

## Nucleophile–Electrophile Interactions in 1,8-Disubstituted Naphthalenes: Structures of Three 1-Naphthaldehydes and a 1-Naphthyl Methyl Ketone

JUDITH C. GALLUCCI, DAVID J. HART\* AND DAVID G. J. YOUNG

Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210, USA. E-mail: hart.10@osu.edu

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### Abstract

4,8-Dimethoxy-5-(tosyloxy)-1-naphthaldehyde (1) and 8-methoxy-5-(tosyloxy)-1-naphthaldehyde (2) crystallize such that the formyl groups approach coplanarity with the naphthalene rings. 4',8'-Dimethoxy-5'-(tosyloxy)-1'-acetone (4), however, crystallizes such that the acetyl group approaches orthogonality to the naphthalene ring. In all three compounds the methoxy group and carbonyl groups exhibit a leaning effect typical of nucleophile–electrophile interactions in 1,8-disubstituted naphthalenes. 8-(Benzoyloxy)-4-methoxy-1-naphthaldehyde (3) crystallizes with the formyl group nearly coplanar to the naphthalene ring and does not exhibit the leaning effect. It is suggested that these structural differences are largely due to differences in the steric requirements of formyl and acetyl groups.

### 1. Introduction

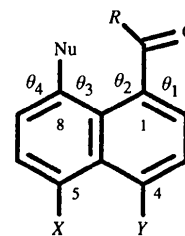
Crystallographic studies have been used in an elegant manner to gain insight into nucleophile–electrophile interactions in organic reactions (Burgi & Dunitz, 1983) and to study interactions between functional groups (Britton & Cramer, 1996; Cordes *et al.*, 1994; Procter *et al.*, 1981; Wallis *et al.*, 1993). For example, such studies have been used to probe possible nucleophile–electrophile approach trajectories in carbonyl addition reactions (Burgi, Dunitz & Shefter, 1974; Burgi, Dunitz, Lehn & Wipff, 1974). Crystallographic studies of 1,8-disubstituted naphthalenes (Schweizer *et al.*, 1978), as well as other molecules (Burgi *et al.*, 1973; Kafory & Dunitz, 1975*a,b,c*), have played important roles in this regard. Herein are reported crystallographic studies of four 1,8-disubstituted naphthalenes [(1)–(4)], which show that 1-naphthaldehydes with nucleophiles in the 8-position display crystallographic properties quite different from those of 1-naphthyl methyl ketones with nucleophiles in the 8-position (Fig. 1).

### 2. Experimental

Compounds (1)–(4) were prepared during the course of studies directed toward a synthesis of the gilvocarin and chrysomycin C-aryl glycoside antitumor antibiotics

(Balitz *et al.*, 1981; Takahashi *et al.*, 1981; Weiss *et al.*, 1982). The synthesis of aldehyde (1) required two steps from the known 4,8-dimethoxy-1-naphthol (Hannan *et al.*, 1979), as did the synthesis of ketone (4) (Hart *et al.*, 1996; Young, 1994). Aldehyde (2) was prepared from methyl 8-methoxynaphthalene-1-carboxylate using a six-step sequence [(i)  $\text{TiCl}_4$ ,  $\text{MeOCHCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ ; (ii)  $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$ ,  $\text{CH}_2\text{Cl}_2$ ; (iii)  $\text{NaOH}$ ,  $\text{MeOH}$ ; (iv)  $\text{TsCl}$ ,  $\text{K}_2\text{CO}_3$ , acetone; (v)  $\text{Bu}_2^i\text{-AlH}$ , toluene; (vi)  $\text{MnO}_2$ , benzene], as described elsewhere (Young, 1994). Aldehyde (3) was prepared by the reaction of 8-hydroxy-4-methoxy-1-naphthaldehyde (Hannon *et al.*, 1979) with benzoyl chloride (Young, 1994). 4,8-Dimethoxy-5-(tosyloxy)-1-naphthaldehyde (1) was crystallized from petroleum ether–ethyl acetate; 8-methoxy-5-(tosyloxy)-1-naphthaldehyde (2) was crystallized from petroleum ether–dichloromethane; 8-(benzoyloxy)-4-methoxy-1-naphthaldehyde (3) was crystallized from petroleum ether–chloroform; 4',8'-dimethoxy-5'-(tosyloxy)-1'-acetone (4) was crystallized from dichloromethane. Crystal data are given in Table 1.†

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: BK0045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



	Nu	R	X	Y
(1)	OMe	H	OTs	OMe
(2)	OMe	H	OTs	H
(3)	OCOPh	H	H	OMe
(4)	OMe	Me	OTs	OMe
(5)	OMe	Me	H	H

Fig. 1. 1,8-Disubstituted naphthalenes.

