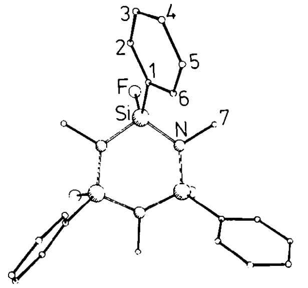

Fig. 1. Structure of the molecule, showing the atom numbering.

and −6·0 (7)°. The slight deviation from planarity is towards a chair rather than a boat conformation (as required by the crystallographic symmetry).

Previous attempts to determine the conformation of Si_3N_3 rings have been fraught with problems. $(SiCl_2.NH)_3$ (Mootz, Fayos & Zinnius, 1972) was found to be disordered in such a way that the average structure determined has a planar ring. An electron diffraction study of $(SiMe_2.NH)_3$ 'does not yield unambiguous information on the ring conformation ... except that the deviation from planarity is not very large' (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastyukov, 1975); chair and boat models were found to fit the data equally well, but a twist-boat conformation was ruled out. $(SiMe_2.NSiMe_3)_3$ (Adamson & Daly, 1970) has a boat conformation but this is probably due to the bulky $SiMe_3$ substituents. Spectroscopic evidence (see references in Rozsondai *et al.*, 1975) is ambiguous and, indeed, contradictory.

We thank Dr U. Klingebiel for providing a sample, and the Verband der Chemischen Industrie for financial support. All computer programs were written by WC and GMS.

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Acta Cryst. (1980). B**36**, 2462–2465

1,8-Dibenzoyl-2,7-dimethylnaphthalene

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(*Received* 25 *April* 1980; *accepted* 20 *May* 1980)

Abstract. $C_{26}H_{20}O_2$, $M_r = 364$, monoclinic, $P2_1/n$, $a = 15{\cdot}024\ (3)$, $b = 14{\cdot}101\ (2)$, $c = 9{\cdot}375\ (2)$ Å, $\beta = 90{\cdot}42\ (1)°$, $U = 1986{\cdot}1$ Å^3, $Z = 4$, $D_c = 1{\cdot}217$ Mg m^{-3}, $\mu(\mathrm{Mo}\ K\alpha) = 0{\cdot}041$ mm^{-1}, $F(000) = 832$. The structure was solved from diffractometer data by direct methods and gave a final $R = 0{\cdot}072$ for 1234 observed reflections. The molecule has the *transoid* configuration for the 1,8-dibenzoyl groups.

Introduction. Although *peri* interactions in 1,8-disubstituted naphthalenes are well known (Anderson, Franck & Mandella, 1972; Herbstein, 1979), little information is available on the detailed molecular structure of compounds possessing additional neighbouring groups. White, Carnduff, Guy & Bovill (1977*a*) have discussed the parameters thought to be indicative of *peri* strain in 1,8-disubstituted naphthalenes, and concluded that the only consistent indicator of steric crowding is the C(1)–C(9)–C(8) angle $[\theta_{1-9-8}]$, which opens with respect to the normal angle in naphthalene itself (121·5°, Cruickshank, 1957). The effect of neighbouring substituents in the 2 and 7 positions on the geometry of 1,8-naphthalene derivatives has not been studied, nor have cases where rotation of the groups away from the naphthalene ring can result in geometrical isomerism. In the title compound the acyl groups cannot be expected to be coplanar with the naphthalene moiety, and two geometric isomers are possible. A single isomer of unknown configuration was obtained by synthesis (Gore, Miri & Siddiquei, 1973).

Data were collected from a crystal 0·26 × 0·32 × 0·18 mm. 3498 intensities were recorded (3·0 <

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$\theta < 25\cdot0°$) on a Philips PW 1100 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, a θ–2θ scan mode, and a constant scan width of 0·86°. Lp corrections were applied. No absorption correction was made. Equivalent reflections were averaged to give 1234 unique observed intensities $[F > 6\sigma(F)]$. Cell dimensions were derived from the angular measurements of 25 strong reflections ($10\cdot0 < \theta < 15\cdot0°$). The structure was solved by multisolution Σ_2 sign expansion for terms with $E > 1\cdot2$. All the non-hydrogen atoms were located from the E map with the highest combined figure of merit (1·437). The structure was refined by full-matrix least-squares calculation with *SHELX* 76 (Sheldrick, 1976). All the H atoms were located from difference maps; however, with a data/parameter ratio of 10 the sp^2 C—H atoms were set geometrically (with C—H = 1·08 Å) and for refinement these atoms were assumed to ride on their respective C atoms. Neutral-atom scattering factors were used (Cromer & Mann, 1968), those for C and O being corrected for anomalous dispersion (Cromer, 1965). The refinement converged to $R = 0\cdot072$ and $R_w = \sum w^{\frac{1}{2}}||F_o| - |F_c||/\sum w^{\frac{1}{2}}|F_o| = 0\cdot081$. The final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2.*

