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Diethyl 2-[cyano(toluene-4-sulfinyl)-methylene]propanedioate and its Diels–Alder adduct with cyclopentadiene

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The thermal Diels–Alder cycloadditon reaction of diethyl 2-[cyano(toluene-4-sulfinyl)methylene]propanedioate, $C_{16}H_{17}NO_5S$, with cyclopentadiene gave the pure racemates of two of the four possible diastereomers, with a complete π-facial selectivity and a high (80:20) *endo*/*exo*-sulfinyl selectivity. X-ray diffraction studies of diethyl 2-[cyano(toluene-4-sulfinyl)methylene]propanedioate and the major isomer of the cycloaddition product, namely diethyl 3-cyano-3-(toluene-4-sulfinyl)bicyclo[2.2.1]hepta-5-ene-2,2-dicarboxylate, $C_{21}H_{23}NO_5S$, reveal that the conformation of the substituents on the acrylonitrile moiety produces both steric and electronic effects, which affect the stereoselectivity of the reaction.

Comment

When sulfinylethylenes are used as dienophiles in Diels–Alder reactions, their reactivity and *endo* selectivity are both moderate or low, unless they bear additional electron-withdrawing groups at the double bond (Arai *et al.*, 1991), the alkoxycarbonyls being the most widely studied such group. The reactivity and stereoselectivity of sulfinyl maleates are usually satisfactory when the reactions are conducted in the presence of a $TiCl_4$ catalyst, which also frequently promotes the undesirable polymerization of the dienes (Alonso *et al.*, 1994). The incorporation of a third alkoxycarbonyl group into the double bond does not solve these problems, since such compounds exhibit lower reactivity than vinyl sulfoxides as well as low π-facial selectivity, probably due to a non-planar structure (Carretero *et al.*, 1995). In diethyl 2-[cyano(toluene-4-sulfinyl)methylene]propanedioate, (I), the replacement of one of the ester groups by a cyano group substantially increases both the reactivity and the stereoselectivity of the cycloaddition reaction. In order to gain an insight into the stereochemistry of this dienophile molecule, we determined its crystal structure, as well as that of its Diels–Alder adduct with cyclopentadiene, namely diethyl 3-cyano-3-(toluene-4-sulfinyl)bicyclo[2.2.1]hepta-5-ene-2,2-dicarboxylate, (II).

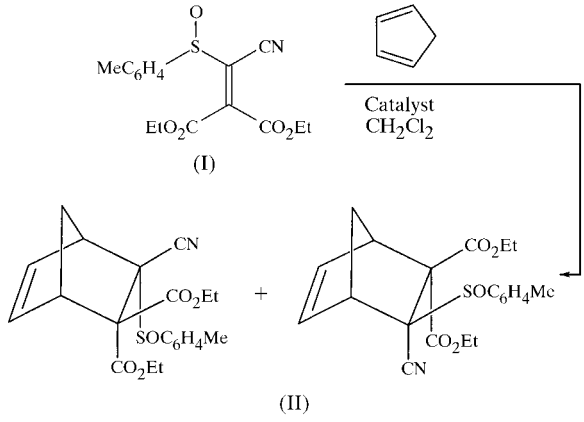

Fig. 1 shows that the acrylonitrile moiety and the ethoxycarbonyl group *syn* to the cyano group in (I) are essentially coplanar [maximum deviation −0.282 (1) Å for O2], with an *S-cis* conformation for the C═C—C═O moiety [O1—C1—C2—C4 164.1 (4)°]. The mean plane of the second ethoxycarbonyl group makes a dihedral angle of −59.89 (3)° with the mean plane of the acrylonitrile moiety, while the orientation of the planar *p*-tolylsulfinyl group is almost perpendicular [89.02 (2)°] to the same plane. This conformation puts atom O5 of the sulfinyl group and O3 of the ethoxy group 0.890 (1) and 1.034 (1) Å, respectively, above the C═C double-bond plane, while the bulky *p*-tolyl substituent and atom O4 of the carbonyl group point in the opposite direction. This will render only one face of the dienophile double bond exposed and thus the Diels–Alder cycloaddition will be facially selective.