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	C <sub>20</sub> H <sub>18</sub> O <sub>6</sub> S	C <sub>19</sub> H <sub>16</sub> O <sub>5</sub> S	C <sub>19</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>21</sub> H <sub>20</sub> O <sub>6</sub> S
Chemical formula weight	386.42	356.39	306.32	400.45
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	8.489 (1)	7.922 (1)	8.075 (1)	10.586 (2)
<i>b</i> (Å)	13.433 (2)	14.664 (2)	15.441 (1)	7.727 (1)
<i>c</i> (Å)	15.802 (1)	14.473 (2)	12.239 (2)	24.361 (2)
$\beta$ (°)	97.431 (8)	94.26 (1)	102.43 (1)	99.29 (1)
<i>V</i> (Å <sup>3</sup> )	1786.9 (6)	1676.6 (4)	1490.2 (3)	1966.4 (9)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.436	1.412	1.365	1.353
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25
$\theta$ range (°)	12.6–15.0	11.0–13.8	10.6–15.0	12.5–15.0
$\mu$ (mm <sup>-1</sup> )	0.206	0.209	0.089	0.189
Temperature (K)	296	296	296	296
Crystal form	Rectangular rod	Rectangular chunk	Rectangular rod	Rectangular rod
Crystal size (mm)	0.540 × 0.190 × 0.150	0.420 × 0.310 × 0.310	0.310 × 0.230 × 0.230	0.460 × 0.270 × 0.230
Crystal color	Pale yellow	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Rigaku AFC-5S	Rigaku AFC-5S	Rigaku AFC-5S	Rigaku AFC-5S
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega$ scans
Absorption correction	None	None	None	None
No. of measured reflections	4564	4305	3822	5102
No. of independent reflections	4284	4026	3579	4848
No. of observed reflections	2553	2426	1854	2752
Criterion for observed reflections	$I > 1\sigma(I)$	$I > 1\sigma(I)$	$I > 1\sigma(I)$	$I > 1\sigma(I)$
<i>R</i> <sub>int</sub>	0.016	0.016	0.017	0.015
$\theta_{\max}$ (°)	27.50	27.56	27.56	27.49
Range of <i>h, k, l</i>	0 → <i>h</i> → 11 0 → <i>k</i> → 17 -20 → <i>l</i> → 20	0 → <i>h</i> → 10 0 → <i>k</i> → 19 -18 → <i>l</i> → 18	0 → <i>h</i> → 10 0 → <i>k</i> → 20 -15 → <i>l</i> → 15	0 → <i>h</i> → 13 0 → <i>k</i> → 10 -31 → <i>l</i> → 31
No. of standard reflections	6	6	6	6
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
Intensity decay (%)	-0.99	-3.21	-3.56	0.25
Refinement				
Refinement on	<i>F</i>	<i>F</i>	<i>F</i>	<i>F</i>
<i>R</i>	0.0508	0.0477	0.0553	0.0480
<i>wR</i>	0.0516	0.0494	0.0457	0.0486
<i>S</i>	1.536	1.535	1.640	1.508
No. of reflections used in refinement	2553	2426	1854	2752
No. of parameters used	248	231	213	254
H-atom treatment	See text	See text	See text	See text
Weighting scheme	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$
( $\Delta/\sigma$ ) <sub>max</sub>	0.0003	0.007	0.005	0.005
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.25	0.24	0.19	0.21
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.35	-0.31	-0.20	-0.28
Extinction method	None	Zachariasen (1963)	Zachariasen (1963)	Zachariasen (1963)
Extinction coefficient	—	1.9 (2) × 10 <sup>-6</sup>	3.2 (2) × 10 <sup>-6</sup>	1.0 (1) × 10 <sup>-6</sup>
Source of atomic scattering factors	Stewart <i>et al.</i> (1965), Creagh & McAuley (1992), Cromer & Waber (1974)	Stewart <i>et al.</i> (1965), Creagh & McAuley (1992), Cromer & Waber (1974)	Stewart <i>et al.</i> (1965), Creagh & McAuley (1992), Cromer & Waber (1974)	Stewart <i>et al.</i> (1965), Creagh & McAuley (1992), Cromer & Waber (1974)
Computer programs				
Data collection	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)
Cell refinement	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)	<i>MSC/AFC</i> (MSC, 1988)
Data reduction	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)
Structure solution	<i>SHELXS86</i> (Sheldrick, 1990)	<i>SHELXS86</i> (Sheldrick, 1990)	<i>SHELXS86</i> (Sheldrick, 1990)	<i>SHELXS86</i> (Sheldrick, 1990)
Structure refinement	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)
Preparation of material for publication	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)	<i>TEXSAN</i> (MSC, 1993)

Each structure was solved by the direct methods procedure in *SHELXS86* (Sheldrick, 1990). Data reduction and least-squares refinement were performed with the *TEXSAN* package (Molecular Structure Corporation, 1993). A small linear decay correction was applied to the data sets for (2) and (3). *ORTEPII* (Johnson, 1976) was used to draw the molecular structures. Some geometrical calculations were carried out with *PLATON* (Spek, 1990).

All the non-H atoms were refined anisotropically. For (1), (2) and (3) the aldehyde hydrogen was refined isotropically, while the other H atoms were included in each model as fixed contributions at calculated positions with C—H = 0.98 Å. For (4) all the H atoms were fixed at C—H = 0.98 Å. In (2) the methyl group C17 has a disordered arrangement of H atoms, which was modeled in terms of two sets of three hydrogens with an occupancy factor of 0.5 each. In (4) there are disordered methyl-group hydrogens on C10 and C19, which are treated in the same manner as above. A secondary extinction parameter was introduced into the final stages of refinement for (2), (3) and (4) (Zachariasen, 1963).

### 3. Discussion

#### 3.1. General discussion

Tables 2–5 contain the final positional parameters for structures (1)–(4). Final metrical parameters are given in Tables 6–9. *ORTEPII* drawings (Johnson, 1976) for each molecule are shown in Fig. 2.

In each structure the pattern of bond lengths within the naphthalene ring is similar to the pattern observed in the naphthalene molecule (Brock & Dunitz, 1982). Each naphthalene ring is slightly distorted from planarity. As a measure of this distortion, the mean deviation from a least-squares plane through the naphthalene ring is 0.029 (13) Å for (1), 0.028 (16) Å for (2), 0.021 (15) Å for (3) and 0.020 (10) Å for (4). The methoxy group at the 8-position lies very close to the naphthalene ring: the dihedral angle between the least-squares plane through the naphthalene and the plane defined by a methoxy group is 10.6 (2)° for (1), 5.7 (3)° for (2) and 9.6 (2)° for (4).

#### 3.2. The leaning effect

Disubstituted naphthalenes with electrophile–nucleophile pairs at the 1,8-positions tend to show a leaning effect. For example, Dunitz has shown that the C1—C9 bond in ketone (5) is splayed away from the C8 methoxy group, which in turn is splayed toward the C1 acetyl group (Schweizer *et al.*, 1978). This pattern has been observed for a number of 1,8-disubstituted naphthalenes and has been suggested to be a consequence of an attractive interaction between the electrophile and nucleophile. In 1,8-disubstituted naphthalenes where

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for (1)

