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4,4-Bis(4-methylphenylsulfanyl)-1,1-diphenyl-2-azabuta-1,3-diene

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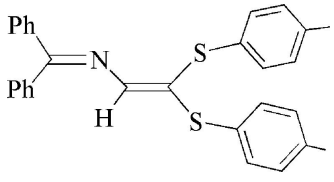
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.090; data-to-parameter ratio = 16.8.

In the title compound, $C_{29}H_{25}NS_2$, both the Cl atoms of the azadiene precursor 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene are replaced by two vicinal *S*-*p*-tolyl substituents attached to the terminal C atom of a π-conjugated 2-azabutadiene array. The azadiene chain is planar to within 0.01 Å. One of the phenyl rings seems to be slightly π-conjugated with the azadiene core [dihedral angle 5.1 (2)°].

Related literature

Some related structures of alkoxo- (Jacquot *et al.*, 2000), cyano- (Jacquot-Rousseau *et al.*, 2002) and ^{i}PrS-substituted (Jacquot-Rousseau *et al.*, 2005) 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-dienes (Jacquot *et al.*, 1999) have been reported. For related literature, see: Tanimoto *et al.* (1976); Truce & Boudakian (1956).



Experimental

Crystal data

$C_{29}H_{25}NS_2$
M_r = 451.66
Triclinic, $P\overline{1}$
a = 6.9340 (10) Å
b = 12.3009 (2) Å
c = 14.4247 (3) Å
α = 101.7371 (8)°
β = 98.2522 (7)°
γ = 93.0400 (10)°
V = 1187.90 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 120 (2) K
0.2 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
7710 measured reflections
5329 independent reflections
4695 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.04
5329 reflections
317 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2031).

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supplementary materials

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4,4-Bis(4-methylphenylsulfanyl)-1,1-diphenyl-2-azabuta-1,3-diene

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Comment

The investigations of Truce and Boudakian on the reactivity of 1,1-dichloroethylene (1) towards an excess of sodium *p*-toluenethiolate have shown that this reaction affords exclusively *cis*-1,2-bis-(*p*-tolylmercapto) ethane (2). The intermediacy of an alkyne species ArSCCH has been suggested to rationalize this interesting rearrangement reaction which implies some addition–elimination sequences (Truce & Boudakian, 1956). Another research group has later confirmed these findings (Tanimoto *et al.*, 1976) (Fig. 2). In the context of our interest in developing novel π-conjugated dithioether compounds as ligands for coordination chemistry, we have recently reported on the synthesis and crystal structure of $[(i\text{-}PrS)_2C{=}C(H){-}N{=}CPh_2]$ (4a), obtained by reaction of an excess of sodium i-propylthiolate with 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (3) in DMF as solvent (Jacquot-Rousseau *et al.*, 2005). In the light of the results mentioned above, we were intrigued whether the reaction of (3) (Jacquot *et al.*, 1999) with sodium *p*-toluenethiolate would lead to $[(p\text{-tolylS})_2C{=}C(H){-}N{=}CPh_2]$ (4 b) or to an rearranged product bearing the two *–S-p*-tolyl substituents on two different carbon atoms, similar to the case of olefin (**2**) (Fig. 3).

The molecular structure of (4 b) is shown in Fig. 1. The *transoid* conformation of the azabutadiene chain found in precursor (3) and in the *S*-i-propyl derivative (4a) is also observed in the crystal structure of (4 b). In contrast to compound (2), both the *S-p*-tolyl substituents are attached to the same C(3) atom.

One may expect that one of the two phenyl groups bound to C(1) makes part of the phenyl/azadiene chain π-conjugation. In fact, a dihedral angle between C10–C15 phenyl plane and that of azadiene chain C1—N—C2—C3 is equal only to 5.1 (2)°. Note that these dihedral angles amount to 28.7 (1)° in precursor (3) and 38.8 (3)° in (4a). An obvious question arises: the reported values of dihedral angles are due to the electronic structures of compounds (3) and (4) or to the packing in the crystals? This problem requires some calculations on the electronic structure of (4 b) and will be separately treated elsewhere.

