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Structure of (*Z*,*Z*)-3,11-Diiodo-*N*,*N*-ditosyl-1,9-diazacyclohexadeca-3,11-diene

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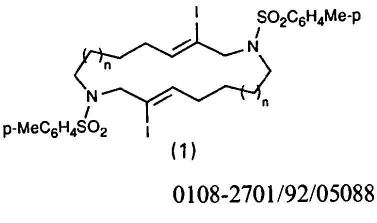
Abstract. $C_{28}H_{36}I_2N_2O_4S_2$, $M_r = 782.5$, orthorhombic, $P2_12_12_1$, $a = 11.153\,(4)$, $b = 14.833\,(3)$, $c = 19.332\,(5)$ Å, $V = 3198.0$ Å^3, $Z = 4$, $D_x = 1.62$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 21.03$ cm^{-1}, $F(000) = 1552$, room temperature, $R = 0.0776$ for 1582 unique reflections. The 16-membered diaza heterocycle has (*Z*) stereochemistry about each of the two double bonds; the two N atoms exhibit a more planar geometry than usually observed in sulfonamides.

Introduction. The iodine-mediated cyclization of *N*-sulfonyl allenic amines [ω-(4-toluenesulfonamido)-1,2-alkadienes] provides an efficient entry into functionalized medium-ring nitrogen heterocycles. In addition to monoaza heterocycles, the diaza derivatives (1) (n = 1–4) have also been synthesized in up to 40% yield (Shaw, Anderson & Gallagher, 1990). The structure of (1) (n = 1), (*Z*,*Z*)-3,11-diiodo-*N*,*N*-ditosyl-1,9-diazacyclohexadeca-3-11-diene, a 16-membered diaza macrocycle, is reported in this paper.



(1)

Experimental. The synthesis of the title compound has been reported previously (Shaw, Anderson & Gallagher, 1990). Crystals were obtained by recrystallization from benzene.

A diamond-shaped crystal of approximate dimensions 0.35 × 0.35 × 0.35 mm was selected and used for data collection. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 < \theta < 24°$ using ω–2θ scans, covering the ranges $h\,0 \rightarrow 12$, $k\,0 \rightarrow 15$, $l\,0 \rightarrow 20$. Cell dimensions were based on 12 accurately centred reflections with $13 < \theta < 16°$. 2815 reflections were collected of which 1582 were unique and observed with $I \geq 3\sigma(I)$. A standard reflection measured after every 50 reflections showed no systematic crystal decay throughout data collection. Data were corrected for Lorentz and polarization effects and also for absorption (Walker & Stuart, 1983). Absorption maximum and minimum: 1.06, 0.90. The structure was solved by conventional Patterson methods and refined using full-matrix least squares based on *F*, using the *SHELX* suite of programs (Sheldrick, 1976, 1986). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-H atoms were treated anisotropically; H atoms were included at calculated positions (C—H = 1.08 Å) with a common fixed thermal parameter ($U = 0.05$ Å^2).

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for* (1)

$$U_{eq} = \sum_{i=1}^{i=3} U_{ii}/3.$$

	x	y	z	U_{eq}
I1	1.0501 (3)	0.5589 (2)	0.2983 (1)	0.092 (2)
I2	0.9161 (3)	0.2580 (2)	0.4053 (2)	0.125 (2)
S1	0.8995 (9)	0.7571 (6)	0.4449 (4)	0.073 (6)
S2	0.5251 (9)	0.2069 (5)	0.2398 (4)	0.065 (5)
O1	1.0163 (18)	0.7888 (13)	0.4215 (11)	0.076 (15)
O2	0.8892 (34)	0.7158 (13)	0.5119 (10)	0.128 (24)
O3	0.4455 (18)	0.2491 (13)	0.1919 (10)	0.075 (13)
O4	0.4818 (21)	0.1877 (14)	0.3082 (11)	0.087 (17)
N1	0.8413 (18)	0.6831 (14)	0.3901 (12)	0.048 (15)
N2	0.6399 (27)	0.2740 (15)	0.2462 (11)	0.071 (19)
C1	0.7446 (32)	0.6308 (19)	0.4069 (18)	0.072 (23)
C2	0.7771 (39)	0.5324 (19)	0.4217 (17)	0.083 (26)
C3	0.6621 (37)	0.4871 (18)	0.4491 (16)	0.075 (25)
C4	0.6764 (42)	0.3804 (23)	0.4558 (15)	0.094 (29)
C5	0.6718 (33)	0.3344 (20)	0.3879 (15)	0.062 (22)
C6	0.7663 (43)	0.2931 (20)	0.3552 (15)	0.086 (27)
C7	0.7391 (31)	0.2397 (20)	0.2914 (15)	0.074 (22)
C8	0.6784 (38)	0.3255 (21)	0.1863 (15)	0.086 (27)
C9	0.7365 (34)	0.4109 (21)	0.2090 (15)	0.087 (25)
C10	0.7715 (54)	0.4706 (26)	0.1456 (18)	0.135 (41)
C11	0.8619 (33)	0.5422 (23)	0.1609 (16)	0.079 (25)
C12	0.8338 (34)	0.6094 (21)	0.2168 (17)	0.072 (24)
C13	0.8902 (38)	0.6297 (20)	0.2712 (15)	0.077 (24)
C14	0.8563 (29)	0.7050 (20)	0.3154 (15)	0.065 (22)
C16	0.8336 (15)	0.9262 (13)	0.4086 (10)	0.074 (23)
C17	0.7584 (15)	1.0013 (13)	0.4085 (10)	0.069 (23)
C18	0.6505 (15)	0.9991 (13)	0.4450 (10)	0.067 (23)
C19	0.6178 (15)	0.9218 (13)	0.4814 (10)	0.077 (24)
C20	0.6930 (15)	0.8467 (13)	0.4815 (10)	0.084 (27)
C15	0.8009 (15)	0.8489 (13)	0.4450 (10)	0.057 (20)
C21	0.5774 (37)	1.0834 (21)	0.4538 (20)	0.103 (29)
C23	0.6072 (21)	0.1002 (11)	0.1356 (10)	0.084 (27)
C24	0.6508 (21)	0.0203 (11)	0.1070 (10)	0.092 (29)
C25	0.6572 (21)	−0.0576 (11)	0.1473 (10)	0.142 (40)
C26	0.6201 (21)	−0.0556 (11)	0.2162 (10)	0.093 (27)
C27	0.5765 (21)	0.0243 (11)	0.2448 (10)	0.070 (22)
C22	0.5700 (21)	0.1022 (11)	0.2045 (10)	0.053 (17)
C28	0.7255 (40)	−0.1449 (21)	0.1214 (20)	0.106 (33)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for the macrocyclic ring of* (1)