	x	y	z	$U_{eq}$
S	0.03628 (9)	0.23141 (6)	0.68151 (5)	0.0501 (2)
O1	0.4147 (3)	−0.0734 (2)	0.2801 (1)	0.0804 (8)
O2	0.3642 (2)	−0.1474 (1)	0.4990 (1)	0.0498 (6)
O3	0.0779 (2)	0.2623 (1)	0.4738 (1)	0.0498 (6)
O4	0.0033 (2)	0.1629 (1)	0.5993 (1)	0.0423 (5)
O5	0.0843 (3)	0.1708 (2)	0.7542 (1)	0.0712 (8)
O6	−0.1056 (3)	0.2890 (2)	0.6769 (2)	0.0729 (8)
C1	0.3146 (3)	0.0157 (2)	0.3905 (2)	0.0375 (7)
C2	0.2862 (4)	0.0985 (2)	0.3411 (2)	0.0472 (8)
C3	0.2086 (4)	0.1822 (2)	0.3671 (2)	0.0477 (8)
C4	0.1535 (3)	0.1828 (2)	0.4446 (2)	0.0379 (7)
C4a	0.1749 (3)	0.0977 (2)	0.4996 (2)	0.0323 (7)
C5	0.1119 (3)	0.0894 (2)	0.5787 (2)	0.0354 (7)
C6	0.1342 (3)	0.0076 (2)	0.6292 (2)	0.0424 (8)
C7	0.2233 (3)	−0.0722 (2)	0.6049 (2)	0.0426 (8)
C8a	0.2609 (3)	0.0141 (2)	0.4731 (1)	0.0330 (7)
C8	0.2827 (3)	−0.0703 (2)	0.5285 (2)	0.0371 (7)
C9	0.4051 (5)	−0.0635 (3)	0.3532 (2)	0.063 (1)
C10	0.3685 (4)	−0.2402 (2)	0.5423 (2)	0.068 (1)
C11	0.0548 (4)	0.3478 (2)	0.4207 (2)	0.066 (1)
C12	0.1961 (3)	0.3078 (2)	0.6645 (2)	0.0412 (8)
C13	0.3477 (3)	0.2693 (2)	0.6748 (2)	0.0459 (8)
C14	0.4733 (4)	0.3294 (2)	0.6602 (2)	0.0513 (9)
C15	0.4496 (4)	0.4285 (2)	0.6369 (2)	0.0502 (9)
C16	0.2965 (4)	0.4659 (2)	0.6291 (2)	0.058 (1)
C17	0.1695 (4)	0.4067 (2)	0.6419 (2)	0.0549 (9)
C18	0.5872 (4)	0.4941 (3)	0.6223 (2)	0.072 (1)
H1	0.485 (4)	−0.102 (3)	0.393 (2)	0.11 (1)†

† Refined isotropically.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for (2)

	x	y	z	$U_{eq}$
S	0.10108 (9)	0.33383 (5)	0.41287 (5)	0.0482 (2)
O1	0.3841 (4)	−0.1421 (2)	0.7059 (2)	0.105 (1)
O2	0.3002 (3)	−0.0964 (1)	0.4599 (1)	0.0645 (7)
O3	0.0231 (2)	0.2501 (1)	0.4668 (1)	0.0485 (5)
O4	0.1318 (3)	0.3055 (1)	0.3218 (1)	0.0622 (6)
O5	−0.0163 (2)	0.4052 (1)	0.4267 (1)	0.0637 (6)
C1	0.3043 (3)	−0.0041 (2)	0.6307 (2)	0.0470 (8)
C2	0.2983 (4)	0.0446 (2)	0.7112 (2)	0.0554 (9)
C3	0.2323 (4)	0.1330 (2)	0.7114 (2)	0.0580 (9)
C4	0.1703 (3)	0.1732 (2)	0.6312 (2)	0.0505 (8)
C4a	0.1703 (3)	0.1248 (2)	0.5462 (2)	0.0407 (7)
C5	0.0979 (3)	0.1626 (2)	0.4620 (2)	0.0431 (7)
C6	0.0876 (4)	0.1154 (2)	0.3816 (2)	0.0536 (9)
C7	0.1569 (4)	0.0275 (2)	0.3796 (2)	0.0551 (9)
C8	0.2310 (3)	−0.0114 (2)	0.4577 (2)	0.0469 (8)
C8a	0.2386 (3)	0.0354 (2)	0.5449 (2)	0.0421 (7)
C9	0.3857 (5)	−0.0957 (3)	0.6400 (3)	0.072 (1)
C10	0.3127 (5)	−0.1414 (2)	0.3730 (2)	0.072 (1)
C11	0.2941 (3)	0.3555 (2)	0.4750 (2)	0.0421 (7)
C12	0.4416 (3)	0.3228 (2)	0.4426 (2)	0.0525 (8)
C13	0.5932 (3)	0.3399 (2)	0.4934 (2)	0.0596 (9)
C14	0.5998 (4)	0.3881 (2)	0.5756 (2)	0.0515 (8)
C15	0.4498 (4)	0.4205 (2)	0.6057 (2)	0.0585 (9)
C16	0.2967 (4)	0.4049 (2)	0.5561 (2)	0.0560 (9)
C17	0.7658 (4)	0.4038 (2)	0.6308 (2)	0.074 (1)
H1	0.466 (5)	−0.112 (3)	0.590 (3)	0.13 (2)†

† Refined isotropically.

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (3)

	x	y	z	$U_{\text{eq}}$
O1	0.2431 (3)	1.1866 (2)	0.2180 (2)	0.0942 (10)
O2	0.1724 (2)	0.9384 (1)	0.2508 (1)	0.0504 (6)
O3	-0.0074 (2)	0.8941 (2)	0.0948 (2)	0.0780 (7)
O4	-0.3697 (2)	1.1053 (1)	0.4505 (2)	0.0644 (7)
C1	0.0390 (3)	1.1098 (2)	0.2928 (2)	0.0471 (8)
C2	-0.0429 (4)	1.1845 (2)	0.3106 (2)	0.0555 (9)
C3	-0.1827 (4)	1.1867 (2)	0.3605 (2)	0.0567 (9)
C4	-0.2408 (3)	1.1109 (2)	0.3961 (2)	0.0485 (8)
C4a	-0.1655 (3)	1.0299 (2)	0.3783 (2)	0.0415 (7)
C5	-0.2273 (3)	0.9521 (2)	0.4153 (2)	0.0477 (8)
C6	-0.1573 (3)	0.8744 (2)	0.3985 (2)	0.0511 (9)
C7	-0.0236 (3)	0.8709 (2)	0.3422 (2)	0.0484 (8)
C8	0.0369 (3)	0.9452 (2)	0.3062 (2)	0.0435 (8)
C8a	-0.0256 (3)	1.0285 (2)	0.3240 (2)	0.0419 (7)
C9	0.1950 (5)	1.1209 (2)	0.2514 (3)	0.078 (1)
C10	-0.4362 (4)	1.1849 (2)	0.4846 (3)	0.088 (1)
C11	0.1346 (3)	0.9100 (2)	0.1425 (2)	0.0482 (8)
C12	0.2873 (3)	0.9023 (2)	0.0962 (2)	0.0421 (7)
C13	0.4481 (3)	0.9218 (2)	0.1574 (2)	0.0467 (8)
C14	0.5867 (3)	0.9136 (2)	0.1096 (2)	0.0516 (9)
C15	0.5670 (4)	0.8860 (2)	0.0009 (3)	0.0547 (9)
C16	0.4078 (4)	0.8662 (2)	-0.0607 (2)	0.0575 (10)
C17	0.2674 (4)	0.8745 (2)	-0.0140 (2)	0.0534 (9)
H1	0.281 (5)	1.074 (2)	0.261 (3)	0.12 (1)†

