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Structure of 7-(2,4-Dinitrophenylthio)-5-*exo*-nitrobicyclo[2.2.1]hept-2-*exo*-yl Acetate

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Abstract. $C_{15}H_{15}N_3O_8S$, M_r=397·4, monoclinic, $P2_1/c$, a = 12·132 (2), b = 15·430 (2), c = 10·033 (2) Å, β = 111·04 (1)°, V = 1752·9 (2) Å^3, Z = 4, D_x = 1·506 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 20·764 cm^{-1}, F(000) = 824, room temperature, R = 0·055 for 2489 observed reflections. The conformation of the bicyclo[2.2.1]heptane framework is synchro-twist to relieve the steric strain imposed by the presence of the substituents. The molecule contains two short S···O non-bonded distances of 2·788 (2) and 2·987 (2) Å whose directions are close to the C—S bond vectors [C—S···O angles 162·1 (1) and 172·8 (1)°, respectively].

Introduction. 8,9,10-Trinorbornane is a traditional model for studying electrophilic addition to the C—C double bond. Disubstituted 8,9,10-trinorbornanes formed in these reactions can be identified unambiguously on the basis of their ^{1}H NMR spectra and some reliable criteria exist (Start, 1958; Zefirov *et al.*, 1980) for assignment of the NMR signals in these systems. However, analogous criteria for trisubstituted 8,9,10-trinorbornanes, adducts of electrophiles to monosubstituted 8,9,10-trinorbornenes, are as yet lacking.

The reaction of 5-*endo*-nitro-8,9,10-trinorbornene (I) with 2,4-dinitrophenylsulfenyl chloride under the 'doping addition' conditions (CH_3COOH + $LiClO_4$) (Zefirov, Sadovaya, Maggerramov, Bodrikov & Kartachov, 1975; Zefirov, Sadovaya, Novgorodtseva & Bodrikov, 1978), proceeds to give the trisubstituted 8,9,10-trinorbornane, $C_{15}H_{15}N_3O_8S$ (IV) (Fig. 1), whose structure is proved unambiguously by X-ray diffraction in this paper.

Experimental. Prismatic crystal of dimensions 0·2 × 0·3 × 0·2 mm used for measurement of unit-cell parameters (from 24 reflections with θ between 35 and 37°) and intensities of 3182 reflections (h = 0 to 14, k = 0 to 18, l = 10 to 10) using a Hilger & Watts four-circle automatic diffractometer (293 K, Cu $K\alpha$, graphite monochromator, $\theta/2\theta$ scan, θ_{max} = 66°). Two standard reflections (170 and $\bar{3}04$) measured after every 98 reflections showed no noticeable intensity variations. No absorption or secondary-extinction

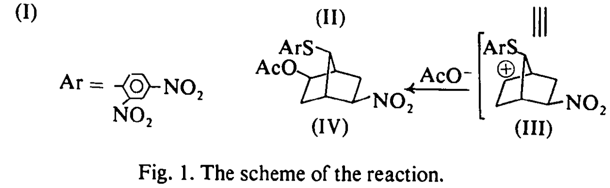

Fig. 1. The scheme of the reaction.

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corrections applied. Structure solved by direct methods using *MULTAN*75 (Main, Woolfson & Germain, 1975) and refined by least squares with anisotropic temperature factors for non-H atoms. 2489 independent reflections with $I \geq 2\sigma$ included in refinement. Function $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$, minimized. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms located in difference Fourier map and refined isotropically. Final discrepancy factors: $R = 0{\cdot}055$, $wR = 0{\cdot}063$, goodness-of-fit $S = 6{\cdot}62$. Max. shift/e.s.d. 0·4, largest and smallest peak heights in final difference synthesis $\pm 0{\cdot}3$ e Å^{-3}. All calculations performed with an Eclipse S/200 computer using *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Discussion. The geometry of molecule (IV) and the bond lengths are shown in Fig. 2. The atomic coordinates and the equivalent isotropic temperature factors are listed in Table 1, and the bond angles in Table 2.*

The present study proved product (IV) to be 7-(2,4-dinitrophenylthio)-5-*exo*-nitrobicyclo[2.2.1]hept-2-*exo*-yl acetate. It follows that the product is formed in the *exo*-attack by the electrophile upon (I) followed by the 1,2-shift (II → III) and, at the final reaction step, the *exo*-attack by the acetoxy anion at the carbocationic centre in (III) (see Fig. 1).