Experimental

4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (3) (1.1 mmol) was stirred with an excess of 4-toluenethiolate (8 mmol) in dry DMF (10 ml). The reaction mixture was kept at room temperature for 8 h, then poured into water (100 ml) and extracted with diethyl ether (150 ml). The organic solution was washed three times with water, dried over anhydrous sodium sulfate and evaporated. The crude residue was recristallized from ethanol (75% yield). 1H NMR: δ = 2.30 p.p.m. (s, 3H, Ar—CH3); 2.33 p.p.m. (s, 3H, Ar—CH3);), 6.99–7.02 p.p.m. (m, 8H, phenyl) 7.10 p.p.m. (s, 1H, C=CH), 7.23–7.28 p.p.m. (m, 10H, Ar—H).

Refinement

The hydrogen H(2) bound to the carbon C(2) of the azadienic chain as well as those of *p*-methyl groups (C22 and C29) were located from difference Fourier map and isotropically refined. Other aromatic H atoms were included in calculated positions and treated in a riding model with isotropic displacement parameters set to 1.2 times those of carbon atoms bearing them.

Figures

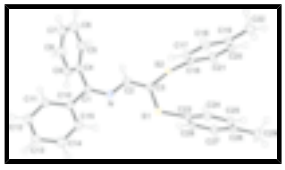

Fig. 1. View of (4 b) with ellipsoids at the 30% probability level.

Fig. 2. *p*-*S*-tolyl substitution on 1,1-dichloroethylene.

Fig. 3. *p*-*S*-tolyl substitution on an azadienic chain.

4,4-Bis(4-methylphenylsulfanyl)-1,1-diphenyl-2-azabuta-1,3-diene

Crystal data

$C_{29}H_{25}NS_2$	$Z = 2$
$M_r = 451.66$	$F_{000} = 476$
Triclinic, $P\bar{1}$	$D_x = 1.263$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 382 K
$a = 6.9340$ (10) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 12.3009$ (2) Å	Cell parameters from 3954 reflections
$c = 14.4247$ (3) Å	$\theta = 1.0$–27.5º
$\alpha = 101.7371$ (8)º	$\mu = 0.24$ mm^{-1}
$\beta = 98.2522$ (7)º	$T = 120$ (2) K
$\gamma = 93.0400$ (10)º	Irregular, yellow
$V = 1187.90$ (4) Å^3	0.2 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer	4695 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.019$
Monochromator: graphite	$\theta_{max} = 27.4$º
$T = 120(2)$ K	$\theta_{min} = 1.5$º
CCD scans	$h = -8 \rightarrow 8$
Absorption correction: none	$k = -12 \rightarrow 15$
7710 measured reflections	$l = -18 \rightarrow 18$
5329 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 0.5208P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
5329 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
317 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.22781 (5)	0.37867 (3)	0.35024 (2)	0.02290 (9)
S2	0.43297 (4)	0.52776 (3)	0.23783 (2)	0.02161 (9)
N	0.48657 (16)	0.21771 (9)	0.26950 (8)	0.0221 (2)
C1	0.58163 (18)	0.13424 (11)	0.23639 (9)	0.0204 (3)
C2	0.50043 (19)	0.31661 (11)	0.23787 (10)	0.0227 (3)
C3	0.39300 (18)	0.40002 (11)	0.27163 (9)	0.0200 (3)
C4	0.71038 (19)	0.13495 (10)	0.16171 (9)	0.0206 (3)
C5	0.6304 (2)	0.12895 (14)	0.06658 (11)	0.0328 (3)
H5	0.4953	0.1238	0.0489	0.039*
C6	0.7506 (3)	0.13066 (16)	−0.00219 (12)	0.0415 (4)
H6	0.6960	0.1270	−0.0656	0.050*
C7	0.9508 (2)	0.13778 (14)	0.02340 (12)	0.0364 (4)
H7	1.0312	0.1378	−0.0230	0.044*
C8	1.0317 (2)	0.14488 (13)	0.11728 (12)	0.0350 (3)
H8	1.1670	0.1506	0.1345	0.042*
C9	0.9128 (2)	0.14354 (12)	0.18644 (11)	0.0287 (3)
H9	0.9686	0.1484	0.2499	0.034*
C10	0.56071 (18)	0.03303 (11)	0.27658 (9)	0.0207 (3)