† Refined isotropically.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (4)

	x	y	z	$U_{\text{eq}}$
S	0.85663 (7)	0.54865 (9)	0.13231 (3)	0.0478 (2)
O1	1.4725 (2)	1.1168 (3)	0.12943 (9)	0.0778 (8)
O2	1.4385 (2)	0.7058 (3)	0.10315 (8)	0.0679 (7)
O3	0.9891 (2)	0.7963 (2)	0.22081 (7)	0.0558 (6)
O4	0.9884 (2)	0.5016 (2)	0.17158 (7)	0.0474 (5)
O5	0.8743 (2)	0.7012 (2)	0.10194 (8)	0.0596 (6)
O6	0.7645 (2)	0.5416 (3)	0.16859 (8)	0.0679 (7)
C1	1.3298 (2)	0.9346 (3)	0.16761 (10)	0.0421 (7)
C2	1.2649 (3)	1.0507 (3)	0.1945 (1)	0.0499 (8)
C3	1.1486 (3)	1.0100 (3)	0.2118 (1)	0.0498 (8)
C4	1.0959 (2)	0.8498 (3)	0.20195 (10)	0.0426 (7)
C4a	1.1554 (2)	0.7245 (3)	0.17074 (9)	0.0375 (6)
C5	1.1046 (2)	0.5577 (3)	0.15602 (9)	0.0413 (7)
C6	1.1672 (3)	0.4412 (3)	0.1285 (1)	0.0493 (8)
C7	1.2832 (3)	0.4845 (4)	0.1110 (1)	0.0519 (8)
C8	1.3328 (2)	0.6457 (4)	0.12198 (10)	0.0461 (8)
C8a	1.2747 (2)	0.7682 (3)	0.15388 (9)	0.0382 (7)
C9	1.4609 (3)	0.9924 (4)	0.1581 (1)	0.0501 (8)
C10	1.5748 (3)	0.9095 (4)	0.1925 (1)	0.0612 (9)
C11	1.4938 (3)	0.6021 (5)	0.0648 (1)	0.088 (1)
C12	0.9253 (3)	0.9137 (4)	0.2523 (1)	0.070 (1)
C13	0.8341 (2)	0.3742 (3)	0.0863 (1)	0.0452 (7)
C14	0.8783 (3)	0.3835 (4)	0.0362 (1)	0.0584 (9)
C15	0.8650 (3)	0.2421 (5)	0.0013 (1)	0.068 (1)
C16	0.8069 (3)	0.0923 (4)	0.0149 (1)	0.067 (1)
C17	0.7590 (4)	0.0886 (4)	0.0643 (2)	0.084 (1)
C18	0.7719 (3)	0.2278 (4)	0.1003 (1)	0.071 (1)
C19	0.7930 (4)	-0.0626 (5)	-0.0232 (1)	0.098 (1)

the substituents are not an electrophile-nucleophile pair, the substituents tend to both splay outward, presumably to minimize steric interactions (Bright *et al.*, 1973; Schweizer *et al.*, 1978). Aldehydes (1)-(2) and ketone (4) show a splaying effect comparable to that reported for ketone (5) and other relevant 1,8-disubstituted naphthalenes (Schweizer *et al.*, 1978). This is documented in Table 10 which lists relevant bond angles and inter-nuclear distances. The behavior of aldehyde (3), however, is different. Both the C1-C9 and C8-O2 bonds are splayed outward ( $\theta_2 > \theta_1$  and  $\theta_3 > \theta_4$ ) and the distance between the nucleophilic and electrophilic atoms (C9...O2) is much longer than in aldehydes (1)-(2) and ketones (4)-(5). This observation is consistent with the notion that an ester oxygen should be a worse nucleophile than an ether oxygen.

### 3.3. Geometric relationships of the nucleophile and electrophile

In addition to the leaning effect, electrophile-nucleophile interactions in 1,8-disubstituted naphthalenes have been analyzed in terms of the geometric relationships defined in Fig. 3 (Schweizer *et al.*, 1978). As documented in Table 11, ketones (4)-(5) have similar geometric relationships, but they differ drastically from those displayed by aldehydes (1)-(3).

Most relevant is the angle  $\alpha$ , which has been suggested to represent a nucleophile-electrophile approach trajectory. Whereas  $\alpha$  is 113.2 and 107.6° for ketones (4) and

(5), respectively, it varies from 141 to 151° for aldehydes (1)-(3). The physical reason for this difference is that the acetyl group in ketones (4) and (5) approaches orthogonality (90° twist angle) to the plane defined by the naphthalene, while the formyl group in aldehydes (1)-(3) is closer to being parallel (0° twist angle) to the naphthalene plane.

### 3.4. Trends in carbonyl compounds (1)-(4)

The first compound examined during the course of this study was aldehyde (1). Since aldehydes are good electrophiles, it was anticipated that this compound might display properties similar to those of ketone (5), and in some ways it does, but in others it does not. As noted above, (1) and (5) both show the leaning effect, but the approach trajectory of the nucleophile (OMe) to the electrophile [CHO in (1) and COMe in (5)] is very different. Owing to this large difference, we next prepared ketone (4) to see if the C4 and C5 substituents in (1) were somehow responsible for this difference. Since ketone (4) is structurally similar to ketone (5), the results show that the C4 and C5 substituents have little effect on the nucleophile-electrophile relationship. Aldehyde (2) was prepared next to examine the effect of the C4 methoxy group on the twist angle. There does appear to be a small effect as (2) shows a slightly greater twist angle than (1). It is notable that this trend also

shows up when comparing the twist angles of ketones (4) (C4 methoxy present) and (5) (C4 methoxy absent). This effect is consistent with the notion that the smaller twist angles in (1) and (4) allow for better overlap of the carbonyl  $\pi$ -bond with the more electron-rich naphthalene. The last compound studied was aldehyde (3). This compound, which has a C4 methoxy group, shows the smallest twist angle and fails to show any evidence of an electrophile-nucleophile interaction.