As required by the *exo*-orientation of the acetoxy and nitro groups, the torsion angles C(1)—C(6)—C(5)—C(1) = 128·0 (3)° and C(4)—C(3)—C(2)—O(1) = 119·2 (2)° are smaller than 180°. The introduction of substituents into 8,9,10-trinorbornane causes some distortions of the framework. Thus the C(1)C(7)C(4) and C(2)C(3)C(5)C(6) planes form the dihedral angle of 88·6 (2)° rather than an ideal 90° angle, and the C(6)—C(1)—C(7) bond angle of 98·4 (2)° is narrowed noticeably in comparison with the analogous angle in the unsubstituted bicyclo[2.2.1]heptane [101·8 (6)°] (Dallinga & Toneman, 1968). Also, the C(1)—C(7) and C(4)—C(7) bond lengths, 1·572 (5) and 1·523 (4) Å, respectively, differ significantly from each other.

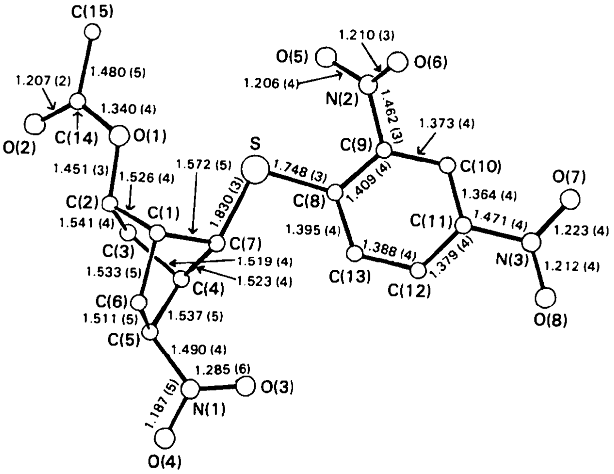

Fig. 2. The molecular structure of the title compound. Distances are in Å.

Table 1. *Atomic coordinates* (×10^4, ×10^5 *for* S) *and their equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)
S	64211 (6)	93632 (5)	16657 (9)	3·72 (2)
O(1)	8484 (2)	8880 (1)	861 (2)	4·03 (6)
O(2)	8940 (2)	9030 (2)	−1097 (3)	5·82 (9)
O(3)	7407 (3)	12125 (2)	3443 (5)	11·54 (19)
O(4)	8784 (4)	12861 (2)	3116 (6)	14·02 (25)
O(5)	5087 (2)	7871 (1)	1518 (3)	5·60 (9)
O(6)	4911 (3)	7599 (2)	3514 (3)	6·73 (10)
O(7)	2007 (2)	9668 (2)	4096 (3)	5·91 (9)
O(8)	2636 (2)	10978 (2)	4487 (3)	6·29 (9)
N(1)	8285 (2)	12189 (2)	3018 (4)	5·90 (10)
N(2)	4909 (2)	8092 (1)	2576 (3)	3·71 (7)
N(3)	2684 (2)	10248 (2)	4064 (3)	4·34 (8)
C(1)	8800 (3)	9945 (2)	2725 (3)	4·07 (9)
C(2)	8850 (2)	9769 (2)	1251 (3)	3·54 (8)
C(3)	7957 (3)	10424 (2)	290 (3)	4·05 (9)
C(4)	7532 (2)	10943 (2)	1299 (3)	4·05 (9)
C(5)	8605 (2)	11473 (2)	2229 (4)	4·50 (10)
C(6)	9406 (3)	10819 (2)	3239 (4)	4·98 (10)
C(7)	7485 (3)	10244 (2)	2350 (4)	4·11 (9)
C(8)	5340 (2)	9651 (2)	2358 (3)	3·02 (7)
C(9)	4684 (2)	9009 (2)	2744 (3)	2·84 (7)
C(10)	3833 (2)	9193 (2)	3308 (3)	3·07 (7)
C(11)	3615 (2)	10043 (2)	3494 (3)	3·19 (7)
C(12)	4244 (2)	10708 (2)	3184 (3)	3·61 (8)
C(13)	5095 (2)	10506 (2)	2609 (3)	3·61 (8)
C(14)	8585 (3)	8585 (2)	−347 (4)	4·43 (10)
C(15)	8169 (4)	7680 (2)	−659 (5)	6·96 (16)

Table 2. *Bond angles* (°)