Table 1. *Atomic fractional coordinates* (× 10⁴)

	x	y	z
C(1)	1461 (4)	3247 (4)	8059 (8)
C(2)	2006 (5)	3433 (5)	9197 (8)
C(3)	2544 (6)	4229 (8)	9135 (12)
C(4)	2536 (5)	4823 (7)	8039 (15)
C(5)	1977 (7)	5247 (7)	5633 (15)
C(6)	1487 (7)	5077 (7)	4512 (13)
C(7)	895 (6)	4259 (6)	4372 (9)
C(8)	904 (5)	3631 (5)	5555 (8)
C(9)	1422 (4)	3816 (4)	6798 (8)
C(10)	2004 (6)	4639 (6)	6836 (11)
C(11)	871 (4)	2395 (4)	8224 (7)
C(12)	77 (4)	2473 (5)	9124 (7)
C(13)	−304 (7)	1652 (7)	9655 (10)
C(14)	−1102 (8)	1783 (9)	10514 (12)
C(15)	−1421 (7)	2641 (11)	10794 (11)
C(16)	−1034 (7)	3395 (10)	10259 (12)
C(17)	−281 (5)	3339 (6)	9447 (8)
C(18)	292 (4)	2795 (5)	5384 (7)
C(19)	599 (5)	1991 (5)	4488 (8)
C(20)	19 (6)	1257 (7)	4119 (10)
C(21)	328 (10)	510 (7)	3284 (13)
C(22)	1167 (11)	472 (8)	2808 (11)
C(23)	1766 (7)	1167 (7)	3226 (9)
C(24)	1495 (5)	1931 (5)	4057 (8)
C(25)	2061 (5)	2813 (6)	10518 (8)
C(26)	343 (6)	4088 (7)	3055 (9)
O(1)	1095 (3)	1633 (3)	7710 (5)
O(2)	−410 (3)	2794 (4)	5956 (5)
H atom coordinates at calculated positions			
H(3)	2997	4379	10006
H(4)	2933	5461	8080
H(5)	2379	5882	5644
H(6)	1520	5574	3638
H(13)	−14	965	9449
H(14)	−1451	1177	10937
H(15)	−2001	2692	11463
H(16)	−1337	4075	10470
H(17)	67	3961	9074
H(20)	−648	1238	4540
H(21)	−126	−40	2939
H(22)	1363	−107	2125
H(23)	2455	1100	2920
H(24)	1954	2485	4366
Methyl H atom coordinates from a difference map			
H(25*a*)	2452	2799	10781
H(25*b*)	1981	1989	10466
H(25*c*)	1628	2941	11396
H(26*a*)	−85	4295	2771
H(26*b*)	−433	3448	3331
H(26*c*)	369	3338	2450

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·365 (10)	C(11)–O(1)	1·225 (8)
C(1)–C(9)	1·429 (10)	C(11)–C(12)	1·470 (9)
C(1)–C(11)	1·503 (9)	C(12)–C(13)	1·386 (12)
C(2)–C(3)	1·384 (13)	C(12)–C(17)	1·369 (11)
C(2)–C(25)	1·518 (11)	C(13)–C(14)	1·460 (15)
C(3)–C(4)	1·326 (17)	C(14)–C(15)	1·329 (19)
C(4)–C(10)	1·402 (16)	C(15)–C(16)	1·314 (20)
C(5)–C(6)	1·301 (18)	C(16)–C(17)	1·370 (13)
C(5)–C(10)	1·417 (16)	C(18)–O(2)	1·188 (8)
C(6)–C(7)	1·462 (13)	C(18)–C(19)	1·487 (10)
C(7)–C(8)	1·419 (11)	C(19)–C(20)	1·395 (12)
C(7)–C(26)	1·502 (12)	C(19)–C(24)	1·412 (11)
C(8)–C(9)	1·420 (10)	C(20)–C(21)	1·395 (15)
C(8)–C(18)	1·503 (10)	C(21)–C(22)	1·341 (21)
C(9)–C(10)	1·454 (10)	C(22)–C(23)	1·386 (17)
		C(23)–C(24)	1·392 (12)