### 3.5. Differences between the aldehydes and ketones

One difference between the aldehydes and ketones described above involves steric effects. A hydrogen is smaller than a methyl group and, thus, the formyl group can adopt a conformation which provides some overlap between the naphthalene and carbonyl  $\pi$ -systems, whereas the acetyl group cannot. A search of the Cambridge Structural Database (Allen & Kennard,

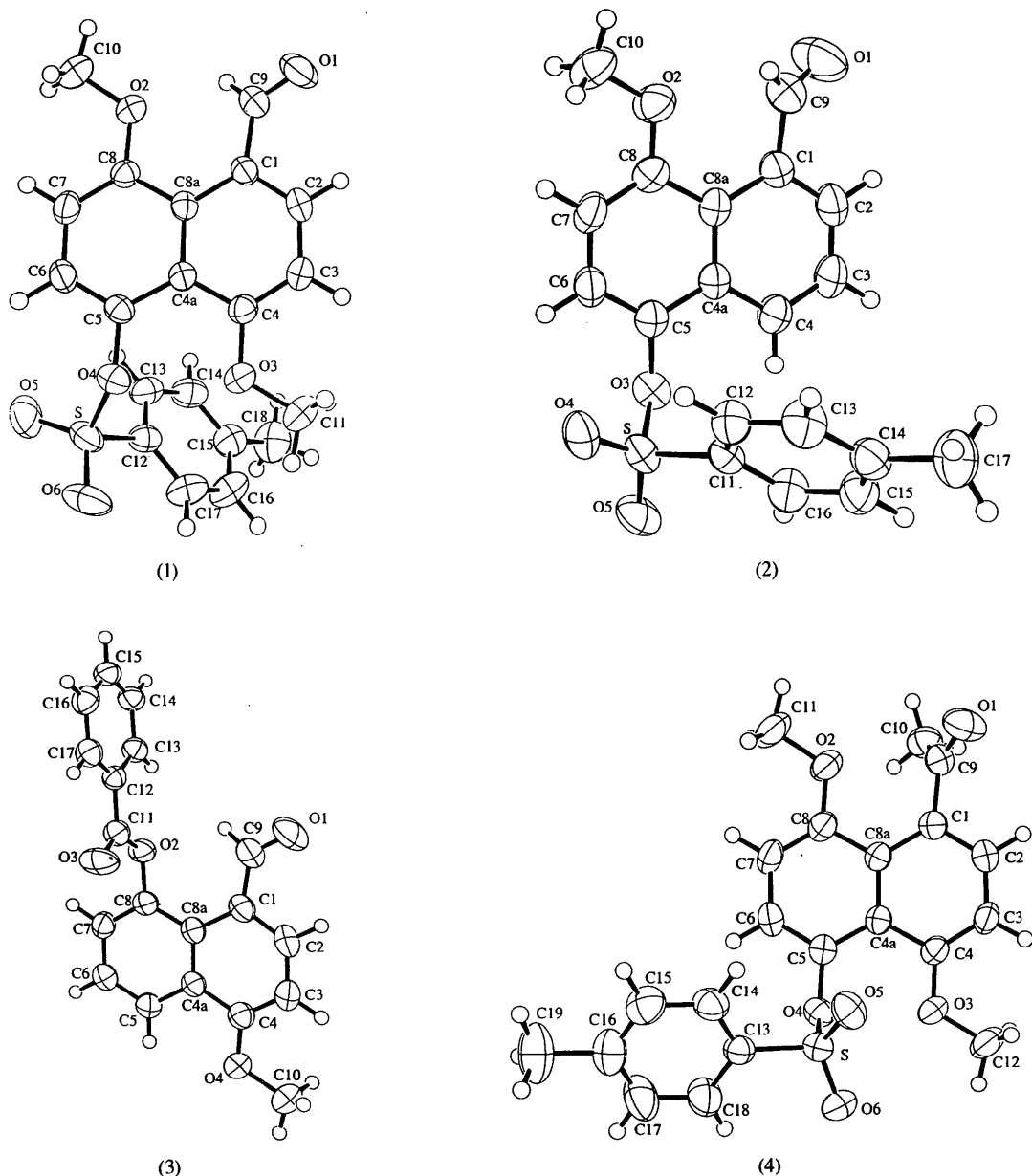


Fig. 2. ORTEPII (Johnson, 1976) drawings for (1)–(4). Non-H atoms are drawn with 50% probability displacement ellipsoids. The H atoms are represented by an arbitrary radius. Only one set of disordered methyl group H atoms is shown on C17 for (2) and on C10 and C19 for (4).

Table 6. Selected geometric parameters for (1)

S—O4	1.587 (2)	C4—C4a	1.432 (3)
S—O5	1.423 (2)	C4a—C5	1.425 (3)
S—O6	1.426 (2)	C4a—C8a	1.432 (3)
S—C12	1.749 (3)	C5—C6	1.358 (4)
O1—C9	1.176 (3)	C6—C7	1.394 (4)
O2—C8	1.361 (3)	C7—C8	1.367 (3)
O2—C10	1.420 (3)	C8a—C8	1.431 (3)
O3—C4	1.357 (3)	C12—C13	1.377 (4)
O3—C11	1.422 (3)	C12—C17	1.388 (4)
O4—C5	1.417 (3)	C13—C14	1.381 (4)
C1—C2	1.362 (4)	C14—C15	1.388 (4)
C1—C8a	1.436 (3)	C15—C16	1.384 (4)
C1—C9	1.479 (4)	C15—C18	1.505 (4)
C2—C3	1.391 (4)	C16—C17	1.375 (4)
C3—C4	1.367 (4)	C9—H1	1.00 (4)
O4—S—O5	109.3 (1)	O4—C5—C6	118.3 (2)
O4—S—O6	102.4 (1)	C4a—C5—C6	122.6 (2)
O4—S—C12	105.8 (1)	C5—C6—C7	120.0 (2)
O5—S—O6	120.3 (1)	C6—C7—C8	120.2 (2)
O5—S—C12	108.2 (1)	C1—C8a—C4a	119.2 (2)
O6—S—C12	109.9 (1)	C1—C8a—C8	122.5 (2)
C8—O2—C10	119.0 (2)	C4a—C8a—C8	118.2 (2)
C4—O3—C11	118.1 (2)	O2—C8—C7	123.4 (2)
S—O4—C5	122.8 (2)	O2—C8—C8a	115.1 (2)
C2—C1—C8a	118.6 (2)	C7—C8—C8a	121.5 (2)
C2—C1—C9	114.9 (2)	O1—C9—C1	125.3 (3)
C8a—C1—C9	126.4 (2)	S—C12—C13	119.6 (2)
C1—C2—C3	123.0 (2)	S—C12—C17	119.9 (2)
C2—C3—C4	120.0 (2)	C13—C12—C17	120.5 (3)
O3—C4—C3	122.7 (2)	C12—C13—C14	119.4 (3)
O3—C4—C4a	116.8 (2)	C13—C14—C15	121.1 (3)
C3—C4—C4a	120.5 (2)	C14—C15—C16	118.3 (3)
C4—C4a—C5	124.2 (2)	C14—C15—C18	120.9 (3)
C4—C4a—C8a	118.5 (2)	C16—C15—C18	120.8 (3)
C5—C4a—C8a	117.3 (2)	C15—C16—C17	121.5 (3)
O4—C5—C4a	118.4 (2)	C12—C17—C16	119.1 (3)

