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12-Formyl-9,10-dimethyl-9,10-dihydro-11-thia-9,10-ethanoanthracene

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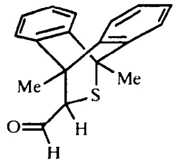
Abstract

The structure of the title compound, $C_{18}H_{16}OS$, is described. Two conformers co-exist in the crystal structure with a very near spatial arrangement.

Comment

Thiaethanoanthracenes are convenient precursors for thioaldehydes (Pelloux-Léon & Vallée, 1997). Upon heating, they undergo cyclo-reversion and give anthracene and a compound containing a carbon–sulfur double bond. The title compound, (1), is a precursor for monothioglyoxal and can also be used as an intermediate in the synthesis of various thiaethanoanthracenes (Arnaud *et al.*, 1994; Pelloux-Léon *et al.*, 1997). We have recently reported the nucleophilic attack of an enolate on the monothioglyoxal precursor (Minassian *et al.*, 1999). To understand the stereoselectivity observed in such additions, knowledge of the preferred conformation of (1) would be of interest. We have thus determined its atomic arrangement.



(1)

The present determination shows the existence of two conformers (Fig. 1) with very similar spatial conformations. Owing to this similarity, we think that both would give the same diastereoselectivity results. If one supposes that these conformers are also predominantly present in solution, then, according to Fig. 2, and assuming that the attack would occur from the less hindered side, the preferred face would be the *S* one. If the entering nucleophilic (Nu) group ranks third in the CIP priority rule (Cahn *et al.*, 1996), the relative configuration of the obtained product will be *R**,*S**. In order to simplify the text, we note the $C_{18}H_{16}OS$ conformer as *C* and the $C'_{18}H'_{16}O'S'$ conformer as *C'* hereafter.

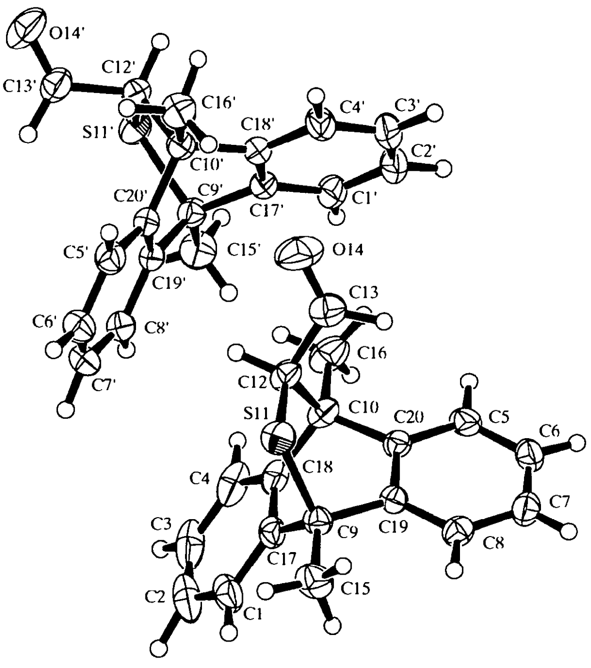


Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the two conformers of (1) shown with 40% probability displacement ellipsoids.

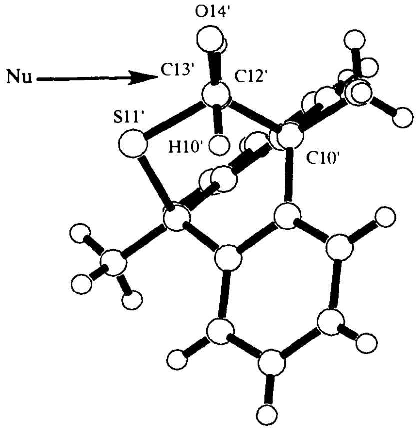


Fig. 2. A *CHARON* (Lauher, 1989) drawing showing the preferred face for the attack of a nucleophile on aldehyde (1).