C5—C6	1.37 (5)	C13—I1	2.14 (4)
C12—C13	1.26 (4)	N1—S1	1.66 (2)
C6—I2	2.00 (4)	N2—S2	1.63 (3)
C7—C6—I2	115 (2)	C1—N1—C14	116 (2)
I2—C6—C5	122 (2)	C1—N1—S1	122 (2)
C6—C5—C4	126 (3)	C14—N1—S1	115 (2)
C14—C13—I1	117 (2)	C7—N2—C8	115 (3)
I1—C13—C12	120 (3)	C7—N2—S2	115 (2)
C14—C13—C12	123 (3)	C8—N2—S2	120 (2)
S1—N1—C14—C13	137.0	C6—C7—N2—S2	−116.2
S1—N1—C1—C2	−105.5	C7—N2—C8—C9	−65.8
N1—C1—C2—C3	172.5	N2—C8—C9—C10	−176.4
C1—C2—C3—C4	171.1	C8—C9—C10—C11	−162.1
C2—C3—C4—C5	−75.2	C9—C10—C11—C12	−56.9
C3—C4—C5—C6	110.1	C10—C11—C12—C13	122.9
C4—C5—C6—C7	171.2	C11—C12—C13—C14	172.3
C5—C6—C7—N2	34.0	C12—C13—C14—N1	128.0
C6—C7—N2—C8	99.1	C13—C14—N1—C1	−67.7
C15—S1—N1—C1	−76.0	I2—C6—C5—C4	17.6
C15—S1—N1—C14	75.7	I2—C6—C7—N2	−169.9
C22—S2—N2—C7	−60.1	I1—C13—C12—C11	−3.2
C22—S2—N2—C8	83.0	I1—C13—C14—N1	−56.4

Aromatic rings (C15–C20 and C22–C27) were treated as rigid hexagons to minimize the number of variables. The final ratio of data/variables (1582/319) was 4.96. Final residuals after 14 cycles of full-matrix least-squares refinement were $R = wR = 0.0776$ for unit weights. Maximum shift/e.s.d. was 0.016, though >95% of the parameters had a maximum shift/e.s.d. of <0.005, and the maximum and minimum residual electron densities were 0.35 and −0.34 e Å^{-3} respectively, in the region of the I atoms. The chirality of the space group was examined by the usual inversion of all the x, y, z coordinates, which yielded a final $R = 0.0828$ for a parallel refinement sequence. Although the geometric parameters arising from this second refinement sequence were essentially the same, the structure did not converge as well (maximum shift/e.s.d. = −0.400). The Hamilton test (Hamilton, 1965) indicates better than 95% confidence in the choice of chirality.

Final fractional atomic coordinates and isotropic thermal parameters are given in Table 1. Selected bond lengths and angles, as well as torsion angles within the 16-membered diaza heterocycle are given in Table 2.* The asymmetric unit is shown in Fig. 1, along with the atomic labelling scheme.