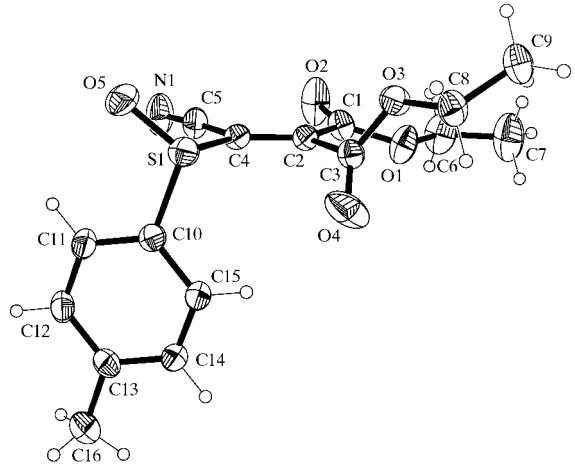

Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii.

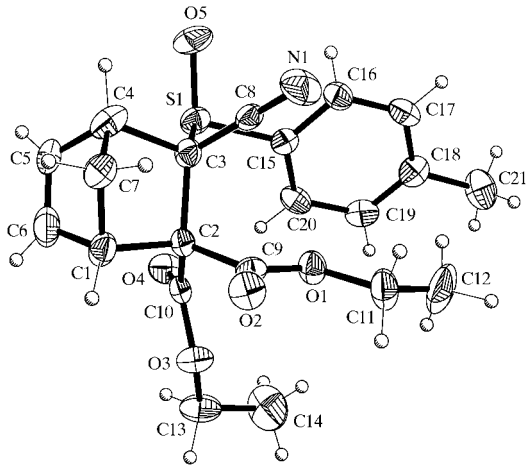

Figure 2
The molecular structure of the Diels–Alder adduct, (II), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii.

Fig. 2 clearly shows the *endo*-sulfinyl nature of the major isomer of (II) obtained from the Diels–Alder reaction. Upon cycloaddition, besides the change in hybridization of atoms C2 and C3, the major change in the dienophile moiety is observed in the orientation of the ethoxycarbonyl group *syn* to the cyano group, which turns from a nearly coplanar conformation to an almost perpendicular conformation [74.77 (1)°]. The S1—O5 bond is *trans* to C2—C3 and approximately coplanar with the phenyl ring. The two C—S bonds are unequal, S1—C15 being shorter than S1—C3, because of the different hybridization. The endocyclic torsion angles show that the approximate mirror symmetry of the norbornene skeleton is only slightly distorted. The *exo*-ethoxycarbonyl substituent at C2 adopts a fully extended conformation, while the *endo* one is twisted, probably due to packing interactions.

The orientation of the phenyl ring in both compounds seems to be stabilized by intramolecular hydrogen bonds involving the *ortho*-H atoms of the aromatic ring, and the carbonyl O4 and sulfinyl O5 atoms [C15—H15···O4 2.47 Å and C11—H11···O5 2.52 Å in (I), and C20—H20···O4 2.38 Å and C16—H16···O5 2.61 Å in (II)]. In addition, weak intermolecular hydrogen bonds are observed for (I) [C14—H14···O5($x-1$, y, z) 2.54 Å] and (II) [C19—H19···N1(x, $1-y$, $z-\frac{1}{2}$) 2.62 Å].

The observed high π-facial selectivity (80:20 *endo*/*exo*-sulfinyl) may be explained by invoking the possibility of these reactions taking place on organized structures, (*A*) or (*B*) (Fig. 3), resulting from intermolecular hydrogen bonding of molecules. Superposition of the structure of cyclopentadiene (Haumann *et al.*, 1996) over the diethyl 2-[cyano(toluene-4-sulfinyl)methylene]propanedioate showed that the organized structure (*A*) favours a closer approximation [2.47 (1) *versus* 2.70 (1) Å], by fitting the space between atoms O3 and O5 [5.027 (4) Å] better than does structure (*B*).