Table 7. Selected geometric parameters for (2)

S—O3	1.603 (2)	C4a—C5	1.420 (3)
S—O4	1.420 (2)	C4a—C8a	1.419 (4)
S—O5	1.424 (2)	C5—C6	1.351 (4)
S—C11	1.745 (3)	C6—C7	1.402 (4)
O1—C9	1.173 (4)	C7—C8	1.360 (4)
O2—C8	1.360 (3)	C8—C8a	1.434 (3)
O2—C10	1.430 (3)	C11—C12	1.377 (4)
O3—C5	1.416 (3)	C11—C16	1.378 (4)
C1—C2	1.372 (4)	C12—C13	1.384 (4)
C1—C8a	1.433 (3)	C13—C14	1.381 (4)
C1—C9	1.491 (4)	C14—C15	1.380 (4)
C2—C3	1.397 (4)	C14—C17	1.505 (4)
C3—C4	1.360 (4)	C15—C16	1.382 (4)
C4—C4a	1.420 (3)	C9—H1	1.03 (4)
O3—S—O4	109.1 (1)	C5—C6—C7	119.3 (3)
O3—S—O5	102.4 (1)	C6—C7—C8	121.0 (2)
O3—S—C11	104.1 (1)	O2—C8—C7	123.6 (3)
O4—S—O5	120.3 (1)	O2—C8—C8a	115.3 (2)
O4—S—C11	109.1 (1)	C7—C8—C8a	121.1 (3)
O5—S—C11	110.5 (1)	C1—C8a—C4a	118.4 (2)
C8—O2—C10	117.1 (2)	C1—C8a—C8	123.9 (3)
S—O3—C5	119.5 (1)	C4a—C8a—C8	117.6 (2)
C2—C1—C8a	119.5 (3)	O1—C9—C1	124.4 (4)
C2—C1—C9	115.7 (3)	S—C11—C12	119.6 (2)
C8a—C1—C9	124.7 (3)	S—C11—C16	119.5 (2)
C1—C2—C3	121.5 (2)	C12—C11—C16	120.9 (2)
C2—C3—C4	120.7 (3)	C11—C12—C13	118.7 (2)
C3—C4—C4a	120.0 (3)	C12—C13—C14	121.8 (3)
C4—C4a—C5	121.5 (3)	C13—C14—C15	118.0 (3)
C4—C4a—C8a	119.8 (2)	C13—C14—C17	120.8 (3)
C5—C4a—C8a	118.6 (2)	C15—C14—C17	121.2 (3)
O3—C5—C4a	117.1 (2)	C14—C15—C16	121.5 (3)
O3—C5—C6	120.5 (2)	C11—C16—C15	119.1 (3)
C4a—C5—C6	122.3 (3)		

1993a,b) revealed several structures relevant to this argument (Fig. 4). For example, 1-acetylanthracene (6), a 1-acetylnaphthalene mimic in which steric interactions would not be expected to inhibit the coplanarity of the naphthalene ring and acetyl group, crystallizes with a twist angle of 28° [the carbonyl group points toward C9 (Langer & Becker, 1993a)]. This number is similar to those observed for aldehydes (1)–(3). On the other hand, 1-acetyl-2,7-dimethoxynaphthalene (7) crystallizes with a twist angle of 62° [the carbonyl group points toward C8

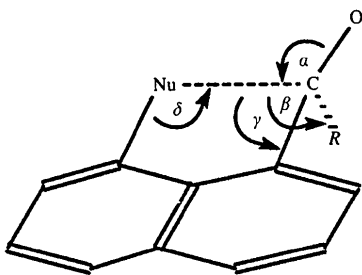


Fig. 3. Geometric relationships between nucleophile and electrophile.

(Prince *et al.*, 1989)]. In this case the twist angle could be a consequence of steric effects and/or an electronic interaction between the adjacent acetyl and methoxy groups ( $\text{MeO} \cdots \text{C}=\text{O}$  angle = 127°). Naphthalene-1-carboxylic acid (8) crystallizes with a twist angle of 8° (Fitzgerald & Gerkin, 1993), compared with a twist angle of 85° for 8-methoxynaphthalene-1-carboxylic acid (9) (Schweizer *et al.*, 1978). Once again one can argue differences between (8) and (9) on the basis of a steric effect and/or an electronic interaction. The CSD search also revealed structures of several aldehydes of relevance to this study. Naphthaldehyde (10) crystallizes with a twist angle of 10° for the C1 formyl group, using a best plane through the naphthalene, although the naphthalene is distorted from planarity due to steric interactions between the two dimethylamino groups (Pozharskii *et al.*, 1991). In addition, anthracene (11) (Langer & Becker, 1993b) and phenanthrene (12) (Wilson *et al.*, 1995) crystallize with twist angles of 20 and 1°, respectively. These data suggest that in the absence of peri substituents, 1-naphthaldehydes crystallize with the formyl group nearly coplanar with the aromatic ring.