C11	0.6700 (2)	−0.05758 (11)	0.25308 (10)	0.0250 (3)
H11	0.7553	−0.0568	0.2089	0.030*
C12	0.6528 (2)	−0.14933 (12)	0.29507 (11)	0.0293 (3)
H12	0.7284	−0.2087	0.2799	0.035*
C13	0.5238 (2)	−0.15238 (12)	0.35923 (11)	0.0285 (3)
H13	0.5126	−0.2136	0.3874	0.034*
C14	0.4112 (2)	−0.06400 (13)	0.38151 (12)	0.0322 (3)
H14	0.3228	−0.0664	0.4240	0.039*
C15	0.4296 (2)	0.02781 (12)	0.34092 (11)	0.0290 (3)
H15	0.3537	0.0869	0.3566	0.035*
C16	0.19592 (18)	0.55484 (11)	0.18701 (9)	0.0200 (3)
C17	0.05190 (19)	0.47143 (11)	0.13858 (10)	0.0231 (3)
H17	0.0744	0.3969	0.1344	0.028*
C18	−0.1256 (2)	0.50030 (12)	0.09652 (10)	0.0258 (3)
H18	−0.2222	0.4443	0.0652	0.031*
C19	−0.1623 (2)	0.61123 (12)	0.10010 (10)	0.0249 (3)
C20	−0.0167 (2)	0.69289 (12)	0.14901 (10)	0.0269 (3)
H20	−0.0387	0.7675	0.1528	0.032*
C21	0.1609 (2)	0.66593 (11)	0.19237 (10)	0.0255 (3)
H21	0.2563	0.7221	0.2249	0.031*
C22	−0.3522 (2)	0.64249 (15)	0.05100 (12)	0.0328 (3)
C23	0.16434 (19)	0.51460 (10)	0.39797 (9)	0.0195 (3)
C24	−0.02989 (19)	0.53814 (11)	0.38031 (9)	0.0217 (3)
H24	−0.1223	0.4848	0.3408	0.026*
C25	−0.08547 (19)	0.64104 (11)	0.42158 (10)	0.0233 (3)
H25	−0.2158	0.6559	0.4098	0.028*
C26	0.0502 (2)	0.72288 (11)	0.48054 (9)	0.0222 (3)
C27	0.2438 (2)	0.69758 (11)	0.49862 (9)	0.0231 (3)
H27	0.3362	0.7509	0.5383	0.028*
C28	0.30109 (19)	0.59443 (11)	0.45858 (9)	0.0218 (3)
H28	0.4305	0.5786	0.4721	0.026*
C29	−0.0105 (3)	0.83537 (13)	0.52391 (12)	0.0316 (3)
H2	0.587 (2)	0.3271 (13)	0.1916 (11)	0.023 (4)*
H221	−0.460 (3)	0.6112 (18)	0.0711 (16)	0.060 (6)*
H222	−0.370 (3)	0.6152 (19)	−0.0180 (18)	0.065 (7)*
H223	−0.357 (3)	0.722 (2)	0.0618 (17)	0.075 (7)*
H291	−0.049 (3)	0.8755 (17)	0.4753 (15)	0.050 (5)*
H292	0.094 (3)	0.8815 (18)	0.5682 (15)	0.055 (6)*
H293	−0.120 (3)	0.8270 (19)	0.5548 (16)	0.066 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02781 (18)	0.01708 (16)	0.02706 (18)	0.00498 (12)	0.01078 (13)	0.00695 (13)
S2	0.01964 (16)	0.02080 (17)	0.02704 (18)	0.00391 (12)	0.00537 (12)	0.00951 (13)
N	0.0233 (5)	0.0201 (5)	0.0235 (6)	0.0061 (4)	0.0038 (4)	0.0045 (4)
C1	0.0199 (6)	0.0198 (6)	0.0200 (6)	0.0040 (5)	0.0010 (5)	0.0021 (5)
C2	0.0229 (6)	0.0226 (6)	0.0235 (7)	0.0053 (5)	0.0042 (5)	0.0059 (5)

