X-Ray Determination of the Stereochemistry and Molecular Structure of 2,6-Dinitrato-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide

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The molecular geometry of the title compound, $C_8H_{12}N_2O_6S$, has been determined by *X*-ray diffraction. The molecule has a twin-chair conformation with the nitrato-groups in equatorial positions on the thiacyclohexane rings. The C(3) ··· C(7) transannular separation is 3.128(2) Å and the H ··· H 3,7-separation is *ca.* 1.9 Å. Crystallographic data are a = 15.144(3), b = 7.851(3), c = 19.958(4) Å, β = 90.295(14)°, Z = 8, space group $A2/a$. Diffractometer intensity measurements were made with both Cu-K_α and Mo-K_α radiation and least-squares adjustment of the atomic parameters converged at R 0.080 for 1 872 Cu-K_α reflexions and at R 0.040 for 2 718 Mo-K_α reflexions.

A RECENT *X*-ray study[1] of 2,6-dichloro-9-thiabicyclo-[3.3.1]nonane 9,9-dioxide (1)[2] confirmed that the chloro-substituents occupy equatorial positions on the thiacyclohexane rings. This stereochemistry is an outcome of the *trans*-addition of SCl_2 to the double bonds of *Z*,*Z*-cyclo-octa-1,5-diene to form (2), from which (1) was derived by peracid oxidation.[2]

The chloro-substituents of (2) are quantitatively replaced under mild conditions by nitrato-groups[3] and the question arises as to whether the substitution occurs with retention or inversion of configuration. Anchimeric assistance to the leaving halide by the β-sulphide group with nucleophilic attack of nitrate on the intermediate thiiranium cation would lead to retention of the C(2) and C(6) configurations, as in (3a). The appearance of the H–C–O ^{1}H n.m.r. signal (δ 5.3—5.8) as a broad multiplet,[4] incorporating a C(2),C(3) diaxial H–H coupling, is consistent with the retention of stereochemistry but the presence of the diastereoisomer (3b) with inverted configuration is not precluded as its C(2),C(3) equatorial-axial and diequatorial couplings could be hidden.

2,6-Dinitrato-9-thiabicyclo[3.3.1]nonane was converted in quantitative yield by peracid oxidation into 2,6-dinitrato-9-thiabicyclo[3.3.1]nonane 9,9-dioxide which crystallized as a homogeneous material.[3] We undertook an *X*-ray analysis of this compound to define the stereochemistry unambiguously and to characterize the molecular conformation. The crystal structure was determined by direct phasing procedures and the atomic co-ordinates were adjusted by full-matrix least-squares calculations with two sets of *X*-ray intensities, one obtained with Cu-K_α and the other with Mo-K_α radiation. The results from these agree well and hence only the atomic co-ordinates, bond lengths, interbond angles, and torsion angles from the Mo-K_α analysis are in Tables 1—3.

The molecular structure is illustrated in the Figure. This shows that the nitrato-groups occupy equatorial positions on the thiacyclohexane rings and the compound is therefore formulated as (4a) rather than (4b), confirming that replacement of the chloro-substituents in (2) occurred with retention of configuration to give (3a).

Several *X*-ray diffraction studies of bicyclo[3.3.1]-nonane derivatives have established that the twin-chair conformer is characterized by a C(3) ··· C(7) separation of *ca.* 3.1 Å and that the H ··· H 3,7-separation is shorter than 2 Å.[5] Molecular mechanics calculations have produced estimates for the transannular H ··· H separation in the range 1.97—2.20 Å,[6] and the geometry of the twin-chair conformer accordingly provides a useful test of the relative merits of the empirical force-fields employed in conformational calculations.