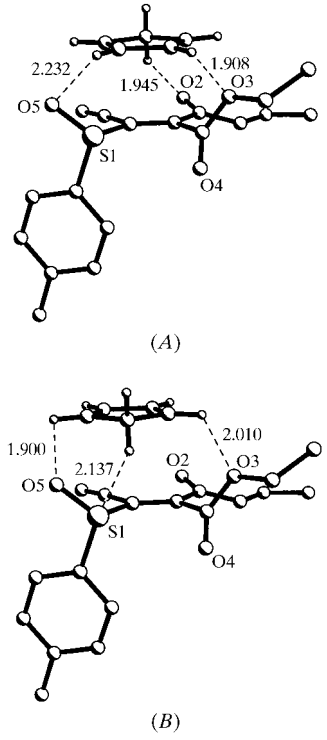

Figure 3
The hypothetical transition state of the reactants during the Diels–Alder reaction; (*A*) is the *endo* arrangement and (*B*) the *exo* arrangement.

Experimental

For the preparation of compound (I), cyanomethyl-*p*-tolylsulfoxide (5.6 mmol, 1 equivalent) in tetrahydrofuran (10 ml) was deprotonzated using a solution of Li–HMDS [*n*-BuLi (6.7 mmol, 1.2 equivalents) and hexamethyldisilazane (HMDS; 6.7 mmol, 1.2 equivalents) in tetrahydrofuran (40 ml)] at 195 K for 30 min. The resulting anion was further reacted with diethyl oxomalonate (6.2 mmol, 1.1 equivalents), added slowly and stirred for 2 h at 195 K. The reaction was quenched with saturated ammonium chloride solution and extracted with dichloromethane, followed by purification by column chromatography to give 3,3-diethoxycarbonyl-3-hydroxy-2-*p*-tolylsulfinylpropionitrile in 78% yield as white crystals (m.p. 394–397 K). Dehydration of this alcohol (4.7 mmol, 1 equivalent) in dichloromethane (65 ml) was performed under an argon atmosphere by treatment with methylsulfonyl chloride (18.8 mmol, 4 equivalents) and diisopropylethylamine (18.8 mmol, 4 equivalents) at 195 K with constant stirring for 2 h. Water (30 ml) was then added, the organic layer separated and the aqueous layer extracted with dichloromethane (2 × 20 ml). The combined layers were dried with sodium sulfate and concentrated. The residue was purified by column chromatography and recrystallized from hexane–dichloromethane to afford compound (I) in 66% yield as yellow crystals (m.p. 375–377 K). For compound (II), cyclopentadiene (1.79 mmol, 6 equivalents) was added to a solution of (I) (0.298 mmol, 1 equivalent) in dichloromethane (2 ml) at room temperature under an argon atmosphere. The resulting solution was stirred for 2.5 h. Evaporation of the volatiles under vacuum gave a residue that was analyzed by ^{1}H NMR (isomer ratio 80:20 *endo*-sulfinyl/*exo*-sulfinyl) and purified by flash chromatography using hexane–ethyl acetate (85:15), yielding compound (II) as a white solid which decomposed at 384–386 K.

Compound (I)

Crystal data

$C_{16}H_{17}NO_5S$
$M_r = 335.37$
Triclinic, $P\overline{1}$
$a = 8.167$ (2) Å
$b = 8.666$ (1) Å
$c = 13.004$ (2) Å
$\alpha = 104.01$ (1)°
$\beta = 103.11$ (1)°
$\gamma = 98.40$ (1)°
$V = 849.8$ (3) Å^3
$Z = 2$
$D_x = 1.311$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 5.0$–12.5°
$\mu = 0.21$ mm^{-1}
$T = 293$ (2) K
Prism, light yellow
0.40 × 0.40 × 0.24 mm