C3	0.0207 (6)	0.0193 (6)	0.0206 (6)	0.0035 (5)	0.0028 (5)	0.0056 (5)
C4	0.0235 (6)	0.0162 (6)	0.0228 (6)	0.0048 (5)	0.0053 (5)	0.0037 (5)
C5	0.0273 (7)	0.0471 (9)	0.0257 (7)	0.0121 (6)	0.0035 (6)	0.0095 (7)
C6	0.0454 (9)	0.0584 (11)	0.0255 (8)	0.0162 (8)	0.0095 (7)	0.0144 (7)
C7	0.0398 (9)	0.0389 (9)	0.0375 (9)	0.0084 (7)	0.0209 (7)	0.0126 (7)
C8	0.0250 (7)	0.0377 (8)	0.0433 (9)	−0.0011 (6)	0.0105 (6)	0.0080 (7)
C9	0.0258 (7)	0.0311 (7)	0.0268 (7)	−0.0012 (6)	0.0014 (6)	0.0035 (6)
C10	0.0217 (6)	0.0198 (6)	0.0197 (6)	0.0033 (5)	0.0022 (5)	0.0023 (5)
C11	0.0285 (7)	0.0229 (7)	0.0259 (7)	0.0064 (5)	0.0090 (5)	0.0056 (5)
C12	0.0346 (8)	0.0218 (7)	0.0345 (8)	0.0089 (6)	0.0100 (6)	0.0077 (6)
C13	0.0342 (7)	0.0225 (7)	0.0306 (8)	0.0016 (6)	0.0057 (6)	0.0095 (6)
C14	0.0349 (8)	0.0300 (8)	0.0360 (8)	0.0042 (6)	0.0166 (6)	0.0093 (6)
C15	0.0305 (7)	0.0251 (7)	0.0351 (8)	0.0092 (6)	0.0137 (6)	0.0070 (6)
C16	0.0212 (6)	0.0232 (6)	0.0190 (6)	0.0062 (5)	0.0068 (5)	0.0087 (5)
C17	0.0270 (7)	0.0213 (6)	0.0227 (7)	0.0051 (5)	0.0055 (5)	0.0064 (5)
C18	0.0252 (7)	0.0292 (7)	0.0233 (7)	0.0024 (5)	0.0025 (5)	0.0072 (6)
C19	0.0240 (7)	0.0330 (7)	0.0224 (7)	0.0093 (5)	0.0078 (5)	0.0123 (6)
C20	0.0304 (7)	0.0232 (7)	0.0320 (8)	0.0095 (5)	0.0087 (6)	0.0131 (6)
C21	0.0260 (7)	0.0218 (7)	0.0300 (7)	0.0026 (5)	0.0052 (6)	0.0079 (5)
C22	0.0273 (8)	0.0437 (9)	0.0318 (8)	0.0108 (7)	0.0044 (6)	0.0166 (7)
C23	0.0243 (6)	0.0185 (6)	0.0183 (6)	0.0044 (5)	0.0066 (5)	0.0070 (5)
C24	0.0220 (6)	0.0224 (6)	0.0209 (6)	0.0011 (5)	0.0037 (5)	0.0049 (5)
C25	0.0212 (6)	0.0270 (7)	0.0244 (7)	0.0069 (5)	0.0068 (5)	0.0084 (5)
C26	0.0287 (7)	0.0217 (6)	0.0188 (6)	0.0058 (5)	0.0088 (5)	0.0057 (5)
C27	0.0269 (7)	0.0222 (6)	0.0196 (6)	0.0000 (5)	0.0025 (5)	0.0047 (5)
C28	0.0205 (6)	0.0243 (6)	0.0226 (6)	0.0040 (5)	0.0031 (5)	0.0092 (5)
C29	0.0381 (8)	0.0249 (7)	0.0323 (8)	0.0083 (6)	0.0112 (7)	0.0021 (6)

Geometric parameters (Å, °)