TABLE 1

Atomic co-ordinates

	x	*y*	*z*
S	0.350 63(2)	0.214 39(5)	0.775 92(2)
C(1)	0.269 38(8)	0.157 50(18)	0.835 97(7)
C(2)	0.216 37(8)	0.320 28(19)	0.850 10(7)
C(3)	0.268 50(9)	0.465 52(20)	0.882 41(8)
C(4)	0.355 90(9)	0.506 52(18)	0.847 22(7)
C(5)	0.414 30(8)	0.355 76(18)	0.826 35(7)
C(6)	0.455 92(9)	0.245 93(19)	0.881 59(7)
C(7)	0.390 24(10)	0.166 90(23)	0.930 08(8)
C(8)	0.315 47(10)	0.068 31(19)	0.894 77(8)
N(1)	0.069 02(9)	0.217 31(18)	0.872 05(9)
N(2)	0.582 69(9)	0.288 07(20)	0.952 26(7)
O(1)	0.310 02(9)	0.307 09(17)	0.721 75(6)
O(2)	0.402 30(8)	0.066 37(15)	0.758 94(6)
O(3)	0.148 02(7)	0.282 40(15)	0.899 01(6)
O(4)	0.067 51(11)	0.183 27(26)	0.813 24(9)
O(5)	0.013 02(9)	0.201 05(19)	0.913 20(8)
O(6)	0.512 81(8)	0.365 10(16)	0.917 37(6)
O(7)	0.597 85(10)	0.139 79(21)	0.942 15(9)
O(8)	0.619 93(10)	0.385 54(23)	0.988 56(7)
H(1)	0.233 8(13)	0.078 5(26)	0.813 4(10)
H(2)	0.190 3(13)	0.362 3(27)	0.807 7(11)
$H(3_1)$	0.232 9(13)	0.576 1(28)	0.880 6(11)
$H(3_2)$	0.279 2(13)	0.440 8(25)	0.930 7(11)
$H(4_1)$	0.390 9(14)	0.573 2(25)	0.878 4(10)
$H(4_2)$	0.347 9(14)	0.592 6(26)	0.810 0(11)
H(5)	0.462 0(14)	0.399 6(26)	0.799 9(11)
H(6)	0.488 9(12)	0.163 6(28)	0.862 1(10)
$H(7_1)$	0.418 8(16)	0.102 7(31)	0.958 2(12)
$H(7_2)$	0.372 3(13)	0.258 8(27)	0.965 5(11)
$H(8_1)$	0.273 0(17)	0.043 0(30)	0.926 4(12)
$H(8_2)$	0.339 0(14)	−0.036 2(27)	0.876 1(10)

The C(3) ··· C(7) and $H(3_2)$ ··· $H(7_2)$ separations in (4a) obtained from the co-ordinates of Table 1 are 3.128(2) and 2.071(28) Å. The C(3)–$H(3_2)$ and C(7)–$H(7_2)$ distances of 1.00 and 0.93 Å, however, are shorter than the normal spectroscopic value for C(sp^3)–H bonds, a well known artifact of the *X*-ray diffraction method, and when $H(3_2)$ and $H(7_2)$ are displaced along the C–H vectors to make these C–H distances 1.10 Å, the H ··· H

TABLE 2

Bond lengths (Å) and angles (°)

S–O(1)	1.439(1)	S–O(2)	1.442(1)
S–C(1)	1.779(1)	S–C(5)	1.779(1)
C(1)–C(2)	1.536(2)	C(5)–C(6)	1.533(2)
C(2)–C(3)	1.528(2)	C(6)–C(7)	1.523(2)
C(3)–C(4)	1.536(2)	C(7)–C(8)	1.539(2)
C(4)–C(5)	1.536(2)	C(8)–C(1)	1.532(2)
C(2)–O(3)	1.457(2)	C(6)–O(6)	1.456(2)
N(1)–O(3)	1.405(2)	N(2)–O(6)	1.401(2)
N(1)–O(4)	1.204(3)	N(2)–O(7)	1.204(2)
N(1)–O(5)	1.190(2)	N(2)–O(8)	1.193(2)
C(1)–H(1)	0.94(2)	C(5)–H(5)	0.96(2)
C(2)–H(2)	0.99(2)	C(6)–H(6)	0.91(2)
C(3)–H(3_1)	1.02(2)	C(7)–H(7_1)	0.87(2)
C(3)–H(3_2)	1.00(2)	C(7)–H(7_2)	0.93(2)
C(4)–H(4_1)	0.97(2)	C(8)–H(8_1)	0.92(3)
C(4)–H(4_2)	1.01(2)	C(8)–H(8_2)	0.97(2)
C(1)–S–C(5)	98.6(1)	O(1)–S–O(2)	117.5(1)
C(1)–S–O(1)	109.8(1)	C(5)–S–O(2)	110.0(1)
C(1)–S–O(2)	109.5(1)	C(5)–S–O(1)	109.7(1)
S–C(1)–C(2)	106.2(1)	S–C(5)–C(6)	106.0(1)
S–C(1)–C(8)	108.5(1)	S–C(5)–C(4)	108.8(1)
C(2)–C(1)–C(8)	118.4(1)	C(6)–C(5)–C(4)	118.3(1)
C(1)–C(2)–C(3)	115.4(1)	C(5)–C(6)–C(7)	114.8(1)
C(1)–C(2)–O(3)	109.1(1)	C(5)–C(6)–O(6)	103.4(1)
O(3)–C(2)–C(3)	103.7(1)	O(6)–C(6)–C(7)	109.7(1)
C(2)–C(3)–C(4)	114.1(1)	C(6)–C(7)–C(8)	113.3(1)
C(3)–C(4)–C(5)	117.5(1)	C(7)–C(8)–C(1)	116.9(1)
C(2)–O(3)–N(1)	115.1(1)	C(6)–O(6)–N(2)	114.2(1)
O(3)–N(1)–O(4)	117.8(1)	O(6)–N(2)–O(7)	118.6(1)
O(3)–N(1)–O(5)	112.5(2)	O(6)–N(2)–O(8)	112.2(1)
O(4)–N(1)–O(5)	129.7(2)	O(7)–N(2)–O(8)	129.2(2)

