Table 1. *Selected bond lengths (Å)*

O1—C4	1.214 (3)	C2—C3	1.348 (4)
O2—C17	1.208 (3)	C3—C4	1.455 (4)
O3—C17	1.339 (3)	C4—C5	1.527 (4)
O3—C12	1.459 (3)	C6—C7	1.472 (3)
O4—C15	1.360 (4)	C7—C8	1.329 (3)
O4—C14	1.366 (3)	C13—C14	1.345 (4)
C1—C2	1.457 (4)	C13—C16	1.428 (4)
C1—C10	1.534 (3)	C15—C16	1.319 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H···O1^{i}	0.93	2.45	3.226 (4)	141

Symmetry code: (i) $-\frac{1}{2}-x, -y, \frac{1}{2}+z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Though all H atoms were located from a difference Fourier map, due to the low ratio of reflections to parameters they were fixed and allowed to ride on the atoms to which they are attached. Since the absolute structure cannot be reliably determined, a configuration similar to fibraurin was used for the refinement. Fibraurin was isolated from the same plant and its absolute configuration was established by Dampawan *et al.* (1986). The postulated biogenetic relationship suggests that the absolute configuration may be that depicted here.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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References

Bakhari, N. A., Wah, S. T., Chinnakali, K., Fun, H.-K. & Razak, I. A. (1998). *Acta Cryst.* C**54**, 1649–1651.
Barton, D. H. R. & Elad, D. (1956). *J. Chem. Soc.* pp. 2085–2090.
Dampawan, P., Engelhardt, L. M., Taylor, W. C., White, A. H. & Wiriyachitra, P. (1986). *Aust. J. Chem.* **39**, 177–181.
Ito, K. & Furukawa, H. (1969). *J. Chem. Soc. Chem. Commun.* pp. 653–654.
Nakanishi, K., Sasaki, S., Kiang, A. K., Goh, J., Kakisawa, H., Dhashi, M., Goto, M., Watanabe, J., Yokotani, H., Matsumura, C. & Togashi, M. (1965). *Chem. Pharm. Bull.* **13**, 882–890.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Seebach, D., Hungerbuhler, R. N., Naef, R., Schnurrenberger, P., Weidman, E. & Zuger, M. (1982). *Synthesis*, p. 138.
Sheldrick, G. M. (1996). *SHELXTL. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Systems Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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1,4-Bis[4-(1-pyridinium)styryl]benzene ditosylate

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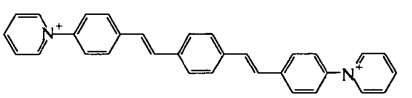
Abstract

The crystal structure of the title compound {alternative name: 1,1′-[*p*-phenylenebis(4-styryl)]dipyridinium ditosylate}, $C_{32}H_{26}N_2^{2+}\cdot 2C_7H_7O_3S^-$, provides an energy-minimum conformation which can be related to its DNA-binding properties.

Comment

The title cation (Auckland Cancer Laboratory synthesis number SN 18071) has been shown in assays to bind weakly in the minor groove of DNA, being totally released from the groove by competitive netropsin binding (Luck *et al.*, 1987). It has been shown to stabilize triplex DNA (Fortsch *et al.*, 1996) and also to inhibit the action of restriction endonucleases by binding in specific four or six base-pair DNA sequences (Kittler *et al.*, 1996).



SN 18071

Cocrystallization experiments of SN 18071 with DNA oligonucleotides were undertaken to characterize the minor-groove binding. These experiments showed the binding to be weak and disordered (Clark & Squire,