As already mentioned, the two independent molecules have very similar geometries. Thus, the dihedral angles between the two benzenic planes differ by less than 2° [53.8 (1)° in conformer *C* and 52.3 (1)° in conformer *C'*]. Another noticeable feature is that in both molecules, the mean plane of the S11, C9, C10, C12, C15 and C16 (or S11', C9', C10', C12', C15' and C16') atoms is within less than 2° of the bisector plane of the two benzenic planes. In addition, one should also note that inside this bisector plane, the C15, C9, C10 and C16 (or S11', C9', C10', C12', C15' and C16') atoms are almost perfectly aligned and located on the intersecting line of the two benzenic ring planes. In each of the two molecules, the two C···S distances are significantly different [1.869 (1) and 1.824 (1) Å in *C*, and 1.870 (1) and 1.812 (1) Å in *C'*] and the C—S—C angles quite comparable [98.16 (6)° in *C* and 98.48 (6)° in *C'*]. A survey of 23 accurate structural investigations (Cambridge Structural Database, 1998) of compounds including similar C—S—C atomic groups shows that for 13 of them, similar differences are observed for the C···S distances, while in the remaining ones, these two distances are almost similar. The values observed in the title compound for both C···S distances and C—S—C angles lie within the ranges of values obtained from this survey.

Experimental

The title compound was synthesized by reduction of the corresponding nitrile (Arnaud *et al.*, 1995) with diisobutylaluminium hydride. It was purified by liquid chromatography over silica gel using a 40/60 chloroform/pentane mixture as the eluent. The oil obtained was kept at 278 K and within a few days crystals appeared.

Crystal data

$C_{18}H_{16}OS$
$M_r = 280.38$
Monoclinic
$P2_1/n$
$a = 14.149\ (5)$ Å
$b = 12.760\ (3)$ Å
$c = 16.754\ (7)$ Å
$\beta = 107.68\ (3)°$
$V = 2882\ (2)$ Å^3
$Z = 8$
$D_x = 1.292$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 10.8–12.0°$
$\mu = 0.217$ mm^{-1}
$T = 293$ K
Prism
$0.32 \times 0.30 \times 0.28$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
8999 measured reflections
8818 independent reflections
5969 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.007$
$\theta_{\rm max} = 29.96°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 23$
2 standard reflections every 120 reflections intensity decay: −1.17%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.057$
$S = 1.937$
5969 reflections
489 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o) + 0.00051|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.031$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S11—C9	1.869 (1)	S11'—C9'	1.870 (1)
S11—C12	1.824 (1)	S11'—C12'	1.812 (1)
C9—C15	1.526 (2)	C9'—C15'	1.516 (2)
C9—C17	1.503 (2)	C9'—C17'	1.513 (2)
C9—C19	1.504 (2)	C9'—C19'	1.513 (2)
C10—C12	1.565 (2)	C10'—C12'	1.583 (2)
C12—C13	1.498 (2)	C12'—C13'	1.511 (2)
C9—S11—C12	98.16 (6)	S11'—C9'—C17'	105.30 (8)
S11—C9—C15	106.13 (9)	S11'—C9'—C19'	105.19 (8)
S11—C9—C17	104.89 (8)	C15'—C9'—C17'	115.4 (1)
S11—C9—C19	105.88 (8)	C15'—C9'—C19'	115.6 (1)
C15—C9—C17	115.9 (1)	C12'—C10'—C16'	108.1 (1)
C15—C9—C19	115.2 (1)	C12'—C10'—C18'	106.39 (9)
C17—C9—C19	107.86 (9)	C12'—C10'—C20'	107.39 (9)
C12—C10—C16	107.1 (1)	C18'—C10'—C20'	107.07 (9)
S11—C12—C10	111.69 (8)	S11'—C12'—C10'	111.72 (8)
S11—C12—C13	105.2 (1)	S11'—C12'—C13'	106.26 (9)
C10—C12—C13	113.2 (1)	C10'—C12'—C13'	111.9 (1)
C9'—S11'—C12'	98.48 (6)	C9'—C17'—C18'	115.0 (1)
S11'—C9'—C15'	105.90 (9)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997). Program(s) used to solve structure: *SIR*92 (Altomare *et al.* 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1032). Services for accessing these data are described at the back of the journal.

