5)
C202	0.8365 (1)	-0.1144 (1)	0.0944 (1)	0.0583 (6)
C203	0.8053 (1)	-0.1214 (1)	-0.0397 (2)	0.0646 (7)
C204	0.7337 (1)	-0.1308 (1)	-0.0532 (2)	0.0624 (7)
C205	0.6933 (1)	-0.1342 (1)	0.0771 (2)	0.0620 (6)
C206	0.7234 (1)	-0.1282 (1)	0.2117 (2)	0.0577 (6)
N207	0.7082 (1)	-0.1364 (1)	-0.1938 (2)	0.0802 (8)
N208	0.8256 (1)	-0.1106 (1)	0.3596 (1)	0.0577 (5)
O209	0.6445 (1)	-0.1432 (1)	-0.2052 (2)	0.0945 (9)
C210	0.7847 (1)	-0.1185 (1)	0.4950 (2)	0.0680 (8)
C211	0.8990 (1)	-0.0962 (2)	0.3801 (2)	0.0832 (10)

C108—C109—N112—C114	10.7 (3)
C110—C109—N112—C113	1.9 (2)
C101—N115—C116—C121	170.2 (1)
C206—C201—N208—C210	2.9 (2)
C202—C201—N208—C211	2.4 (2)
C205—C204—N207—O209	1.4 (3)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55647 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1020]

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Table 2. Geometric parameters (Å, °)

C101—C102	1.522 (2)	C116—C117	1.388 (2)
C101—N115	1.353 (2)	C116—C121	1.389 (2)
C101—O122	1.218 (2)	C117—C118	1.395 (2)
C102—C103	1.497 (2)	C118—C119	1.364 (3)
C102—N105	1.287 (2)	C119—C120	1.379 (3)
C103—C104	1.501 (2)	C120—C121	1.391 (2)
C103—O123	1.212 (2)	C201—C202	1.428 (2)
N105—C106	1.395 (2)	C201—C206	1.428 (2)
C106—C107	1.404 (2)	C201—N208	1.331 (2)
C106—C111	1.404 (2)	C202—C203	1.359 (2)
C107—C108	1.378 (2)	C203—C204	1.399 (2)
C108—C109	1.408 (2)	C204—C205	1.416 (2)
C109—C110	1.411 (2)	C204—N207	1.367 (2)
C109—N112	1.361 (2)	C205—C206	1.354 (2)
C110—C111	1.372 (2)	N207—O209	1.243 (3)
N112—C113	1.453 (2)	N208—C210	1.462 (2)
N112—C114	1.441 (2)	N208—C211	1.449 (2)
N115—C116	1.406 (2)		
N115—C101—O122	126.2 (1)	C101—N115—C116	128.1 (1)
C102—C101—O122	121.7 (1)	N115—C116—C121	116.6 (1)
C102—C101—N115	112.1 (1)	N115—C116—C117	123.9 (1)
C101—C102—N105	126.2 (1)	C117—C116—C121	119.5 (1)
C101—C102—C103	115.2 (1)	C116—C117—C118	119.1 (2)
C103—C102—N105	118.7 (1)	C117—C118—C119	121.4 (2)
C102—C103—O123	119.4 (1)	C118—C119—C120	119.8 (2)
C102—C103—C104	118.1 (1)	C119—C120—C121	119.8 (2)
C104—C103—O123	122.5 (2)	C116—C121—C120	120.4 (2)
C102—N105—C106	125.0 (1)	C206—C201—N208	120.9 (1)
N105—C106—C111	126.9 (1)	C202—C201—N208	121.8 (1)
N105—C106—C107	116.3 (1)	C202—C201—C206	117.4 (1)
C107—C106—C111	116.7 (1)	C201—C202—C203	120.5 (1)
C106—C107—C108	122.2 (1)	C202—C203—C204	121.7 (2)
C107—C108—C109	120.8 (1)	C203—C204—N207	116.4 (2)
C108—C109—N112	122.7 (1)	C203—C204—C205	118.5 (2)
C108—C109—C110	116.9 (1)	C205—C204—N207	125.1 (2)
C110—C109—N112	120.4 (1)	C204—C205—C206	120.7 (1)
C109—C110—C111	121.7 (1)	C201—C206—C205	121.3 (1)
C106—C111—C110	121.6 (1)	C204—N207—O209	116.1 (2)
C109—N112—C114	122.2 (2)	C201—N208—C211	122.8 (2)
C109—N112—C113	121.2 (1)	C210—N208—C211	121.5 (1)
C113—N112—C114	116.0 (2)	C210—N208—C211	115.7 (2)
C102—C101—N115—C116	174.8 (1)		
N115—C101—C102—N105	-81.3 (2)		
O122—C101—C102—C103	-83.5 (2)		
C101—C102—N105—C106	-1.2 (2)		
N105—C102—C103—O123	-177.8 (1)		
C102—N105—C106—C107	161.0 (1)		