C(2)–C(1)–C(9)	124·0 (6)	C(1)–C(11)–O(1)	119·8 (6)
C(2)–C(1)–C(11)	115·1 (6)	C(1)–C(11)–C(12)	118·7 (6)
C(9)–C(1)–C(11)	120·9 (6)	O(1)–C(11)–C(12)	121·2 (6)
C(1)–C(2)–C(3)	118·0 (8)	C(11)–C(12)–C(13)	118·8 (7)
C(1)–C(2)–C(25)	123·8 (7)	C(11)–C(12)–C(17)	121·0 (6)
C(3)–C(2)–C(25)	118·2 (8)	C(13)–C(12)–C(17)	120·1 (7)
C(2)–C(3)–C(4)	122·9 (10)	C(12)–C(13)–C(14)	115·8 (9)
C(3)–C(4)–C(10)	120·6 (9)	C(13)–C(14)–C(15)	121·5 (11)
C(10)–C(5)–C(6)	123·0 (10)	C(14)–C(15)–C(16)	120·0 (11)
C(5)–C(6)–C(7)	124·0 (10)	C(15)–C(16)–C(17)	122·4 (12)
C(6)–C(7)–C(8)	114·8 (8)	C(16)–C(17)–C(12)	120·1 (9)
C(6)–C(7)–C(26)	122·2 (8)	C(8)–C(18)–O(2)	119·9 (6)
C(8)–C(7)–C(26)	123·0 (7)	C(8)–C(18)–C(19)	117·8 (6)
C(7)–C(8)–C(9)	122·0 (6)	O(2)–C(18)–C(19)	122·3 (7)
C(7)–C(8)–C(18)	113·8 (6)	C(18)–C(19)–C(20)	120·7 (7)
C(9)–C(8)–C(18)	124·2 (6)	C(18)–C(19)–C(24)	120·5 (7)
C(8)–C(9)–C(10)	119·5 (7)	C(20)–C(19)–C(24)	118·7 (7)
C(8)–C(9)–C(1)	126·5 (6)	C(19)–C(20)–C(21)	119·3 (9)
C(10)–C(9)–C(1)	114·0 (7)	C(20)–C(21)–C(22)	122·3 (11)
C(9)–C(10)–C(4)	120·5 (9)	C(21)–C(22)–C(23)	119·2 (10)
C(9)–C(10)–C(5)	116·7 (9)	C(22)–C(23)–C(24)	120·9 (10)
C(4)–C(10)–C(5)	122·8 (9)	C(23)–C(24)–C(19)	119·3 (8)

Intermolecular contacts (Å)

O(1)···C(4)$^{\rm i}$	3·35 (1)	H(3)···H(20)$^{\rm iv}$	2·26
O(1)···H(4)$^{\rm i}$	2·33	H(13)···H(21)$^{\rm v}$	2·61
H(6)···H(23)$^{\rm ii}$	2·25	O(1)···H(21)$^{\rm v}$	2·74
H(15)···H(24)$^{\rm iii}$	2·52		

