3·30 (1), and C(24)···O(14) $(1-x, -0{\cdot}5+y, -z)$ 3·31 (1) Å. No suitable donors for H-bond formation are available. The molecules are held in the crystal by van der Waals forces.

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Structure of 1-Cyano-3,3-dimethyl-2-thiatricyclo[3.2.1.1^{6,8}]nonane 2,2-Dioxide

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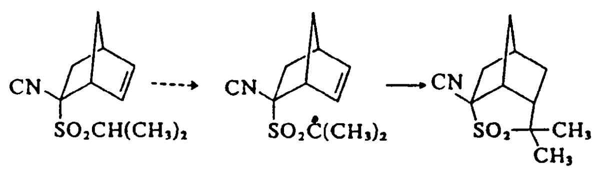
Abstract. $C_{11}H_{15}NO_2S$, $M_r = 225{\cdot}3$, monoclinic, $P2_1/n$, $a = 6{\cdot}382\,(3)$, $b = 14{\cdot}586\,(6)$, $c = 12{\cdot}049\,(13)$ Å, $\beta = 98{\cdot}20\,(6)°$, $V = 1100\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}348$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}6$ cm^{-1}, $F(000) = 480$, $T = 296$ K, $R = 0{\cdot}035$ for 1031 observed diffractometer data. The three five-membered rings adopt an envelope conformation. The S atom has the usual distorted tetrahedral configuration with mean S=O bond length 1·443 (3) Å. The cyano group is almost linear with C—C≡N angle 177·2 (4)° and C≡N bond 1·144 (5) Å. The structure of the title compound is compared with that of its precursor, 5-*exo*-cyano-5-*endo*-isopropylsulfonyl-2-norbornene, an efficient new radical clock.

Introduction. A convenient approach to check for the presence of radical intermediates during organic reactions is to use a radical clock (Griller & Ingold, 1980). Recently, the 5-cyano-substituted 5-*endo*-isopropylsulfonyl-2-norbornene (I) has been synthetized (Vacher, Samat & Chanon, 1985), and the corresponding α-sulfonyl-C-centred radical (II) undergoes an intramolecular addition at the double bond, leading to the tricyclo compound (III).



(I) (II) (III)

In connection with the structure of (I), already reported (Vacher, Samat, Allouche, Laknifli, Baldy & Chanon, 1988), we decided to undertake an X-ray study of (III).

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Experimental. A well formed parallelepiped (0·25 × 0·30 × 0·40 mm) was selected among the light-yellow crystals obtained by recrystallization of $C_{11}H_{15}NO_2S$ in ethanol.

Enraf–Nonius CAD-4 diffractometer. Cell constants by least squares using the setting angles for 25 reflections in the range $10{\cdot}0° \leq \theta < 15{\cdot}1°$. Three standard reflections ($\bar{1}54$, $3\bar{5}\bar{4}$, $02\bar{6}$) were measured every hour and remained constant throughout the data collection. Intensities of 2881 reflections were collected in an ω–2θ scan mode with $h = 0, \pm 6$; $k = 0, \pm 15$; $l = 0$, 12 up to $[(\sin\theta)/\lambda]_{max} = 0{\cdot}528$ Å^{-1} (133 unique reflections). Merging of equivalent data ($R = 0{\cdot}04$) left a set of 1431 data of which 400 reflections with $I < 3\sigma(I)$ were considered unobserved. Lorentz–polarization correction, no absorption correction. All calculations were performed using the *Enraf–Nonius Structure Determination Package* (B. A. Frenz & Associates, Inc., 1985) on a PDP 11/44 computer.

The structure was solved by direct methods using *MULTAN* 11/82 (Main *et al.*, 1982). An *E* map computed with the best set of phases (CFOM = 2·400) revealed the positions of all non-hydrogen atoms. In a difference Fourier map appeared the positions of all H atoms. Refinement by full-matrix least squares based on 181 parameters, all non-hydrogen atoms refined anisotropically and hydrogen atoms refined isotropically with the temperature factors fixed ($B_H = 1{\cdot}3B_C$). The function minimized was $\sum w\Delta F^2$ with individual weights $w = 1/\sigma^2(F)$. Final $R = 0{\cdot}035$, $wR = 0{\cdot}037$ and $S = 0{\cdot}86$; $(\Delta/\sigma)_{max} = 0{\cdot}19$ in final cycle; $\Delta\rho$ peak 0·23 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are given in Table 1 with the numbering scheme in Fig. 1.* Bond distances and angles are given in Table 2.