TABLE 3

Torsion angles (°)

S–C(1)–C(2)–C(3)	−64.0(1)
C(1)–C(2)–C(3)–C(4)	49.4(2)
C(2)–C(3)–C(4)–C(5)	−44.2(2)
C(3)–C(4)–C(5)–S	54.6(1)
C(3)–C(4)–C(5)–C(6)	−66.4(2)
C(4)–C(5)–S–C(1)	−62.0(1)
C(4)–C(5)–S–O(1)	52.7(1)
C(4)–C(5)–S–O(2)	−176.5(1)
C(5)–S–C(1)–C(2)	66.2(1)
O(1)–S–C(1)–C(2)	−48.5(1)
O(2)–S–C(1)–C(2)	−178.8(1)
O(3)–C(2)–C(1)–S	179.8(1)
O(3)–C(2)–C(1)–C(8)	−58.0(2)
O(3)–C(2)–C(3)–C(4)	168.6(1)
C(8)–C(1)–C(2)–C(3)	58.2(2)
C(1)–C(2)–O(3)–N(1)	−85.5(1)
C(3)–C(2)–O(3)–N(1)	151.0(1)
C(2)–O(3)–N(1)–O(4)	7.1(2)
C(2)–O(3)–N(1)–O(5)	−174.5(1)
S–C(5)–C(6)–C(7)	−65.4(1)
C(5)–C(6)–C(7)–C(8)	52.3(2)
C(6)–C(7)–C(8)–C(1)	−47.4(2)
C(7)–C(8)–C(1)–S	56.2(1)
C(7)–C(8)–C(1)–C(2)	−64.8(2)
C(8)–C(1)–S–C(5)	−62.1(1)
C(8)–C(1)–S–O(2)	52.9(1)
C(8)–C(1)–S–O(1)	−176.8(1)
C(1)–S–C(5)–C(6)	66.2(1)
O(2)–S–C(5)–C(6)	−48.3(1)
O(1)–S–C(5)–C(6)	−179.1(1)
O(6)–C(6)–C(5)–S	175.2(1)
O(6)–C(6)–C(5)–C(4)	−62.4(1)
O(6)–C(6)–C(7)–C(8)	168.1(1)
C(4)–C(5)–C(6)–C(7)	57.0(2)
C(5)–C(6)–O(6)–N(2)	−156.3(1)
C(7)–C(6)–O(6)–N(2)	80.9(1)
C(6)–O(6)–N(2)–O(7)	10.9(2)
C(6)–O(6)–N(2)–O(8)	−169.8(1)

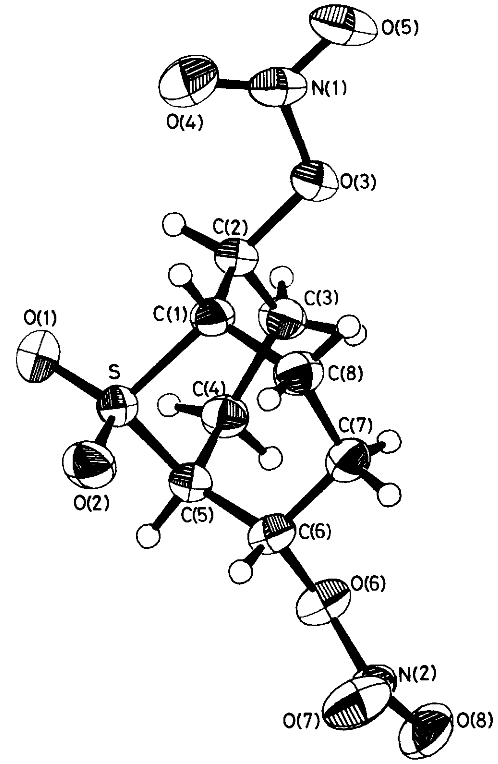
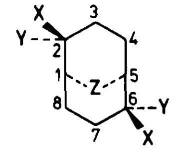


FIGURE Molecular structure of 2,6-dinitrato-9-thiabicyclo[3.3.1]nonane 9,9-dioxide. The thermal ellipsoids of the S, O, N, and C atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å

transannular distance becomes 1.92 Å. The corresponding experimental C ··· C, H ··· H, and corrected H ··· H separations obtained in the analysis with Cu-K_α intensities are 3.128(8), 2.074(68), and 1.91 Å. The agreement between the two sets of results is excellent. Other X-ray studies of bicyclo[3.3.1]nonane derivatives have given similar results[5] and it is now evident that molecular mechanics calculations that estimate the H ··· H 3,7-separation in bicyclo[3.3.1]nonane to be > 2 Å exaggerate the transannular repulsion.