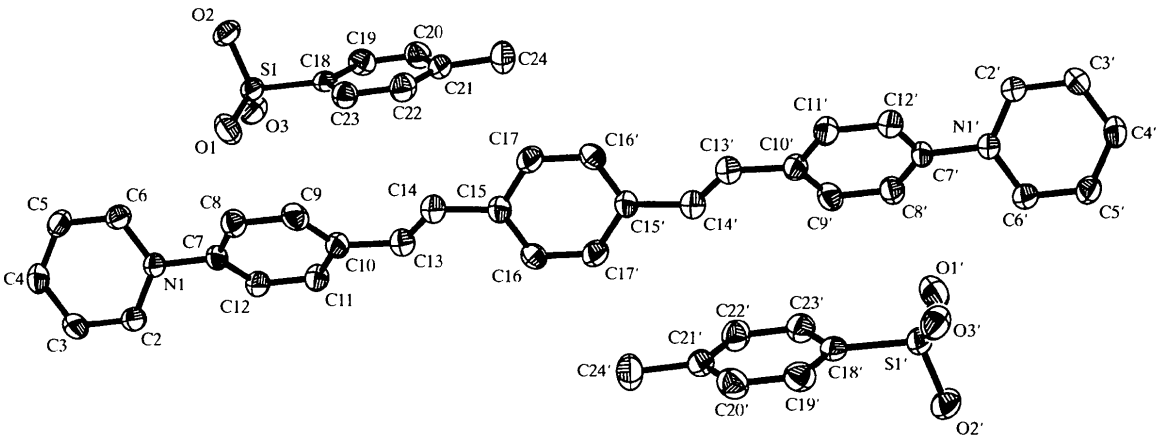


Fig. 1. View of the SN 18071 cation and its tosylate counter-ions (two crystallographic asymmetric units). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

1998). The crystal structure of the SN 18071 molecule was determined in parallel with the DNA experiments to establish an energy-minimum conformation for the uncomplexed ligand.

The structure (Fig. 1) displays inversion symmetry about the centroid of the C15–C20 ring. It contains no unusual bonds lengths, bond angles or torsion angles, and all ring systems are planar. The arrangement about the alkene linkers is *trans* and this in combination with the inversion symmetry results in an overall linear molecule. The geometry about the alkene linkers does deviate from idealized sp^2 bond angles, particularly for the angle C10—C13—C14 [127.6 (2)°], but these distortions do not represent an unusual strain on the molecule. The C13═C14 double-bond length is 1.323 (3) Å and the inter-ring N1—C7 bond is 1.452 (2) Å. Within the tosylate anion, the S1—C18 bond is 1.783 (2) Å and the average S1—O bond length is 1.452 (2) Å.

This free ligand crystal structure represents a minimum-energy conformation of the SN 18071 cation. The angle between the aryl-ring planes and the angles around the alkene linker are given by the following torsion angles: C2—N1—C7—C8 −132.5 (2), C9—C10—C13—C14 −7.9 (3) and C13—C14—C15—C17 158.8 (2)°. The cation is straight and so cannot be expected to bind in the curved minor groove in an isohelical manner like conventional minor-groove binders. This conclusion is consistent with the binding assays.

Experimental

The title compound was synthesized as described previously by Denny *et al.* (1979). The sample was dissolved in hot methanol (323 K) and crystallized by slow evaporation.

Crystal data

$C_{32}H_{26}N_2^{2+}\cdot 2C_7H_7O_3S^-$
M_r = 780.92
Triclinic
$P\bar{1}$
a = 7.2454 (3) Å
b = 9.1927 (4) Å
c = 15.6539 (7) Å
α = 92.418 (1)°
β = 99.687 (1)°
γ = 112.666 (1)°
V = 941.79 (7) Å^3
Z = 1
D_x = 1.377 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6184 reflections
θ = 1.33–28.23°
μ = 0.197 mm^{-1}
T = 203 (2) K
Fragment
0.36 × 0.34 × 0.12 mm
Yellow

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.819, T_{max} = 0.978
9218 measured reflections
4146 independent reflections
3383 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 28.23°
$h = -9 \rightarrow 8$
$k = -12 \rightarrow 11$
$l = 0 \rightarrow 20$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.107
S = 1.021
3654 reflections
305 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.4359P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.083
$\Delta\rho_{max}$ = 0.511 e Å^{-3}
$\Delta\rho_{min}$ = −0.348 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

All non-H atoms were located by direct methods and were refined anisotropically. The methyl-H atoms were included at calculated positions and refined as riding on C24. All other H atoms were located in difference Fourier electron-density maps and were refined with isotropic displacement parameters set to 1.2 times those of the bound C atoms.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SMART*. Data reduction: *SHELXTL* (Siemens, 1994*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1035). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Clark, G. R. & Squire, C. J. (1998). Unpublished results.
Denny, W. A., Atwell, G. J., Baguley, B. C. & Cain, B. F. (1979). *J. Med. Chem.* **22**, 134–151.
Fortsch, I., Birch-Hirschfeld, E., Schutz, H. & Zimmer, C. (1996). *J. Biomol. Struct. Dyn.* **14**, 317–329.
Kittler, L., Bell, A., Baguley, B. C. & Lober, G. (1996). *Biochem. Mol. Biol. Int.* **40**, 263–272.
Luck, G., Reinert, K. E., Baguley, B. C. & Zimmer, C. (1987). *J. Biomol. Struct. Dyn.* **4**, 1079–1094.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994*a*). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Two new compounds by reaction of taurolidine with methylene glycol