The structure of the norbornane part of the molecule may be viewed as a cyclohexane ring locked in a boat conformation by the bridging methylene group at C(8), but also as two interlocked five-membered rings. The carbon C(8) deviates 0·834 (4) and 0·849 (4) Å, respectively, from mean planes C(3)C(4)C(5)C(7) and C(1)C(6)C(5)C(7), thus constituting the common flap of the two envelopes.

A third five-membered heterocyclic ring appears in (III). It also assumes an envelope conformation with the carbon atom C(7) as flap, 0·699 (3) Å away from the C(1)SC(2)C(3) mean plane. As a result of cyclization, strain is induced in the norbornane framework and there is movement whereby the two rings twist in

* Lists of structure factors, anisotropic thermal parameters and positional parameters of hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51713 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²), *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}
S	0·4867 (2)	0·31327 (7)	0·49393 (8)	3·14 (2)
O(1)	0·6546 (5)	0·3339 (2)	0·5834 (2)	5·00 (7)
O(2)	0·2715 (4)	0·3329 (2)	0·5115 (2)	4·45 (6)
N	0·2315 (6)	0·0996 (3)	0·5586 (3)	5·07 (9)
C(1)	0·4961 (5)	0·1920 (3)	0·4540 (3)	2·70 (7)
C(2)	0·5398 (6)	0·3611 (3)	0·3585 (3)	3·17 (8)
C(3)	0·5817 (6)	0·2744 (3)	0·2914 (3)	2·94 (8)
C(4)	0·8108 (6)	0·2328 (3)	0·3115 (3)	3·94 (9)
C(5)	0·7770 (6)	0·1363 (3)	0·3559 (3)	3·65 (9)
C(6)	0·7233 (6)	0·1469 (3)	0·4755 (3)	3·56 (9)
C(7)	0·4438 (5)	0·1934 (3)	0·3235 (3)	2·80 (7)
C(8)	0·5628 (6)	0·1086 (3)	0·2898 (3)	3·73 (9)
C(9)	0·3436 (6)	0·1414 (3)	0·5124 (3)	3·33 (8)
C(10)	0·7269 (7)	0·4281 (3)	0·3803 (4)	5·1 (1)
C(11)	0·3399 (7)	0·4108 (3)	0·3032 (4)	4·9 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°), *with e.s.d.'s in parentheses*

S	O(1)	1·439 (3)	C(1)	C(7)	1·560 (4)	C(3)	C(7)	1·556 (5)
S	O(2)	1·448 (3)	C(1)	C(9)	1·477 (5)	C(4)	C(5)	1·532 (6)
S	C(1)	1·837 (4)	C(2)	C(3)	1·545 (5)	C(5)	C(6)	1·536 (5)
S	C(2)	1·850 (4)	C(2)	C(10)	1·536 (6)	C(5)	C(8)	1·534 (5)
N	C(9)	1·144 (5)	C(2)	C(11)	1·534 (6)	C(7)	C(8)	1·536 (5)
C(1)	C(6)	1·579 (6)	C(3)	C(4)	1·570 (5)			

O(1)	S	O(2)	118·0 (2)	C(3)	C(2)	C(11)	110·9 (3)
O(1)	S	C(1)	110·4 (2)	C(10)	C(2)	C(11)	110·7 (3)
O(1)	S	C(2)	111·8 (2)	C(2)	C(3)	C(4)	117·6 (3)
O(2)	S	C(1)	107·2 (2)	C(2)	C(3)	C(7)	110·2 (3)
O(2)	S	C(2)	110·5 (2)	C(4)	C(3)	C(7)	102·4 (3)
C(1)	S	C(2)	96·6 (2)	C(3)	C(4)	C(5)	103·6 (4)
S	C(1)	C(6)	114·9 (2)	C(4)	C(5)	C(6)	107·2 (3)
S	C(1)	C(7)	104·0 (2)	C(4)	C(5)	C(8)	102·7 (3)
S	C(1)	C(9)	107·9 (2)	C(6)	C(5)	C(8)	102·3 (4)
C(6)	C(1)	C(7)	103·3 (3)	C(1)	C(6)	C(5)	102·1 (3)
C(6)	C(1)	C(9)	111·5 (3)	C(1)	C(7)	C(3)	102·3 (3)
C(7)	C(1)	C(9)	115·2 (3)	C(1)	C(7)	C(8)	102·4 (3)
S	C(2)	C(3)	102·8 (2)	C(3)	C(7)	C(8)	103·1 (3)
S	C(2)	C(10)	108·9 (2)	C(5)	C(8)	C(7)	95·1 (3)
S	C(2)	C(11)	108·4 (3)	N	C(9)	C(1)	177·2 (4)
C(3)	C(2)	C(10)	114·9 (3)				