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2,4,4,6,6-Pentachloro-2-(2,6-di-*tert*-butyl-4-methylphenoxy)cyclo-$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-triphosphazatriene

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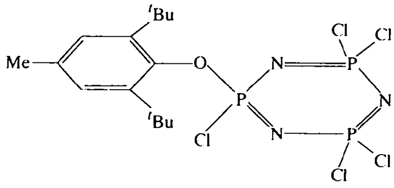
Abstract

The title compound, $C_{15}H_{23}Cl_5N_3OP_3$, consists of a non-planar trimeric phosphazene ring and a bulky 2,6-di-*tert*-butyl-4-methylphenoxy side group in which the phenyl ring shows a small but significant distortion from planarity. The bulky group predominantly determines the molecular shape. The endocyclic angle about the P atom bonded to the substituent is decreased, while the exocyclic angle is increased. The situation is not similar to that of tetrameric phosphazene derivatives.

Comment

Over the last two decades, there have been a number of studies of the bulky phenoxy derivatives of hexachlorocyclo-$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-triphosphazatriene ($N_3P_3Cl_6$) and octachlorocyclo-$2\lambda^5$,$4\lambda^5$,$6\lambda^5$,$8\lambda^5$-tetraphosphazatetraene ($N_4P_4Cl_8$). These phosphazene derivatives have potential use in the preparation of new small-molecule organocyclophosphazenes (Allcock, Dembek *et al.*, 1992; Allen, 1994), and high polymeric phosphazene derivatives with inorganic backbones and aryloxy side groups. These classes of polymers may be useful as high refractive index glasses (Olshavsky & Allcock, 1995), ferroelectric and non-linear optical polymers (Dembek *et al.*, 1991; Allcock *et al.*, 1995), liquid crystalline materials (Allcock & Kim, 1991), biomedical materials (Cohen *et al.*, 1990) and small-molecule models for the corresponding linear phosphazene macromolecules. The structures of the organic, inorganic or organometallic side groups are highly effective in determining the specific physical or chemical properties of phosphazene polymers (Allcock *et al.*, 1996; Allcock, 1985).

$N_3P_3Cl_6$ is a standard compound for trimeric phosphazene derivatives. The crystal structures of $N_3P_3Cl_6$ (Bullen, 1971) and only a few of its derivatives with bulky phenoxy groups, such as [$Cl_5N_3P_3$–$P_3N_3Cl_4(OC_6H_3\text{-}2,6\text{-}{}^t\text{Bu}_2)$] (Hökelek *et al.*, 1994), [$N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$], [$N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$] and [$N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2$] (Allcock, Ngo *et al.*, 1992), and [$N_3P_3(OC_6H_4OCH_2Ph\text{-}4)_6$] (Allcock *et al.*, 1996), have been reported. The study of the title structure, (I), was undertaken in order to understand the influence of the highly hindered side group on the structure of the cyclic trimeric phosphazene ring and is part of a study of the effects of the steric and electronic factors on the nucleophilic substitution patterns found for cyclic trimeric phosphazenes.



(I)

The title molecule is shown in Fig. 1. The structure consists of a non-planar cyclic trimeric phosphazene ring with one 2,6-di-*tert*-butyl-4-methylphenoxy group attached to the P2 atom; the phenyl ring is not strictly planar, the largest displacements from its least-squares plane being *ca* 0.06 Å for C1, C4 and C6. The total puckering amplitude of the phosphazene ring is 0.166 (2) Å (Cremer & Pople, 1975). The three N atoms are displaced on opposite sides (+ and −) with respect to the plane through the P atoms as follows: N1 +0.203 (3), N3 +0.084 (3) and N5 −0.075 (3) Å.