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1,4-Bis(4-chlorobenzoyl)-2,3,5,6-tetramethylbenzene

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Abstract

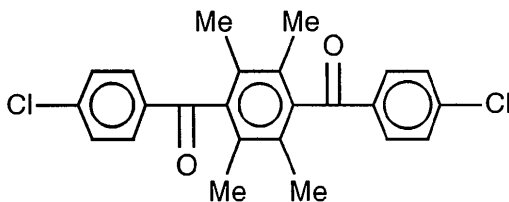
In Cl—C₆H₄—CO—C₆Me₄—CO—C₆H₄—Cl, steric hindrance due to four methyl substituents in the central ring of the title compound causes the two *p*-chlorobenzoyl

units to lie in planes which are almost orthogonal to the plane of the central ring. The conformer present in the crystal lies on an inversion centre and consequently has the two carbonyl groups in a 'trans' orientation.

Comment

The ease with which durene (1,2,4,5-tetramethylbenzene) and other polymethylated benzenes undergo diacylation under Friedel-Crafts conditions, whereas benzene itself and its simple analogues normally only give monoacyl derivatives, has long been regarded (Gore & Hoskins, 1970) as the result of a classical example of 'steric inhibition of resonance'. If, as in durene, the first acyl group is forced to lie appreciably out of the plane of the ring, it cannot exert its normal mesomeric electron-withdrawing effect, and thus cannot so effectively deactivate the ring towards a second acylation step. Several crowded 1-acyl-2,6-dialkylbenzenes have been studied crystallographically, *e.g.* 2-(4-carboxymethyl-2-nitrobenzoyl)-1,3,5-trimethylbenzene (van der Heijden, Chandler & Roberston, 1975) and in this molecule the angle between the mesityl and carbonyl C—C(=O)—C planes is found to be 51.5° . The extent of the steric hindrance has, however, not been previously demonstrated crystallographically in crowded bis(acyl) derivatives [a search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for 1,4-bis(acyl)-2,3,5,6-tetrasubstituted benzenes yielded no hits]; neither has it been known hitherto if the two carbonyl groups in a hindered diacylbenzene can adopt distinct 'cis' and 'trans' orientations (*i.e.* both lying on the same side of the central ring plane, or one above and one below).

Our analysis of the hindered diacylbenzene, 1,4-bis(4-chlorobenzoyl)-2,3,5,6-tetramethylbenzene, (1), shows that this molecule (Fig. 1) lies about a crystallographic inversion centre and consequently has the carbonyl groups in a 'trans' orientation in the solid state. The molecular dimensions (Table 2) are in accord with expected values and the intermolecular contacts correspond to normal van der Waals distances.



The molecule can be thought of as lying in three planes consisting of: (a) the central aromatic ring, (b) the carbonyl group [atoms C(1), C(7), C(1') and O], and (c) the terminal aromatic ring [atoms C(1'), ..., C(6')]. The dihedral angles between these planes are (a)/(b) $85.9(1)$, (b)/(c) $10.0(1)$ and (a)/(c) $82.3(1)^\circ$. The plane of the C—C(=O)—C moiety is thus close to being normal to the

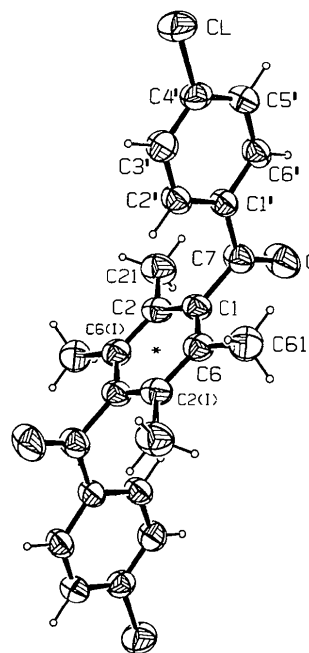


Fig. 1. A view of the centrosymmetric molecule (1) showing the general conformation with the crystallographic numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size. The * represents an inversion centre.

central aromatic ring plane. While the central ring is planar [maximum deviation $0.002(3)$ Å], its substituents are slightly ruffled with C(21) $-0.040(5)$, C(61) $-0.014(4)$ and C(7) $+0.068(4)$ Å from the plane of the central ring.

