Fig. 2. Space-filling molecular model in different orientations (a) and (b), drawn with *PLUTO* (Motherwell & Clegg, 1978). C shaded, O spark, H other.

that the cone cavity is too shallow to include an organic solvent molecule such as xylene. This shallow cavity is shown from the upper and side directions in Fig. 2.

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Structure of 6,6-Dimethyl-1-phenyl-7-thiatricyclo[3.2.1.1³,⁸]nonane 7,7-Dioxide

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Abstract. $C_{16}H_{20}O_2S$, $M_r = 276.4$, orthorhombic, $P2_12_12_1$, $a = 6.175$ (2), $b = 11.102$ (2), $c = 19.862$ (3) Å, $V = 1362$ (6) Å^3, $Z = 4$, $D_x = 1.348$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.2$ cm^{-1}, $F(000) = 592$, $T = 296$ K, $R = 0.066$ for 972 observed diffractometer data. The three five-membered rings adopt an envelope conformation with a 5-*exo*-phenyl substituent and a 5-*endo*-isopropylsulfonyl group, with reference to the norbornane moiety. The structure of the title compound is compared with that of its cyano analogue and with that of its precursor connected to an efficient radical clock.

Introduction. Aiming to check for the presence of elusive radicals during organic reactions, free-radical clocks of ever increasing efficiency have been designed and synthesized (Surzur, 1982). A new kind of radical clock based on the 5-*exo*-substituted-5-*endo*-isopropylsulfonyl-2-norbornene structure (Fig. 1) has recently been described and the X-ray structures of (1*a*) and (1*b*) (Vacher, Samat, Allouche, Laknifli, Baldy & Chanon, 1988) were undertaken in order to explain the enhancement for the cyclization rate of the α-sulfonyl-C-centred intermediate radical (2*b*) as compared to (2*a*).

The intramolecular addition at the double bond led to a new type of tricyclo[3.2.1.1³,⁸]nonane which includes an intracyclic sulfonyl group. In connection with the structure of (3*a*), which has already been reported (Estienne, Baldy, Samat & Vacher, 1989), we decided to undertake an X-ray analysis of (3*b*).

Experimental. White hollowed crystals were obtained by recrystallization of (3*b*) in ethanol. A suitable fragment was cut into a crystalline block (0.30 × 0.30 × 0.40 mm) and was used for the data collection. Enraf–Nonius CAD-4 diffractometer. Cell constants by least-squares refinement using the setting angles for 25 reflections in the range $12.4 < \theta < 17.8°$. Three standard reflections ($3\overline{5}2$, 4,3,10, $\overline{4}27$) were measured every hour with no intensity variation. Intensities of 1018 reflections collected in an ω–2θ-scan mode for h = 0, 6; $k = 0$, 11; $l = 0$, 20 up to $[(\sin\theta)/\lambda]_{max} =$ 0.526 Å^{-1}. Lorentz–polarization correction, no absorption correction. All calculations performed using the Enraf–Nonius *Structure Determination Package* (B. A. Frenz & Associates Inc., 1985) on a MicroVAX station 2000. Direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). An E map computed with the best set of phases revealed the positions of all the non-H atoms. The H atoms were introduced in structure-factor calculations by their computed coordinates (C—H = 0.95 Å) and isotropic temperature factors [$B(H) = 1.3B_{eq}(C)$ Å^2]. The function minimized by full-matrix least squares based on 172 parameters was $\sum w\Delta F^2$ using