Data collection

Siemens *P4*/*PC* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.920$, $T_{max} = 0.948$
3165 measured reflections
2941 independent reflections
1985 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.177$
$S = 1.07$
2941 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0942P)^2 + 0.0905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

S1—O5	1.480 (3)	O4—C3	1.182 (5)
S1—C10	1.803 (4)	N1—C5	1.137 (5)
S1—C4	1.837 (3)	C1—C2	1.511 (4)
O1—C1	1.314 (5)	C2—C4	1.330 (5)
O2—C1	1.189 (5)	C2—C3	1.516 (5)
O3—C3	1.295 (4)	C4—C5	1.447 (5)
O5—S1—C10	107.03 (19)	C1—C2—C3	117.6 (3)
O5—S1—C4	105.26 (18)	O4—C3—O3	126.2 (4)
C10—S1—C4	94.52 (15)	O4—C3—C2	122.9 (3)
O2—C1—O1	125.6 (4)	O3—C3—C2	111.0 (3)
O2—C1—C2	123.6 (4)	C2—C4—C5	125.1 (3)
O1—C1—C2	110.7 (3)	C2—C4—S1	122.6 (3)
C4—C2—C1	121.2 (3)	C5—C4—S1	112.2 (3)
C4—C2—C3	121.2 (3)		
O2—C1—C2—C4	−17.0 (7)	C3—C2—C4—S1	−2.4 (5)
O2—C1—C2—C3	164.5 (4)	O5—S1—C4—C2	−140.8 (3)
C4—C2—C3—O4	−58.5 (6)	C10—S1—C4—C2	110.2 (3)
C1—C2—C3—O4	119.9 (5)	O5—S1—C4—C5	37.3 (3)
C1—C2—C3—O3	−60.2 (4)	O5—S1—C10—C11	0.4 (3)
C1—C2—C4—C5	1.4 (6)	O5—S1—C10—C15	178.3 (3)

Compound (II)

Crystal data

$C_{21}H_{23}NO_5S$
$M_r = 401.46$
Monoclinic, Cc
$a = 8.458$ (1) Å
$b = 15.137$ (2) Å
$c = 15.930$ (3) Å
$\beta = 95.98$ (2)°
$V = 2028.4$ (5) Å^3
$Z = 4$
$D_x = 1.315$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 5.1$–16.1°
$\mu = 0.19$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.28 × 0.20 × 0.06 mm

Data collection

Siemens *P4*/*PC* diffractometer
$\omega/2\theta$ scans
2587 measured reflections
2361 independent reflections (plus 130 Friedel-related reflections)
1072 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 27.6°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = -20 \rightarrow 20$
3 standard reflections
every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.141$
$S = 0.96$
2491 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.024$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.02 (19)

Table 2
Selected geometric parameters (Å, °) for (II).

S1—C15	1.807 (8)	C2—C3	1.630 (10)
S1—C3	1.863 (8)	C5—C6	1.274 (12)
C10—C2—C9	109.2 (6)	C8—C3—C4	107.0 (7)
C10—C2—C1	108.3 (6)	C8—C3—C2	110.4 (7)
C9—C2—C1	111.8 (7)	C4—C3—C2	101.4 (6)
C10—C2—C3	115.3 (6)	C8—C3—S1	107.5 (6)
C9—C2—C3	110.7 (7)	C4—C3—S1	107.6 (5)
C1—C2—C3	101.4 (6)	C2—C3—S1	121.9 (5)
C7—C1—C2—C3	−36.4 (8)	C4—C5—C6—C1	3.0 (11)
C1—C2—C3—C4	−1.1 (8)	C7—C1—C6—C5	29.9 (10)
O5—S1—C3—C2	176.4 (6)	C9—O1—C11—C12	174.9 (7)
C2—C3—C4—C7	38.8 (8)	C10—O3—C13—C14	85.0 (10)
C7—C4—C5—C6	−35.6 (10)	O5—S1—C15—C16	20.3 (8)

For both compounds, data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1028). Services for accessing these data are described at the back of the journal.

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