S1—C3	1.7689 (13)	C14—H14	0.9300
S1—C23	1.7776 (13)	C15—H15	0.9300
S2—C3	1.7572 (13)	C16—C21	1.3892 (19)
S2—C16	1.7781 (13)	C16—C17	1.3919 (19)
N—C1	1.2959 (17)	C17—C18	1.3890 (19)
N—C2	1.3869 (17)	C17—H17	0.9300
C1—C10	1.4851 (18)	C18—C19	1.393 (2)
C1—C4	1.4955 (18)	C18—H18	0.9300
C2—C3	1.3515 (18)	C19—C20	1.388 (2)
C2—H2	0.983 (15)	C19—C22	1.5098 (19)
C4—C9	1.3904 (19)	C20—C21	1.3873 (19)
C4—C5	1.3902 (19)	C20—H20	0.9300
C5—C6	1.387 (2)	C21—H21	0.9300
C5—H5	0.9300	C22—H221	0.93 (2)
C6—C7	1.378 (2)	C22—H222	0.97 (2)
C6—H6	0.9300	C22—H223	0.96 (3)
C7—C8	1.373 (2)	C23—C24	1.3912 (18)
C7—H7	0.9300	C23—C28	1.3936 (18)
C8—C9	1.385 (2)	C24—C25	1.3843 (19)

C8—H8	0.9300	C24—H24	0.9300
C9—H9	0.9300	C25—C26	1.3941 (19)
C10—C11	1.3934 (18)	C25—H25	0.9300
C10—C15	1.3974 (19)	C26—C27	1.3942 (19)
C11—C12	1.3927 (19)	C26—C29	1.5062 (19)
C11—H11	0.9300	C27—C28	1.3864 (19)
C12—C13	1.381 (2)	C27—H27	0.9300
C12—H12	0.9300	C28—H28	0.9300
C13—C14	1.384 (2)	C29—H291	0.95 (2)
C13—H13	0.9300	C29—H292	0.97 (2)
C14—C15	1.382 (2)	C29—H293	0.95 (2)
C3—S1—C23	104.31 (6)	C21—C16—C17	119.68 (12)
C3—S2—C16	103.68 (6)	C21—C16—S2	116.76 (10)
C1—N—C2	121.26 (12)	C17—C16—S2	123.46 (10)
N—C1—C10	117.10 (12)	C18—C17—C16	119.57 (12)
N—C1—C4	123.91 (12)	C18—C17—H17	120.2
C10—C1—C4	118.98 (11)	C16—C17—H17	120.2
C3—C2—N	119.27 (12)	C17—C18—C19	121.53 (13)
C3—C2—H2	119.6 (9)	C17—C18—H18	119.2
N—C2—H2	121.2 (9)	C19—C18—H18	119.2
C2—C3—S2	117.32 (10)	C20—C19—C18	117.82 (12)
C2—C3—S1	119.54 (10)	C20—C19—C22	120.64 (13)
S2—C3—S1	123.10 (8)	C18—C19—C22	121.53 (14)
C9—C4—C5	118.69 (13)	C21—C20—C19	121.59 (13)
C9—C4—C1	120.58 (12)	C21—C20—H20	119.2
C5—C4—C1	120.73 (12)	C19—C20—H20	119.2
C6—C5—C4	120.46 (14)	C20—C21—C16	119.80 (13)
C6—C5—H5	119.8	C20—C21—H21	120.1
C4—C5—H5	119.8	C16—C21—H21	120.1
C7—C6—C5	120.06 (15)	C19—C22—H221	111.6 (13)
C7—C6—H6	120.0	C19—C22—H222	111.9 (13)
C5—C6—H6	120.0	H221—C22—H222	105.5 (18)
C8—C7—C6	120.05 (14)	C19—C22—H223	111.4 (14)
C8—C7—H7	120.0	H221—C22—H223	109.5 (19)
C6—C7—H7	120.0	H222—C22—H223	106.6 (19)
C7—C8—C9	120.25 (14)	C24—C23—C28	119.57 (12)
C7—C8—H8	119.9	C24—C23—S1	118.78 (10)
C9—C8—H8	119.9	C28—C23—S1	121.44 (10)
C8—C9—C4	120.48 (14)	C25—C24—C23	119.96 (12)
C8—C9—H9	119.8	C25—C24—H24	120.0
C4—C9—H9	119.8	C23—C24—H24	120.0
C11—C10—C15	118.28 (12)	C24—C25—C26	121.25 (12)
C11—C10—C1	122.05 (12)	C24—C25—H25	119.4
C15—C10—C1	119.66 (12)	C26—C25—H25	119.4
C12—C11—C10	120.62 (13)	C27—C26—C25	118.15 (12)
C12—C11—H11	119.7	C27—C26—C29	120.85 (13)
C10—C11—H11	119.7	C25—C26—C29	121.01 (13)
C13—C12—C11	120.18 (13)	C28—C27—C26	121.20 (12)
C13—C12—H12	119.9	C28—C27—H27	119.4