Symmetry code

(i) $\frac{1}{2} - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$

(ii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$

(iii) $1\frac{1}{2} + x, 1\frac{1}{2} - y, \frac{1}{2} + z$

(iv) $1\frac{1}{2} + x, 1\frac{1}{2} - y, 1\frac{1}{2} + z$

(v) $-x, -y, 1 - z$

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* Lists of structure factors, anisotropic thermal parameters and equations of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35363 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A perspective view of the molecule is shown in Fig. 1 with the numbering scheme. The analysis establishes the *transoid* configuration for the 1,8-dibenzoyl groups. The non-bonded interactions between the *peri* substituents result in a distortion of the molecular geometry whereby the C atoms of the carbonyl substituents are splayed outwards. The magnitude of this effect can be gauged by the C(11)···C(18) distance (2·85 Å, Fig. 2). In naphthalene the H(1)···H(8) distance is 2·50 Å (Cruickshank, 1957). Similar distances have been reported for 1,8-dimethylnaphthalene [C(11)···C(12) 2·93 Å, Bright, Maxwell & de Boer, 1973], 1,8-dinitronaphthalene [N(1)···N(2) 2·93 Å, Akopian, Kitaigorodskii & Struchkov, 1965], and for 1,8-bis-(dimethylamino)naphthalene [N(1)···N(2) 2·79 Å, Einspahr, Robert, Marsh & Roberts, 1973]. Relief of strain in the present system appears to be achieved partly by distortion from planarity of the naphthalene nucleus, with maximum displacements of individual atoms from the mean C_{10} plane of 0·03 (1) Å. The 2- and 7-methyl substituents lie −0·03 (1) and −0·02 (1) Å respectively from this plane, and the angles θ_{1-2-25} and θ_{8-7-26} have splayed to 123–124 (1)°. The carbonyl C atoms of the 1,8-dibenzoyl groups are displaced unsymmetrically to opposite sides of the mean plane; C(11) by 0·11 (1) Å and C(18) by −0·04 (1) Å.

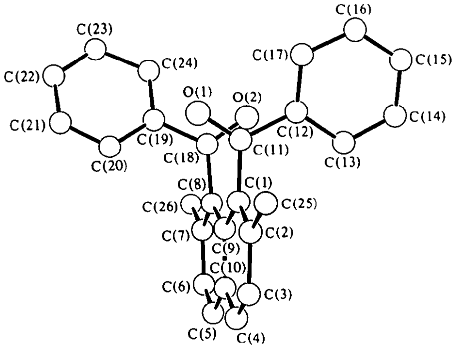

Fig. 1. *ORTEP* (Johnson, 1965) perspective view of 1,8-dibenzoyl-2,7-dimethylnaphthalene.

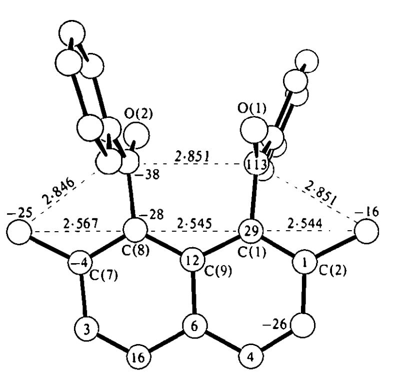

Fig. 2. Geometry of 1,8-dibenzoyl-2,7-dimethylnaphthalene, showing non-bonded interactions and deviations from the least-squares plane defined by the C_{10} nucleus (in units of 10^{-3} Å).

Table 3. *Bond angles* (°) *and angular distortion in* 1,8-*disubstituted naphthalenes*

X and *Y* are substituents at the 1 and 8 positions.

$$\delta\theta = (\theta_{1-9-8} - 121\cdot5) + (121\cdot5 - \theta_{4-10-5}) = \theta_{1-9-8} - \theta_{4-10-5}.$$

Naphthalene *X* =	*Y* =	θ_{1-9-8} (°)	θ_{4-10-5} (°)	$\delta\theta$ (°)	Reference
H	H	121·5	121·5	0	(*a*)
NMe_2	COMe	122·3	121·8	0·5§	(*b*)
Me	H	122·3	121·7	0·6	(*c*)
NMe_2	CO_2Me	122·4	121·3	1·1§	(*b*)
Me_2CH	H	123·2	121·6	1·6	(*d*)
MeO	CO_2H	124·4	121·8	2·6§	(*b*)
COPh	COPh*	126·5	122·8	3·7	(*e*)
F	F	126·5	122·2	4·3	(*f*)
C≡CPh	C≡CPh	125·1	119·6	5·5	(*g*)
C≡CMe	C≡CMe	125·2	119·6	5·6	(*h*)
Me	Me	125·2	119·5	5·7	(*i*)
$BrCH_2$	$BrCH_2$	127·0	121·0	6·0	(*j*)
NMe_2	NMe_2	125·8	119·6	6·2	(*k*)
NO_2	NO_2	127·5	120·7	6·8	(*l*)
Me	Me†	125·9	118·3	7·6	(*m*)
Me	Me‡	126·8	117·4	9·4	(*n*)
NMe_2H^+	CO_2	129·9	116·2	13·7	(*b*)

References: (*a*) Cruickshank (1957). (*b*) Schweizer, Procter, Kaftory & Dunitz (1978). (*c*) White, Carnduff, Guy & Bovill (1977*b*). (*d*) White, Carnduff, Mallinson, Guy & Bovill (1977). (*e*) This work. (*f*) Meresse, Courseille, Leroy & Chanh (1975). (*g*) Jungk & Schmidt (1971, 1972). (*h*) Jungk (1972). (*i*) Bright *et al.* (1973). (*j*) Robert, Sherfinski, Marsh & Roberts (1974). (*k*) Einspahr *et al.* (1973). (*l*) Akopian *et al.* (1965). (*m*) White *et al.* (1977*a*). (*n*) Jameson & Penfold (1965).