(1) X = Cl, Y = H, Z = SO_2

(2) X = Cl, Y = H, Z = S

(3a) X = ONO_2, Y = H, Z = S

(3b) X = H, Y = ONO_2, Z = S

(4a) X = ONO_2, Y = H, Z = SO_2

(4b) X = H, Y = ONO_2, Z = SO_2

The presence of the nitrato-substituents at positions 2 and 6 in (4a) causes the six-membered rings to be skewed to a small extent, the torsion angles S–C(1)–C(2)–C(3) and S–C(5)–C(4)–C(3) differing by 9.4° and S–C(1)–C(8)–C(7) and S–C(5)–C(6)–C(7) by 9.2°. Accordingly, the symmetry of the carbon framework is lowered from C_{2v} and approximates to C_2 (see Table 3); the positions adopted by the nitrato-groups, however, do not conform to C_2 symmetry, *cf.* N(1)–O(3)–C(2)–C(1) and N(2)–O(6)–C(6)–C(5) torsion angles of −85.5 and −156.3°. Bicyclo[3.3.1]nonanes lacking substituents at C(2), C(4), C(6), and C(8) are not skewed in this way.[5]

Within the six-membered rings, the C–C–C angles at C(2) and C(6) are 115.4 and 114.8°, whereas those at C(4) and C(8) are slightly larger, 117.5 and 116.9°, and those at C(3) and C(7) smaller, 114.1 and 113.3°. The S–C–C angles at C(1) and C(5) are appreciably smaller, 106.0—108.8, mean 107.4°. Molecular mechanics calculations, with the White and Bovill force field,[6] for bicyclo[3.3.1]-nonane give angles at C(3), C(7) smaller than those at C(2), C(4), C(6), and C(8), with the C(9)–C–C angles appreciably smaller: C(1)–C(2)–C(3) 114.5°, C(2)–C(3)–C(4) 113.5°, C(9)–C(1)–C(2) 109.6°.

EXPERIMENTAL

Crystal Data.—$C_8H_{12}N_2O_6S$, $M = 264.3$. Monoclinic, space group $A2/a$, $a = 15.144(3)$, $b = 7.851(3)$, $c = 19.958(4)$ Å, $\beta = 90.295(14)°$, $U = 2\,374$ Å^3, $D_c = 1.48$ g cm^{-3}, $Z = 8$, $F(000) = 1\,104$, $\mu(\text{Mo-}K_\alpha) = 2.93$ cm^{-1}, $\mu(\text{Cu-}K_\alpha) = 25.8$ cm^{-1}.

Crystallographic Measurements.—Cell dimensions were derived from least-squares treatment of the setting angles for 25 reflexions measured on an Enraf–Nonius CAD4 diffractometer with Cu-K_α radiation. Two sets of intensity measurements were obtained: set 1 with Cu-K_α radiation and set 2 with another crystal and Mo-K_α radiation. For set 1, 2 342 reflexions hkl and $hk\bar{l}$ were surveyed in the range $\theta \leqslant 72°$ and 1 872 reflexions satisfied the criterion $I > 2.5\sigma(I)$. For set 2, 3 436 reflexions hkl and $hk\bar{l}$ were surveyed in the range $\theta \leqslant 27°$ and 2 718 reflexions satisfied the criterion $I > 2.5\sigma(I)$.

Structure Analysis.—With data set 1, the crystal structure was elucidated by a version of MULTAN,[7] adapted for the Glasgow University ICL 2976 computer by Dr. C. J. Gilmore. The co-ordinates and thermal parameters of the S, C, N, and O atoms were adjusted by full-matrix least-squares calculations with unit weights (R 0.11) after which the H atoms were located in a difference electron-density distribution and included in the least-squares calculations with isotropic thermal parameters. The weighting scheme was changed to $w = [\sigma^2(|F|) + 0.0083|F|^2]^{-1}$ and the calculations converged at R 0.080 and R_w 0.104.

Since this final value of R is rather high, suggesting that there are some systematic errors, another crystal was selected and intensity set 2 collected with Mo-K_α radiation. Least-squares adjustment of the atomic parameters with these intensity data converged at R 0.040 and R_w 0.048. The results from this analysis are summarized in Tables 1—3.

Fourier and least-squares calculations were performed with the SHELX series of programs[8] and the molecular diagram was prepared with ORTEP.[9]

Observed and calculated structure amplitudes, thermal parameters, and the atomic parameters obtained with the Cu-K_α intensity data are listed in Supplementary Publication No. SUP 23292 (19 pp.).*

We thank the S.E.R.C. for a grant towards the purchase of the diffractometer.

[1/1963 *Received*, 21*st December*, 1981]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

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