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5-Allyl-3-methoxy-2-(*p*-tolylsulfonyloxy)-azobenzene

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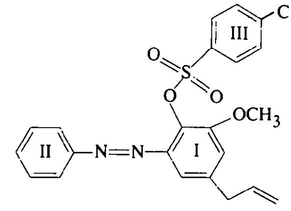
Abstract

The structure of the title compound, 5-allyl-3-methoxy-2-(*p*-tolylsulfonyloxy)diphenyldiazene, $C_{23}H_{22}N_2O_4S$, shows the characteristic features of azobenzene derivatives. The rings in the azobenzene frame are twisted by 16.97 (2) and 5.47 (2)° out of the azo group plane. The larger twist is associated with the 5-allyl-3-methoxy ring. The azobenzene moiety of the molecule has a *trans* configuration.

Comment

As part of a general study of the crystal chemistry of dyes and to provide templates for molecular modelling studies, the crystal structure of the brown–red dye (1) has been determined.



(1)

The bond distances and angles in the three phenyl rings are in good agreement with the expected value for aromatic rings. The N1=N2 bond length [1.237 (3) Å] is short enough to indicate its double-bond character. The angles N2—N1—C1 and N1—N2—C11 are 114.7 (2) and 113.8 (2)°, respectively; the torsion angle N1—N2—C11—C16 is −179.1 (2)°. Similar values have been observed in other *trans*-azo compounds (Özbey, Kendi, Hocaoğlu, Uyar & Mak, 1993; Özbey, Kendi, Hocaoğlu, Uyar, Mak & Cascarano, 1994; Özbey, Kendi & İde, 1995; Howard, Batsanov, Bryce & Chesney, 1994).

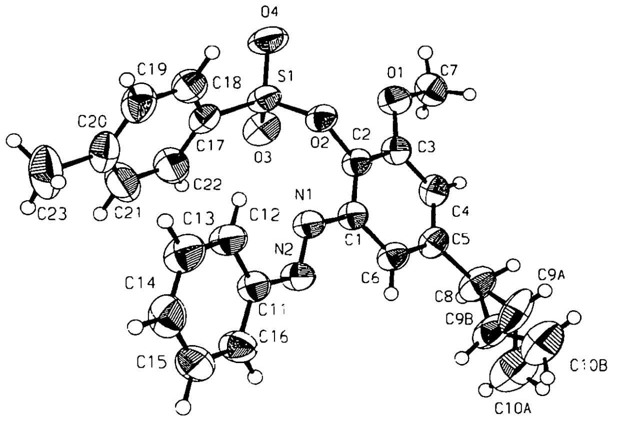


Fig. 1. *ORTEP*II (Johnson, 1976) view of the title compound. Anisotropic displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.

The three phenyl rings are planar within experimental error. The rings in the azobenzene frame are twisted by 16.97 (2) and 5.47 (2)° out of the azo group plane. The larger twist is associated with the 5-allyl-3-methoxy ring. The angles between the least-squares planes of phenyl rings which contain atoms C1–C6 (I), C11–C16 (II) and C17–C22 (III) are I/II 21.40 (1), I/III 51.95 (1) and II/III 33.09 (2)°. The 5-allyl-3-methoxy groups are not coplanar with the C1–C6 ring.

Experimental

Aniline in an acidic medium was diazotized and combined with eugenol. This compound was then reacted with *p*-tolylsulfonic chloride in a basic medium. Single crystals were obtained from diethyl ether. The density D_m was measured using pycnometry.

Crystal data

$C_{23}H_{22}N_2O_4S$
$M_r = 422.49$
Triclinic
$P\bar{1}$
$a = 6.811\ (2)$ Å
$b = 11.079\ (2)$ Å
$c = 14.907\ (2)$ Å
$\alpha = 91.82\ (3)°$
$\beta = 96.53\ (3)°$
$\gamma = 105.41\ (3)°$
$V = 1075.2\ (4)$ Å^3
$Z = 2$
$D_x = 1.305$ Mg m^{-3}
$D_m = 1.33$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.24–28.17°$
$\mu = 0.182$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.8 × 0.48 × 0.32 mm
Brown–red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: none

$\theta_{\max} = 24.03°$
$h = 0 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$

2813 measured reflections
2813 independent reflections
2438 reflections with
$I > 2\sigma(I)$

3 standard reflections
frequency: 20 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.123$
$S = 1.063$
2813 reflections
307 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.3922P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.215$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O4	1.415 (2)	O1—C3	1.349 (3)
S1—O3	1.423 (2)	O1—C7	1.431 (3)
S1—O2	1.595 (2)	N1—N2	1.237 (3)
S1—C17	1.747 (3)	N1—C1	1.426 (3)
O2—C2	1.413 (3)	N2—C11	1.432 (3)
O4—S1—O3	120.76 (13)	O3—S1—C17	109.82 (13)
O4—S1—O2	104.13 (12)	O2—S1—C17	102.83 (11)
O3—S1—O2	108.69 (11)	N2—N1—C1	114.7 (2)
O4—S1—C17	109.02 (12)	N1—N2—C11	113.8 (2)
C17—S1—O2—C2	−111.1 (2)	N2—N1—C1—C6	17.7 (3)
C1—N1—N2—C11	−175.4 (2)	N1—N2—C11—C16	−179.1 (2)
N2—N1—C1—C2	−167.3 (2)	N1—N2—C11—C12	3.7 (4)

Following a sequence of refinements and difference Fourier syntheses, disordered C9 and C10 atoms were recognized in a 60:40 ratio in the allyl group. Their atomic displacement parameters are only slightly larger than those of the other atoms. A riding model was used for all H atoms at calculated positions with isotropic $U_{\rm iso}$.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methanol Solvate of the 1:1 Molecular Complex of Trimethoprim and Sulfadimidine

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Abstract

In the title complex, $C_{14}H_{18}N_4O_3.C_{12}H_{14}N_4O_2S.CH_4O$, the molecular association between trimethoprim {5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine; TMP} and sulfadimidine [4-amino-*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide; SDMD] is maintained by two N—H···N hydrogen bonds with no proton transfer from the sulfonamide imino N atom to the pyrimidine N atom of TMP. The methanol solvate molecule is linked to an O atom of the sulfonamido group through a strong O—H···O interaction and does not seem to play an important role in the crystal-packing stabilization.

Comment

Complexation of TMP with sulfamethoxazole (Giuseppetti, Tadini, Bettinetti, Giordano & La Manna, 1980; Nakai, Takasuka & Shiro, 1984) and sulfametrole (Giuseppetti, Tadini & Bettinetti, 1994) in the solid state involves a proton transfer from the sulfonamide to the pyrimidine N atom of TMP. In the complex between