C(7)SC(8)	101·0 (1)	N(1)C(5)C(4)	113·1 (3)
C(2)O(1)C(14)	116·5 (2)	N(1)C(5)C(6)	111·5 (3)
O(3)N(1)O(4)	119·8 (4)	C(1)C(6)C(5)	104·3 (3)
O(3)N(1)C(5)	121·9 (3)	SC(7)C(1)	113·0 (2)
O(4)N(1)C(5)	118·0 (3)	SC(7)C(4)	117·6 (2)
O(5)N(2)O(6)	123·7 (3)	C(1)C(7)C(4)	94·9 (2)
O(5)N(2)C(9)	118·4 (2)	SC(8)C(9)	120·6 (2)
O(6)N(2)C(9)	117·9 (2)	SC(8)C(13)	123·4 (2)
O(7)N(3)O(8)	123·6 (3)	C(9)C(8)C(13)	116·0 (2)
O(7)N(3)C(11)	118·0 (3)	C(8)C(9)C(10)	123·4 (2)
O(8)N(3)C(11)	118·4 (3)	N(2)C(9)C(8)	120·1 (2)
C(2)C(1)C(6)	107·6 (3)	N(2)C(9)C(10)	116·5 (2)
C(2)C(1)C(7)	102·1 (2)	C(9)C(10)C(11)	117·8 (2)
C(6)C(1)C(7)	98·4 (2)	C(10)C(11)C(12)	122·3 (3)
O(1)C(2)C(1)	108·4 (2)	N(3)C(11)C(10)	118·3 (2)
O(1)C(2)C(3)	111·9 (2)	N(3)C(11)C(12)	119·5 (2)
C(1)C(2)C(3)	103·0 (2)	C(11)C(12)C(13)	118·8 (3)
C(2)C(3)C(4)	105·0 (2)	C(8)C(13)C(12)	121·7 (3)
C(3)C(4)C(5)	105·6 (2)	O(1)C(14)O(2)	122·7 (3)
C(3)C(4)C(7)	101·2 (2)	C(1)C(14)C(15)	112·2 (3)
C(5)C(4)C(7)	101·0 (2)	O(2)C(14)C(15)	125·1 (3)
C(4)C(5)C(6)	104·6 (3)		

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' details and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42828 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

To adapt itself to the steric strain caused by the presence of substituents, the 8,9,10-trinorbornane framework assumes the synchro-twist $S(-,-)$ conformation, as follows from comparison of the absolute values of the torsion angles (Altona & Sundaralingam, 1970): |C(7)–C(1)–C(2)–C(3)| [31·2 (3)°] < |C(7)–C(4)–C(3)–C(2)| [37·2 (3)°]; |C(7)–C(1)–C(6)–C(5)| [39·0 (3)°] > |C(7)–C(4)–C(5)–C(6)| [31·4 (3)°]. The C(1)C(2)C(3)C(4)C(7) five-membered ring is distorted to a somewhat smaller extent than the C(1)C(6)C(5)C(4)C(7) ring, the total puckering amplitudes Q being 0·570 (3) and 0·599 (3) Å, respectively.

Substituted bicyclo[2.2.1]heptane derivatives with 2-nitrophenylthio substituents often show a shortening of the S···O(nitro group) non-bonded distance in comparison with the sum of their van der Waals radii, 3·25 Å (Pauling, 1960). Thus in the structures of 3-*exo*-methoxy-5-*exo*-(2-nitrophenylthio)tricyclo-[2.2.1.$0^{2,6}$]heptane (Garratt, Przybylska & Cygler, 1983), 1-chloromethyl-3-*endo*-(2,4-dinitrophenylthio)-tricyclo[2.2.1.$0^{2,0}$]heptane (Przybylska & Garratt, 1981) and 2-*exo*-chloro-7,7-dimethyl-3-*endo*-(2-nitrophenylthio)bicyclo[2.2.1]heptane (Sergeyeva, Struchkov, Kurkutova, Zemlyanukhina, Sadovaya & Zefirov, 1984) these distances are respectively 2·694 (2), 2·739 (2) and 2·694 (2) Å. Their shortening can be considered as the result of the attractive interaction between the S and O atoms. In molecule (IV) the S···O(5) distance is somewhat longer and the *ortho* nitro group is more significantly rotated out of the benzene plane [the dihedral angle in (IV) is equal to 40·6°, whereas in the structures mentioned above these angles are respectively 25·0, 28·0 and 11·9°]. In molecule (IV), along with the considerably shortened S···O(5) distance, the less significantly shortened non-bonded distance S···O(1) 2·987 (2) Å is also observed. The directions of both shortened contacts are close to the C–S bond vectors [the C(7)–S···O(5) and C(8)–S···O(1) angles are 162·1 (1) and 172·8 (1)°, respectively], *i.e.* the T-type coordination of the S atom, characteristic of molecules with shortened S–nucleophile contacts, is observed.

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1-(4-Chlorophenyl)-2-cyclopentylethanone

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Abstract. $C_{13}H_{15}ClO$, $M_r = 222{\cdot}72$, monoclinic, $P2_1/a$, $a = 7{\cdot}936\ (2)$, $b = 10{\cdot}741\ (3)$, $c = 14{\cdot}001\ (4)$ Å, $\beta = 101{\cdot}52\ (1)°$, $V = 1169{\cdot}4\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}265$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}96$ cm^{-1}, $F(000) = 472$, $T = 295$ K, final $R = 0{\cdot}061$ for 1342 observed reflections. The carbonyl-containing side chain occupies an equatorial position with respect to the five-membered cyclopentane ring; the conformation of the ring is close to C_2 (half-chair or twisted form). The equatorial γ-H atom is 2·76 (4) Å from the carbonyl O atom [axial H 3·46 (4) Å], which is near the upper limit for H abstraction.

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