Another difference between the aldehydes and ketones is that an attractive interaction between the hydrogen of the formyl group and the oxygen of the C(8) substituent

Table 8. Selected geometric parameters for (3)

O1—C9	1.190 (4)	C4a—C8a	1.429 (3)
O2—C8	1.410 (3)	C5—C6	1.360 (3)
O2—C11	1.366 (3)	C6—C7	1.402 (4)
O3—C11	1.194 (3)	C7—C8	1.358 (3)
O4—C4	1.354 (3)	C8—C8a	1.416 (3)
O4—C10	1.439 (3)	C11—C12	1.469 (3)
C1—C2	1.370 (4)	C12—C13	1.386 (3)
C1—C8a	1.441 (3)	C12—C17	1.391 (3)
C1—C9	1.466 (4)	C13—C14	1.376 (3)
C2—C3	1.395 (4)	C14—C15	1.373 (4)
C3—C4	1.366 (4)	C15—C16	1.377 (4)
C4—C4a	1.427 (3)	C16—C17	1.381 (4)
C4a—C5	1.413 (3)	C9—H1	0.99 (4)
C8—O2—C11	117.1 (2)	O2—C8—C8a	118.8 (2)
C4—O4—C10	117.5 (2)	C7—C8—C8a	123.5 (2)
C2—C1—C8a	118.4 (2)	C1—C8a—C4a	118.5 (2)
C2—C1—C9	115.9 (3)	C1—C8a—C8	126.0 (2)
C8a—C1—C9	125.5 (3)	C4a—C8a—C8	115.4 (2)
C1—C2—C3	123.6 (3)	O1—C9—C1	125.9 (4)
C2—C3—C4	119.0 (3)	O2—C11—O3	122.1 (2)
O4—C4—C3	124.4 (3)	O2—C11—C12	111.7 (2)
O4—C4—C4a	114.6 (2)	O3—C11—C12	126.3 (2)
C3—C4—C4a	121.0 (3)	C11—C12—C13	122.7 (2)
C4—C4a—C5	120.3 (2)	C11—C12—C17	117.9 (2)
C4—C4a—C8a	119.3 (2)	C13—C12—C17	119.4 (2)
C5—C4a—C8a	120.3 (2)	C12—C13—C14	120.2 (2)
C4a—C5—C6	121.0 (2)	C13—C14—C15	120.3 (3)
C5—C6—C7	119.8 (2)	C14—C15—C16	119.9 (3)
C6—C7—C8	119.8 (2)	C15—C16—C17	120.4 (3)
O2—C8—C7	117.6 (2)	C12—C17—C16	119.7 (3)

Table 9. Selected geometric parameters for (4)

S—O4	1.601 (2)	C4—C4a	1.437 (3)
S—O5	1.421 (2)	C4a—C5	1.420 (3)
S—O6	1.419 (2)	C4a—C8a	1.430 (3)
S—C13	1.744 (3)	C5—C6	1.357 (3)
O1—C9	1.207 (3)	C6—C7	1.403 (4)
O2—C8	1.359 (3)	C7—C8	1.361 (4)
O2—C11	1.425 (3)	C8—C8a	1.425 (3)
O3—C4	1.352 (3)	C9—C10	1.496 (4)
O3—C12	1.426 (3)	C13—C14	1.379 (3)
O4—C5	1.412 (3)	C13—C18	1.379 (4)
C1—C2	1.361 (3)	C14—C15	1.377 (4)
C1—C8a	1.430 (3)	C15—C16	1.376 (4)
C1—C9	1.511 (3)	C16—C17	1.380 (4)
C2—C3	1.398 (4)	C16—C19	1.506 (4)
C3—C4	1.363 (4)	C17—C18	1.381 (4)
O4—S—O5	108.9 (1)	C4a—C5—C6	122.1 (2)
O4—S—O6	103.8 (1)	C5—C6—C7	120.8 (2)
O4—S—C13	102.9 (1)	C6—C7—C8	119.2 (2)
O5—S—O6	121.2 (1)	O2—C8—C7	124.0 (2)
O5—S—C13	108.8 (1)	O2—C8—C8a	114.1 (2)
O6—S—C13	109.5 (1)	C7—C8—C8a	121.8 (2)
C8—O2—C11	118.5 (2)	C1—C8a—C4a	119.4 (2)
C4—O3—C12	118.9 (2)	C1—C8a—C8	121.9 (2)
S—O4—C5	118.9 (1)	C4a—C8a—C8	118.6 (2)
C2—C1—C8a	119.1 (2)	O1—C9—C1	120.4 (3)
C2—C1—C9	115.3 (2)	O1—C9—C10	121.1 (3)
C8a—C1—C9	125.5 (2)	C1—C9—C10	117.7 (2)
C1—C2—C3	122.3 (2)	S—C13—C14	119.9 (2)
C2—C3—C4	120.4 (2)	S—C13—C18	119.8 (2)
O3—C4—C3	124.0 (2)	C14—C13—C18	120.3 (3)
O3—C4—C4a	115.8 (2)	C13—C14—C15	119.3 (3)
C3—C4—C4a	120.2 (2)	C14—C15—C16	121.6 (3)
C4—C4a—C5	124.4 (2)	C15—C16—C17	117.9 (3)
C4—C4a—C8a	118.4 (2)	C15—C16—C19	121.6 (3)
C5—C4a—C8a	117.2 (2)	C17—C16—C19	120.5 (3)
O4—C5—C4a	121.4 (2)	C16—C17—C18	121.7 (3)
O4—C5—C6	116.4 (2)	C13—C18—C17	119.0 (3)

in the aldehydes may replace an attractive interaction between the C(8) substituent and the acetyl group in the ketones. This suggestion is based on reports of such C—H...O interactions in other crystallographic studies

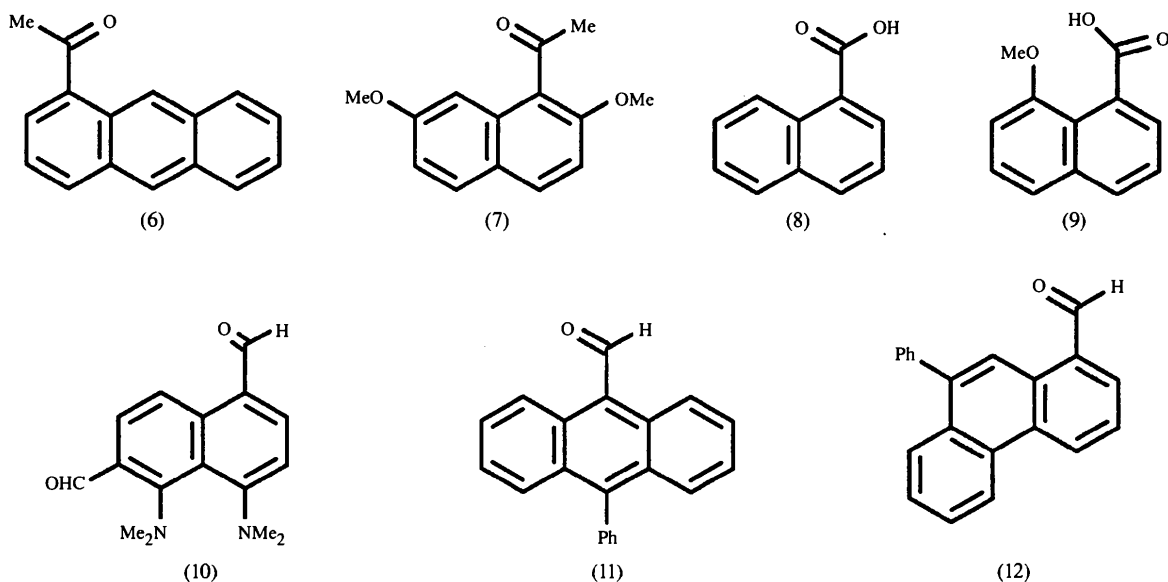


Fig. 4. Relevant compounds from the Cambridge Structural Database.

