Crystal data

$C_{24}H_{24}O_3Si_2$
$M_r = 416.61$
Monoclinic
$P2_1/n$
$a = 10.694\,(1)$ Å
$b = 13.481\,(1)$ Å
$c = 15.307\,(2)$ Å
$\beta = 94.32\,(1)°$
$V = 2200.5\,(4)$ Å^3
$Z = 4$
$D_x = 1.258$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 4.83$–$9.96°$
$\mu = 0.183$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.42 \times 0.38 \times 0.32$ mm
Yellow

Data collection

Siemens $P4$ four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.243$, $T_{\max} = 0.266$
4615 measured reflections
3451 independent reflections

2170 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 24°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.164$
$S = 0.489$
3434 reflections
306 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.2186P)^2 + 2.3095P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.179$
$\Delta\rho_{\max} = 0.182$ e Å^{-3}
$\Delta\rho_{\min} = -0.205$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Si1—O2	1.626 (2)	O1—C9	1.381 (3)
Si2—O2	1.625 (2)	O3—C20	1.376 (4)
Si2—O3	1.647 (2)		
O2—Si1—O1	108.91 (11)	Si2—O2—Si1	151.2 (2)
O2—Si2—O3	108.95 (12)	C20—O3—Si2	126.9 (2)
C9—O1—Si1	121.4 (2)		

All H atoms were fixed at calculated positions with common isotropic displacement parameters ($U_{\rm iso} = 0.08$ Å^2).

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *XL* in *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1062). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 146–148

2-(5-Chloro-2-nitrophenylthio)nicotinoyl Chloride

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Abstract

The two aromatic rings in the title compound, $C_{12}H_6Cl_2N_2O_3S$, form a dihedral angle of 56.7 (1)°. The alkanoyl chloride group lies slightly out of the plane of the aromatic ring with the carbonyl O and alkanoyl Cl atoms lying 0.219 (2) and −0.374 (1) Å, respectively, from the ring. The nitro group deviates from coplanarity with its aromatic ring, displaying a torsion angle along N—C of 34.9 (3)°. The C—S—C angle is 102.85 (9)°. Bond distances C═O and S—C have values of 1.178 (3) Å, and 1.766 (2) and 1.767 (2) Å, respectively.

Comment

The title compound, (I), was prepared as part of a structural study involving heterocyclic fused-ring systems and their key synthetic precursors (Garcia, Haydar & Krapcho, 1997).

The title compound contains two substituted aromatic rings linked by an S atom which form a di-

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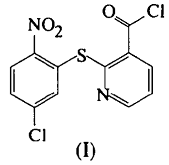

(I)

hedral angle of 56.7 (1)°. The S—C1 and S—C7 bond lengths of 1.766 (2) and 1.767 (2) Å, respectively, are in agreement with those found for 9-nitro-1-azaphenoxathiin [1.768 (7) and 1.756 (7) Å; Hossain *et al.*, 1982], and 7- and 8-chloro-1-azaphenoxathiin [1.759 (3) and 1.766 (2) Å, respectively; Martin *et al.*, 1978]. The S atom deviates slightly from coplanarity with both aromatic rings, torsion angles S—C1—C2—C6 and S—C7—C8—N2 are 1.4 (3) and −1.8 (3)°, respectively. Bond lengths C7—C8 [1.409 (3) Å] and C1—C2 [1.415 (3) Å] are longer than the other C—C aromatic bonds, which lie in the range 1.372 (3)–1.384 (3) Å. These increased values may be attributed to the presence of electron-withdrawing groups α to the sulfur-substituted C atoms. The C2—C6 bond length of magnitude 1.471 (3) Å is in agreement with other C(phenyl)—C(carbonyl) bond lengths, *e.g.* terephthaloyl chloride [1.486 (4) Å; Leser & Rabinovich, 1978*a*], biphenyl-2,2′-dicarbonyl chloride [1.476 (5) Å; Leser & Rabinovich, 1978*b*] and a series of chalcone derivatives [mean value 1.489 (12) Å; Rabinovich & Shakked, 1974]. The C=O length of 1.178 (3) Å agrees well with values obtained for other alkanoyl chlorides, varying from 1.166 in phosgene to 1.21 (4) Å in chloroacetyl chloride (Simonetta & Beltrame, 1972). The C6—Cl2 bond length of 1.771 (2) Å is longer than the accepted value of 1.736 Å for Cl—C_{sp^2} (Dewar & Schmeizing, 1960).

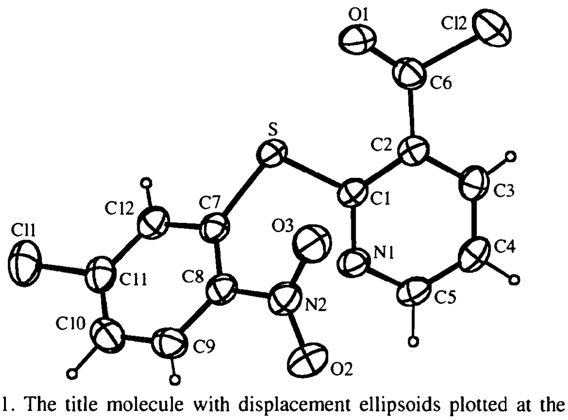

Fig. 1. The title molecule with displacement ellipsoids plotted at the 40% probability level and H atoms represented as circles of arbitrary radii.