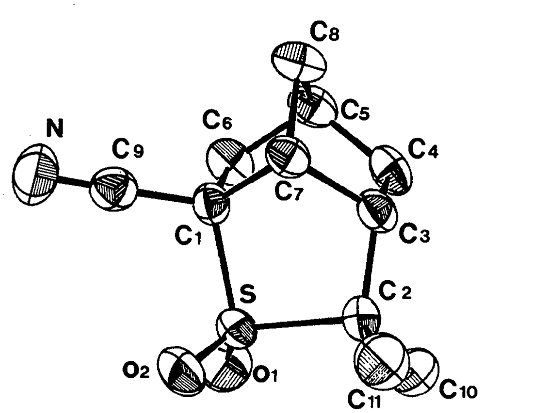

Fig. 1. Illustration of the molecular conformation. The thermal ellipsoids are drawn at the 50% probability level.

opposite directions when viewed along C(5)···C(7), so-called 'contra-twist', according to the values observed for the torsion angles in the six-membered ring defined by C(1), C(7), C(3), C(4), C(5) and C(6).

An interesting overall description of the title molecule can be based on the C(1)SC(2)C(3)C(4)C(5)C(6) seven-membered ring. Indeed the basic conformations of cycloheptane are the chair, twist-chair, boat and twist-boat (Hendrickson, 1961), with the twist-chair corresponding to the lowest-energy minimum (Bocian, Pickett, Rounds & Strauss, 1975).

The present seven-membered-ring conformation is similar to a distorted form of the C_s chair of cycloheptane. The twisting movement is hampered by the junction between C(1), C(3) and C(5) connected *via* the C(7)H—C(8)H_2 group. For this ring the deformation of the chair is a result of this bridging situation with substitution at the three axial positions C(1), C(3) and C(5). The oxygen atoms O(1) and O(2) are eclipsed by C(10) and C(11) when viewed along the S—C(2) bond. Finally, in this description, whereas O(1) and C(10) occupy axial positions, the cyano group, O(2) and C(11) are equatorial.

Conformational calculations have shown that the rotational barrier around the C(1)—S bond is relatively low for compound (I) (25 kJ mol^{-1}). The minimum distance of 2·70 Å, between the reactive site C(2) and C(3) in (III), is at a rotation angle of 80° about this *endo* C—S bond, with regard to the X-ray determination. Cyclization induces rotation about the σ C—S bond and a lessening of C(7)—C(1)—S and C(1)—S—C(2) angles from 117·5 and 108·5° in (I), respectively, to 104·0 and 96·6° in (III). Other structural differences between (I) and (III) are very slight, except for the lengthening of the C(3)—C(4) bond from 1·33 (1) to 1·570 (5) Å.

Intermolecular distances do not indicate any interactions except van der Waals forces.

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Platelet Activating Factor Antagonist Design. 2. X-ray Structure of Dimethyl 2,3,4,5-Tetrahydro-5β-(3,4-methylenedioxyphenyl)-2-oxo-3β-(3,4,5-trimethoxybenzoyl)-3α,4α-furandicarboxylate

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(*Received* 28 *September* 1988; *accepted* 8 *November* 1988)

Abstract. $C_{25}H_{24}O_{12}$, $M_r = 516·46$, triclinic, $P\bar{1}$, $a = 8·780 (3)$, $b = 11·298 (4)$, $c = 13·271 (6)$ Å, $\alpha = 71·77 (4)$, $\beta = 70·31 (3)$, $\gamma = 72·66 (3)°$, $V = 1189$ Å^3, $Z = 2$, $D_x = 1·44$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·74$ cm^{-1}, $F(000) = 540$, $T = 293$ K, final $R = 0·046$ for 2495 observed [$F_o \geq 5\sigma(F_o)$] reflections. The observed structure reveals a *trans* disposition for the methoxycarbonyl and aryl substituents at positions 4 and 5 of the heterocycle and a *cis*-3,4-bis(methoxycarbonyl) relationship. There is no crystallographically

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