* In 1,8-dibenzoyl-2,7-dimethylnaphthalene.

† In 1,8-dimethyl-2-naphthyl acetate.

‡ In 3-bromo-1,8-dimethylnaphthalene.

§ These compounds show a distortion pattern where the exocyclic bond to the electrophilic centre is splayed outward, and the one to the nucleophilic centre is splayed inward.

The opening of the angle θ_{1-9-8}, suggested to be a characteristic feature indicating steric crowding caused by 1,8-naphthyl substituents (White *et al.*, 1977*a*), is accompanied by a compression of θ_{4-10-5}, and since these departures from normal bond angles are not absolutely interrelated, a possible index to steric crowding in 1,8-naphthalene derivatives may be the sum of these angular distortions ($\delta\theta$). In Table 3 these are listed in increasing order of angular distortion.

The phenyl substituents lie almost perpendicular to the naphthalene nucleus, at angles of 93 (1) and 96 (1)°, making an angle of 38 (1)° between their respective least-squares planes. The structure of the title compound consists of discrete molecules with the shortest C···C or C···O contact [3·35 (1) Å] between O(1) and C(4^i), related by the glide plane.

We thank the SRC for financial support for the Rutherford Laboratory computing facilities.

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Acta Cryst. (1980). B**36**, 2465–2467

4,7-Dimethoxy-5-methylphthalide

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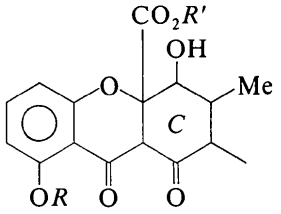
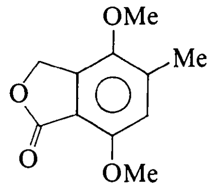
(*Received* 23 *April* 1980; *accepted* 13 *May* 1980)

Abstract. $C_{11}H_{12}O_4$, $M_r = 208{\cdot}2$, m.p. 386 K, monoclinic, $C2/c$, $a = 15{\cdot}475\ (3)$, $b = 10{\cdot}955\ (2)$, $c = 15{\cdot}377\ (5)$ Å, $\beta = 127{\cdot}83\ (2)°$, $V = 2059{\cdot}0$ Å^3, $Z = 8$, $D_c = 1{\cdot}34$ Mg m^{-3}, $F(000) = 440$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}031$ mm^{-1}. $R = 0{\cdot}065$ for 1145 reflexions with $I > 3\sigma(I)$. The analysis establishes the compound to be the 5-methyl derivative.

Introduction. In the course of experiments directed towards the elaboration of molecules of type (I) characteristic of the ergot pigments (Hooper, Marlow, Whalley, Borthwick & Bowden, 1971), we required 4,7-dimethoxy-5-methylphthalide (II) as a potential synthon for ring *C* of these metabolites. The preparation of (II), together with the isomeric 4,7-dimethoxy-6-methylphthalide, has been reported (Ahad, Banham, Whalley, Ferguson & Siew, 1980), but attempts to differentiate between these isomers by chemical and spectroscopic means were unsuccessful. Hence, as a necessary preliminary to our subsequent work, one of the isomers was examined crystallographically and identified as (II).



(I)



(II)

The space group and preliminary unit-cell information were obtained by photographic measurements. The systematic absences (hkl when $h + k = 2n + 1$, $h0l$ when $h = 2n + 1$ and $l = 2n + 1$) are indicative of space groups $C2/c$ or Cc; space group $C2/c$ was confirmed by successful refinement.

The cell dimensions were refined by least squares from the diffractometer angles of 12 reflexions with θ(Mo $K\alpha$) > 10°. Intensities were measured with an acicular (c) crystal $0{\cdot}24 \times 0{\cdot}24 \times 0{\cdot}72$ mm mounted with c parallel to the axis of a Hilger & Watts Y290 four-circle diffractometer (Ferguson & Roberts, 1978).

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