Experimental

Crystal data

C₂₄H₂₀Cl₂O₂

$M_r = 411.32$

Triclinic

P1

$a = 8.1456(19)$ Å

$b = 10.830(3)$ Å

$c = 6.0122(10)$ Å

$\alpha = 103.990(19)^\circ$

$\beta = 97.880(13)^\circ$

$\gamma = 80.760(13)^\circ$

$V = 505.26(20)$ Å³

$Z = 1$

$D_x = 1.352$ Mg m⁻³

Mo K α radiation

$\lambda = 0.70930$ Å

Cell parameters from 25 reflections

$\theta = 10.00-18.00^\circ$

$\mu = 0.34$ mm⁻¹

$T = 293$ K

Colourless

$0.36 \times 0.42 \times 0.51$ mm

Block

Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2184 measured reflections

2184 independent reflections

1666 observed reflections

$[I_{net} > 3.0\sigma(I_{net})]$

$\theta_{max} = 26.88^\circ$

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 13$

$l = -7 \rightarrow 7$

3 standard reflections

frequency: 120 min

intensity variation: none

Refinement

Refinement on F Final $R = 0.040$ $wR = 0.065$ $S = 1.89$

1666 reflections

168 parameters

All H-atom parameters re-

fined

 $w = 1/[\sigma^2(F) + 0.0008F^2]$ $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

Extinction correction: Larson

Extinction coefficient: 844(7)

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

C(21)—C(2)—C(6) ¹	120.17 (20)	C(2')—C(3')—C(4')	118.70 (19)
C(1)—C(6)—C(2) ¹	118.53 (18)	Cl—C(4')—C(3')	118.73 (16)
C(1)—C(6)—C(61)	120.62 (18)	Cl—C(4')—C(5')	119.52 (16)
C(2) ¹ —C(6)—C(61)	120.85 (18)	C(3')—C(4')—C(5')	121.75 (18)
O—C(7)—C(1)	121.82 (18)	C(4')—C(5')—C(6')	118.60 (18)
O—C(7)—C(1')	120.63 (18)	C(1')—C(6')—C(5')	121.18 (19)

C(1)···C(2') 2.926 (3) C(21)···C(61)¹ 2.933 (3)Symmetry code: (i) $-x, -y, -z$.

The synthesis of 1,4-bis(4-chlorobenzoyl)-2,3,5,6-tetramethylbenzene starting from durene, using 4-chlorobenzoyl chloride and aluminium chloride, is described in detail in the supplementary material. Crystals for the X-ray study were obtained on recrystallization from toluene/propan-2-ol. Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction, program used to solve and refine the structures, software used to prepare material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The figure was prepared using *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55624 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1021]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cl	-0.28870 (8)	0.71080 (5)	-0.03649 (12)	0.0706 (5)
O	-0.31211 (25)	0.19557 (17)	0.3764 (3)	0.0789 (12)
C(1)	-0.1125 (3)	0.09638 (16)	0.1098 (3)	0.0437 (9)
C(2)	0.05105 (25)	0.07832 (16)	0.2138 (3)	0.0444 (10)
C(21)	0.1028 (4)	0.1609 (3)	0.4462 (4)	0.0627 (15)
C(6)	-0.16629 (24)	0.01946 (16)	-0.1022 (3)	0.0445 (10)
C(61)	-0.3443 (3)	0.0413 (3)	-0.2069 (5)	0.0591 (13)
C(7)	-0.2327 (3)	0.20609 (19)	0.2261 (3)	0.0506 (11)
C(1')	-0.24564 (23)	0.33118 (17)	0.1581 (3)	0.0425 (9)
C(2')	-0.1736 (3)	0.34135 (19)	-0.0319 (3)	0.0464 (10)
C(3')	-0.1876 (3)	0.45773 (20)	-0.0937 (4)	0.0501 (10)
C(4')	-0.27299 (24)	0.56464 (18)	0.0392 (4)	0.0475 (10)
C(5')	-0.3463 (3)	0.55746 (20)	0.2294 (4)	0.0504 (11)
C(6')	-0.3318 (3)	0.44063 (18)	0.2871 (3)	0.0477 (10)

Table 2. Geometric parameters (\AA , $^\circ$)

Cl—C(4')	1.7309 (19)	C(7)—C(1')	1.491 (3)
O—C(7)	1.2175 (24)	C(1')—C(2')	1.388 (3)
C(1)—C(2)	1.397 (3)	C(1')—C(6')	1.391 (3)
C(1)—C(6)	1.400 (3)	C(2')—C(3')	1.382 (3)
C(1)—C(7)	1.507 (3)	C(3')—C(4')	1.382 (3)
C(2)—C(21)	1.512 (3)	C(4')—C(5')	1.384 (3)
C(2)—C(6) ¹	1.401 (3)	C(5')—C(6')	1.374 (3)
C(6)—C(61)	1.506 (3)		
C(2)—C(1)—C(6)	122.35 (17)	C(1)—C(7)—C(1')	117.49 (16)
C(2)—C(1)—C(7)	118.52 (17)	C(7)—C(1')—C(2')	121.49 (16)
C(6)—C(1)—C(7)	119.08 (18)	C(7)—C(1')—C(6')	119.61 (17)
C(1)—C(2)—C(21)	120.70 (19)	C(2')—C(1')—C(6')	118.90 (18)
C(1)—C(2)—C(6) ¹	119.11 (16)	C(1')—C(2')—C(3')	120.85 (18)

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