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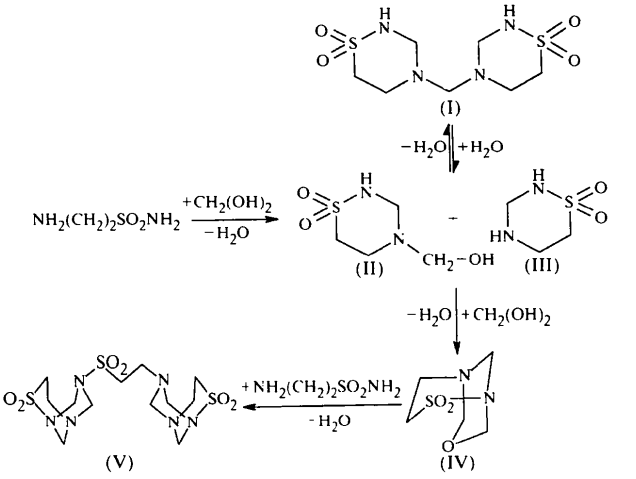
Abstract

The compounds 7-oxa-2[λ]^6-thia-1,5-diazabicyclo-[3.3.1]nonane-2,2-dione ($C_5H_{10}N_2O_3S$) and 7-{[2-(2,2-dioxo-2[λ]^6-thia-1,5,7-triazabicyclo[3.3.1]non-7-yl)ethyl]sulfonyl}-2[λ]^6-thia-1,5,7-triazabicyclo[3.3.1]-nonane-2,2-dione ($C_{12}H_{24}N_6O_6S_3$) are produced when taurolidine is reacted with an excess of methylene glycol. The saturated six-membered heterocyclic rings in both compounds adopt distorted chair conformations.

Comment

Taurolidine is a broad-spectrum bactericide and anti-endotoxin (Browne *et al.*, 1976). The scheme below shows the reaction sequence for the synthesis of taurolidine, (I), *via* compounds (II) and (III) which have been identified by NMR (Myers *et al.*, 1980; Erb *et al.*, 1982; Knight *et al.*, 1983; Hood *et al.*, 1994). We present here



the crystal structures of two new compounds, 7-oxa-2[λ]^6-thia-1,5-diazabicyclo[3.3.1]nonane-2,2-dione [(IV); Fig. 1] and 7-{[2-(2,2-dioxo-2[λ]^6-thia-1,5,7-triazabicyclo[3.3.1]non-7-yl)ethyl]sulfonyl}-2[λ]^6-thia-1,5,7-triazabicyclo[3.3.1]nonane-2,2-dione [(V); Fig. 2], which are formed when the reaction mixture contains an excess of methylene glycol.

Compound (IV) contains two six-membered rings sharing atoms N1, C5 and N2. Both the thiadiaza- and oxadiazacyclohexane rings adopt distorted chair conformations, with puckering parameters Q = 0.586 (3) Å, θ = 12.1 (3)°, φ = 8.8 (10)°, and Q = 0.550 (3) Å, θ = 5.4 (3)°, φ = 342 (3)°, respectively (Cremer & Pople, 1975). Compound (V) contains four six-membered rings, *i.e.* a thiadiaza- and a triazacyclohexane ring fused together across N1—C3—N2, and a thiadiaza- and a triazacyclohexane ring fused together across N5—C10—N6. As in compound (IV), each ring adopts a distorted chair conformation [puckering parameters: ring C3—N2—C4—N3—C5—N1 Q = 0.547 (3) Å, θ = 7.4 (3)° and φ = 359 (2)°; ring C3—N1—S1—C1—C2—N2 Q = 0.583 (2) Å, θ = 13.5 (3)° and φ = 13.6 (9)°; ring C10—N5—C11—C12—S3—N6 Q = 0.589 (3) Å, θ = 13.1 (3)° and φ = 354 (1)°; ring C10—N6—C9—N4—C8—N5 Q = 0.561 (3) Å, θ = 4.0 (3)° and φ = 29 (3)°].

Intermolecular C—H···O and C—H···N close contacts are listed in Tables 2 [compound (IV)] and 4 [compound (V)]. The observed distances are consistent with those commonly observed for weak hydrogen bonds in organic molecular crystals (Jeffrey & Saenger, 1991).