C11—C12—H12	119.9	C26—C27—H27	119.4
C12—C13—C14	119.75 (13)	C27—C28—C23	119.84 (12)
C12—C13—H13	120.1	C27—C28—H28	120.1
C14—C13—H13	120.1	C23—C28—H28	120.1
C15—C14—C13	120.26 (14)	C26—C29—H291	110.6 (12)
C15—C14—H14	119.9	C26—C29—H292	112.6 (13)
C13—C14—H14	119.9	H291—C29—H292	106.3 (17)
C14—C15—C10	120.89 (13)	C26—C29—H293	110.2 (14)
C14—C15—H15	119.6	H291—C29—H293	106.8 (18)
C10—C15—H15	119.6	H292—C29—H293	110.1 (18)

Fig. 1

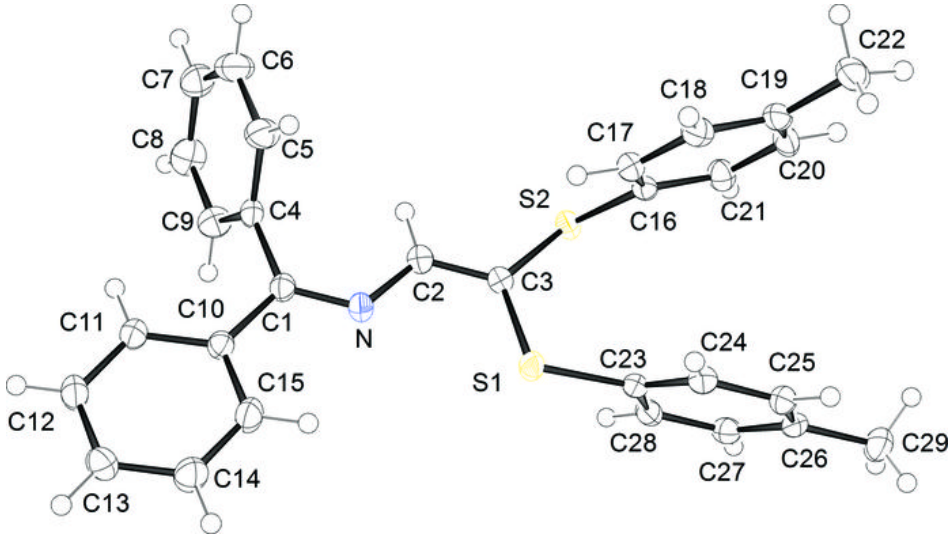
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Fig. 2

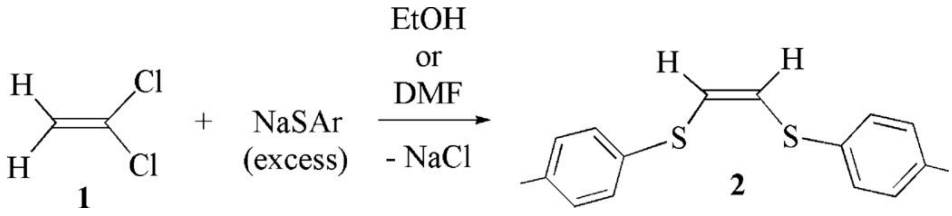
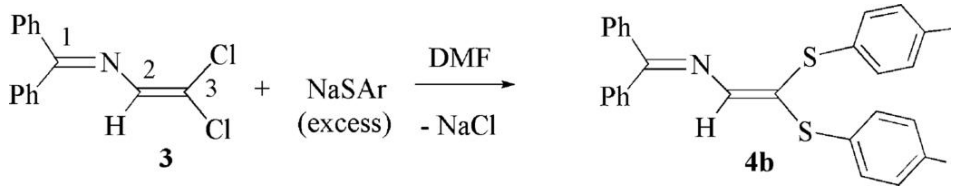
Fig. 3