Experimental

The compound was synthesized by reacting 2-nitro-5-chlorothiophenol (Bourdais, 1966) with 2-chloronicotinic acid (Garcia, Haydar & Krapcho, 1997) following a modification of a reported procedure (Ross, 1966).

Crystal data

$C_{12}H_6Cl_2N_2O_3S$
$M_r = 329.16$
Monoclinic
$P2_1/c$
$a = 11.8721$ (7) Å
$b = 15.406$ (2) Å
$c = 7.1392$ (5) Å
$\beta = 95.361$ (5)°
$V = 1300.1$ (3) Å^3
$Z = 4$
$D_x = 1.682$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 12$–29°
$\mu = 6.2$ mm^{-1}
$T = 298$ K
Irregular fragment
0.35 × 0.30 × 0.25 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.11$, $T_{\max} = 0.22$
2995 measured reflections
2675 independent reflections

2566 reflections with $I > 1\sigma(I)$
$R_{\rm int} = 0.03$
$\theta_{\max} = 74.92°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 120 min
intensity decay: −1.6%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.061$
$S = 1.62$
2566 reflections
206 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.002F_o^4]$
$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $5.6 (3) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C11	1.733 (2)	S—C1	1.766 (2)
Cl2—C6	1.771 (2)	S—C7	1.767 (2)
C1—S—C7	102.85 (9)	Cl2—C6—C2	115.4 (2)
Cl2—C6—O1	117.9 (2)	O1—C6—C2	126.7 (2)

C—H distances are in the range 0.85 (2)–0.99 (3) Å, while $B_{\rm iso}$ values for H atoms range from 3.4 (5) to 4.6 (6) Å^2.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: Direct methods *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1348). Services for accessing these data are described at the back of the journal.

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3,3''-Dimethyl-1,1':4',1''-terphenyl

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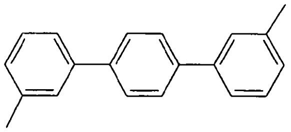
Abstract

The title compound, $C_{20}H_{18}$, is centrosymmetric and adopts a twisted conformation. This result contrasts related unsubstituted systems, where rotational disorder is inevitably found. The different behaviour is rationalized in terms of the absence of π–π interactions in the lattice of the title compound.

Comment

The title compound, (1), was isolated as a by-product from the addition of singlet oxygen to 1-methyl-3-[4-(3-methylphenyl)-1,3-cyclohexadienyl]benzene. The structure of (1) is molecular, with the closest non-hydrogen contact of 3.588 (3) Å occurring between C2' and C6'^{i} [symmetry code: (i) $-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$]; there is no evidence of base stacking, *i.e.* π–π interactions. The molecule is centrosymmetric with significant twists between the constituent rings as seen in the dihedral angle between the inner and outer rings of 35.3 (1)°. Consequently, there is little opportunity for conjugation throughout the molecule and this is reflected in the C1—C1' bond distance of 1.488 (2) Å. This separation compares well with that found in *p*-terphenyl of 1.496 (4) Å (Rietveld *et al.*, 1970). Other geometric parameters are as expected, with the aromatic C—C bonds lying in the range 1.377 (3) to 1.399 (2) Å, and C3'—C3'' is 1.504 (3) Å.



(1)

p-Polyphenyls have received considerable attention owing to their molecular flexibility. Whether a particular structure is planar or twisted depends on a balance between (i) intermolecular forces and (ii) intramolecular repulsions between the *ortho*-H atoms (Saitoh *et al.*, 1993; Baker *et al.*, 1993). Accordingly, while a planar structure is found for *p*-terphenyl and indeed higher homologues at room temperature, these structures undergo phase changes at reduced temperatures to give rise to twisted conformations. In *p*-terphenyl, the dihedral angle between the inner and outer rings at 200 K is 26.6° (Baudour *et al.*, 1986). The absence of extended base stacking in (1) precludes the sort of rotational disorder found in the unsubstituted analogues.

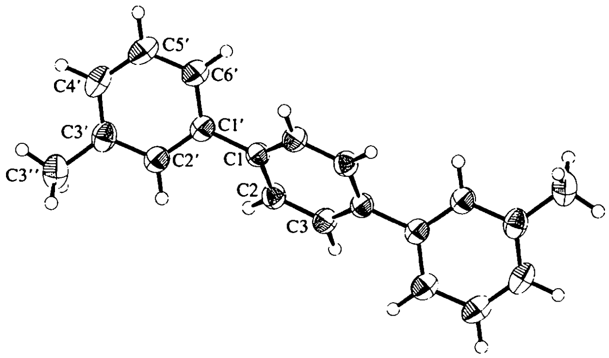


Fig. 1. The title structure is shown with 40% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976).

Experimental

To a solution of 1-methyl-3-[4-(3-methylphenyl)-1,3-cyclohexadienyl]benzene in dichloromethane (100 ml) at 283 K was added rose bengal (5 mg). A gentle stream of oxygen was passed through the solution with concomitant irradiation from