Discussion. The structure (Fig. 1) confirms the formation of a 16-membered ring, and establishes a (*Z*) stereochemistry about the double bonds [C5—C6 and C12—C13, bond lengths 1.37 (5) and 1.26 (4) Å, respectively]. However, there are some distortions in the bond angles about the alkene units, with the angle at the least hindered olefinic C atom (C5 or C12) being relatively large [C4—C5—C6 126 (3), C11—C12—C13 131 (4)°]. Both I atoms are directed towards the same face of the macrocycle, in contrast to the peripheral tolyl groups. Also of note is the apparent near planarity of the formally sp^3 N atoms, with displacements from the C_2S plane being 0.21 and 0.29 Å for N1 and N2, respectively. The confirmation that both double bonds adopt (*Z*) stereochemistry is in accordance with the ^{1}H and ^{13}C NMR data which imply the molecule is symmetrical

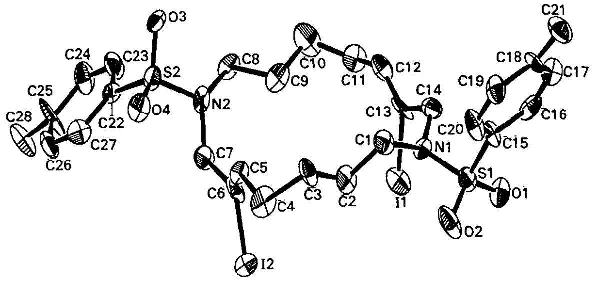

Fig. 1. The asymmetric unit of (1) showing the atomic labelling used in the tables.

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* Lists of structure factors, anisotropic thermal parameters, complete bond lengths and angles, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54732 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and contains only one type of double-bond geometry. Moreover, the finding that this alkene configuration is (*Z*) allows confident spectroscopic assignments to be made in the monoaza series of heterocycles where both (*E*)- and (*Z*)-alkene isomers have been isolated (Shaw, Anderson & Gallagher, 1990). Specifically, the chemical shift of the alkenyl proton in the (*E*) series appears consistently at lower field than the corresponding (*Z*) series ($\Delta\delta_H$ = 0.5–0.1 p.p.m.), while the chemical shifts for the iodo-substituted alkenyl C atoms also differ for the (*E*) (δ_C = 87.4–96.6 p.p.m.) and (*Z*) compounds (δ_C = 99.8–104.6 p.p.m.).

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Spiro[(2,3-époxycyclohexane)-1:4′-(2′,3′-dihydro-8′-méthoxybenzo-4*H*-pyranne)]

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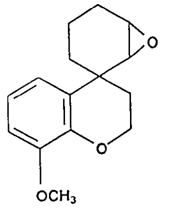
Abstract. 2,3-Dihydro-2′,3′-epoxy-8-methoxyspiro-[4*H*-1-benzopyran-4,1′-cyclohexane], $C_{15}H_{18}O_3$, M_r = 246.3, orthorhombic, *Pbcn*, $a = 26.085$ (7), $b = 7.211$ (2), $c = 13.653$ (6) Å, $V = 2568$ (3) Å^3, $Z = 8$, $D_x = 1.274$ Mg m^{-3}, λ(Cu $K\bar{\alpha}$) = 1.5418 Å, μ = 0.67 mm^{-1}, $F(000) = 1056$, $T = 295$ K, $R = 0.048$ for 1273 unique reflections. Both six-membered rings which share the spiro C atom are approximately 1,2-diplanar (sofa conformation) while the aromatic ring is planar. Owing to steric hindrance, one C—C bond formed by the spiro C atom is slightly longer than usual [1.560 (5) Å], but one of its neighbours in the heterocycle measures only 1.452 (5) Å. The structure can be regarded as constituted of layers of molecules which spread out approximately along the planes $x = \pm\frac{1}{8}$ and $\pm\frac{3}{8}$.

Introduction. Le spiro[(2,3-époxycyclohexane)-1:4′-(2′,3′-dihydro-8′-méthoxybenzo-4*H*-pyranne)] (I) a été obtenu par époxydation du composé éthylénique correspondant selon un mécanisme qui produit un seul des deux couples de diastéréoisomères prévisibles. Il possède la particularité d'être inerte vis à vis des réactifs azotés et de s'ouvrir de manière régiosélective lorsqu'on le traite par $LiAlH_4$. Son étude cristallographique a été entreprise dans le but de préciser la géométrie de sa molécule et, par suite, d'expliquer sa formation et son comportement réactionnel.



(I)

Partie expérimentale. Cristal approximativement parallélépipédique: 0,11 × 0,19 × 0,30 mm. Dimensions de la maille déterminées avec 25 réflexions pour lesquelles $14{,}86 \le \theta \le 26{,}85°$. Diffractomètre Enraf–Nonius CAD-4. Balayage ω d'amplitude $s = (1{,}40 + 0{,}14\mathrm{tg}\theta)°$. $0{,}023 \le (\sin\theta)/\lambda \le 0{,}550$ Å^{-1}; $0 \le h \le 28$, $0 \le k \le 7$, $0 \le l \le 14$. Réflexions de contrôle de l'intensité: $5\bar{1}6$, $\bar{7}30$ et 225. Diminution de *I* au cours des mesures: 3,8%. Correction de décroissance. 1782 réflexions indépendantes mesurées, 509 inobservées [$I < 3\sigma(I)$]. Programme *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H liés à C(10): série de Fourier des ΔF,

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