Table 10. *Distortion of exocyclic bonds in (1)–(5)*

The angles  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  and  $\theta_4$  are defined in Fig. 1.  $d(\text{Nu})$  and  $d(\text{C})$  are the displacements of the nucleophilic and electrophilic atoms from the mean plane of the naphthalene. The numbering of atoms is given in Fig. 2.

	Nu	R	$\theta_1$	$\theta_2$	$\theta_3$	$\theta_4$	$d(\text{Nu})$ (Å)	$d(\text{C})$ (Å)	C9...O2 (Å)	C1...C8 (Å)
(1)	OMe	H	114.9 (2)	126.4 (2)	115.1 (2)	123.4 (2)	0.02	-0.03	2.628 (4)	2.514 (4)
(2)	OMe	H	115.7 (3)	124.7 (3)	115.3 (2)	123.6 (2)	0.04	0.05	2.644 (4)	2.530 (4)
(3)	OCOPh	H	115.9 (3)	125.5 (3)	118.8 (2)	117.6 (2)	0.07	-0.25	2.823 (4)	2.546 (4)
(4)	OMe	Me	115.3 (2)	125.5 (2)	114.1 (2)	124.0 (2)	0.16	-0.20	2.578 (3)	2.496 (4)
(5)	OMe	Me	115.3 (8)	125.5 (8)	115.9 (8)	124.4 (9)	0.08	-0.12	2.61	2.50

Table 11. *Geometric relationships between nucleophilic and electrophilic substituents in (1)–(5)*

The terms  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are defined in Fig. 3.  $\Delta C$  refers to the distance between C9 and a plane passing through C1, R and O1. C9—H and O2...H refer to the aldehyde C—H bond length and the distance between the aldehyde hydrogen and O2, respectively. C9—H...O2 refers to the angle defined by those three atoms. Twist refers to the angle between the mean plane of the naphthalene and the plane defined by the formyl (1)–(3) or acetyl group (4)–(5) and C1. Pyramidalization at the aldehyde carbonyl group could not be accurately determined because of the large error in the H-atom position when determined by X-ray scattering. Pyramidalization of the carbonyl group was observed in ketone (4).

	Nu	R	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\delta$ (°)	$\Delta C$	C9—H (Å)	O2...H (Å)	C9—H...O2 (°)	Twist (°)
(1)	OMe	H	147.8 (3)	52 (2)	79.9 (2)	96.0 (2)	—	1.00 (4)	2.16 (4)	106 (3)	23.9 (4)
(2)	OMe	H	141.4 (3)	55 (2)	80.6 (2)	95.4 (2)	—	1.03 (4)	2.22 (4)	102 (3)	32.9 (4)
(3)	OCOPh	H	151.2 (3)	47 (2)	79.9 (2)	88.9 (2)	—	0.99 (4)	2.26 (3)	115 (3)	12.8 (4)
(4)	OMe	Me	113.1 (2)	85.6 (2)	79.4 (2)	97.4 (2)	0.07	—	—	—	68.3 (1)
(5)	OMe	Me	107.6	87.7	80.0	96.2	0.044	—	—	—	75

(Chaney *et al.*, 1996; Desiraju, 1991; Pedireddi & Desiraju, 1992; Steiner, 1996; Taylor & Kennard, 1984). The leaning effect in the aldehydes may be an attempt to attain an optimum C—H...O bond distance of  $\sim 2.20$  Å (Steiner, 1996).

### 3.6. Conclusions and an additional observation

It is clear that aldehydes (1)–(3), which have an opportunity to show geometric evidence of nucleophile-electrophile interactions between the methoxy and carbonyl groups in the solid state, fail to do so. What is most interesting, however, is that (1) and (2) show the same leaning effect as ketones (4)–(5) and some 1-methoxynaphthalene derivatives (Bideau *et al.*, 1984; Bideau *et al.*, 1991; Linden *et al.*, 1989; van Koten *et al.*, 1980; Schmalte *et al.*, 1986; Siriwardane *et al.*, 1987). Perhaps this leaning effect is simply an indication that

there is an electrostatic attraction between the methoxy group and the formyl C—H bond, although an electrostatic attraction between the methoxy group and the carbonyl carbon may also be present.

Finally, it is notable that the crystal structure of gilvocarcin M (13) also shows a leaning effect, Fig. 5 (Hirayama *et al.*, 1981). For example,  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  and  $\theta_4$  are 116.4, 125.6, 113.4 and 120.3°, respectively. In addition, the O7...C6 internuclear distance is 2.681 Å, the C7...C13 internuclear distance is 2.550 Å and the O7...C6—O3 angle is 161°. This is quite interesting and surprising. First, the electrophile is now a carbon-oxygen sigma bond and the nucleophile is a lactone oxygen. The crystal structure looks remarkably like the lactone (nucleophile) is performing an  $S_N2$  reaction on the C6—O3 sigma bond (electrophile). In this regard, it is notable that the C6—O3 bond in (11) is slightly longer than normal. Although the geometric relationships between O7 and the C6—O3 sigma bond could well be an artifact of steric constraints, the leaning effect could be a consequence of an electrostatic attraction between the C7 and C13 substituents.

We thank Dr Kurt Loening for help with nomenclature. We thank one of the referees for pointing out leaning effects in several 1-methoxynaphthalene derivatives of which we were unaware.

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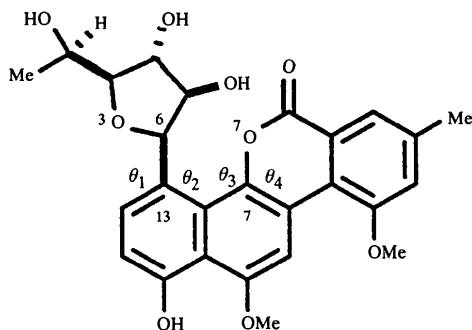


Fig. 5. Gilvocarcin M.



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