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) 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	0.6827 (4)	0.9308 (2)	0.4117 (1)	2.58 (4)
O(1)	0.451 (1)	0.9290 (6)	0.4077 (4)	4.5 (2)
O(2)	0.777 (1)	0.9621 (6)	0.4756 (3)	3.6 (1)
C(1)	0.798 (2)	1.0290 (7)	0.3464 (4)	2.4 (2)
C(2)	0.794 (2)	0.7874 (8)	0.3810 (4)	2.6 (2)
C(3)	0.904 (2)	0.8232 (8)	0.3138 (4)	2.8 (2)
C(4)	0.754 (2)	0.8299 (9)	0.2514 (5)	4.0 (2)
C(5)	0.767 (2)	0.9637 (9)	0.2301 (4)	3.8 (2)
C(6)	0.644 (2)	1.0368 (9)	0.2832 (5)	3.3 (2)
C(7)	0.992 (1)	0.9569 (8)	0.3204 (4)	2.6 (2)
C(8)	1.005 (2)	0.9938 (9)	0.2458 (5)	3.8 (2)
C(9)	0.837 (2)	1.1525 (8)	0.3785 (4)	2.9 (2)
C(10)	0.614 (2)	0.6927 (9)	0.3757 (6)	4.4 (3)
C(11)	0.974 (2)	0.7475 (9)	0.4316 (5)	4.1 (2)
C(12)	0.669 (2)	1.2352 (8)	0.3800 (5)	3.0 (2)
C(13)	0.699 (2)	1.3485 (8)	0.4120 (5)	4.3 (2)
C(14)	0.907 (2)	1.3755 (9)	0.4397 (5)	3.8 (2)
C(15)	1.068 (2)	1.2919 (9)	0.4378 (5)	3.4 (2)
C(16)	1.035 (2)	1.1792 (9)	0.4093 (5)	3.2 (2)

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

|			
S—O(1)	1.431 (7)	C(2)—C(10)	1.54 (1)
S—O(2)	1.439 (6)	C(2)—C(11)	1.56 (1)
S—C(1)	1.837 (9)	C(3)—C(4)	1.54 (1)
S—C(2)	1.839 (9)	C(3)—C(7)	1.59 (1)
C(1)—C(6)	1.58 (1)	C(4)—C(5)	1.55 (1)
C(1)—C(7)	1.53 (1)	C(5)—C(6)	1.53 (1)
C(1)—C(9)	1.53 (1)	C(5)—C(8)	1.54 (2)
C(2)—C(3)	1.55 (1)	C(7)—C(8)	1.54 (1)
C(9)—C(12)	1.39 (1)	C(13)—C(14)	1.43 (2)
C(9)—C(16)	1.40 (1)	C(14)—C(15)	1.36 (2)
C(12)—C(13)	1.42 (1)	C(15)—C(16)	1.39 (1)
O(1)—S—O(2)	117.0 (4)	C(2)—C(3)—C(7)	108.5 (7)
O(1)—S—C(1)	110.8 (4)	C(4)—C(3)—C(7)	103.0 (7)
O(1)—S—C(2)	110.1 (4)	C(3)—C(4)—C(5)	103.6 (8)
O(2)—S—C(1)	108.9 (4)	C(4)—C(5)—C(6)	107.2 (8)
O(2)—S—C(2)	110.4 (4)	C(6)—C(5)—C(8)	102.5 (8)
C(1)—S—C(2)	97.8 (4)	C(4)—C(5)—C(8)	101.7 (8)
S—C(1)—C(6)	111.3 (6)	C(1)—C(6)—C(5)	102.9 (8)
S—C(1)—C(7)	103.3 (5)	C(1)—C(7)—C(3)	104.3 (7)
S—C(1)—C(9)	107.4 (6)	C(1)—C(7)—C(8)	103.0 (7)
C(6)—C(1)—C(7)	103.3 (7)	C(3)—C(7)—C(8)	100.7 (7)
C(6)—C(1)—C(9)	112.1 (7)	C(5)—C(8)—C(7)	95.1 (8)
C(7)—C(1)—C(9)	119.0 (8)	C(1)—C(9)—C(12)	119.1 (9)
S—C(2)—C(3)	103.1 (6)	C(10)—C(9)—C(16)	120.6 (8)
S—C(2)—C(10)	107.3 (6)	C(12)—C(9)—C(16)	120.3 (8)
S—C(2)—C(11)	110.0 (7)	C(9)—C(12)—C(13)	119.8 (9)
C(3)—C(2)—C(10)	108.7 (8)	C(12)—C(13)—C(14)	118.5 (9)
C(3)—C(2)—C(11)	115.6 (8)	C(13)—C(14)—C(15)	120.1 (9)
C(10)—C(2)—C(11)	111.5 (8)	C(14)—C(15)—C(16)	121.5 (9)
C(2)—C(3)—C(4)	116.4 (8)	C(9)—C(16)—C(15)	119.6 (9)
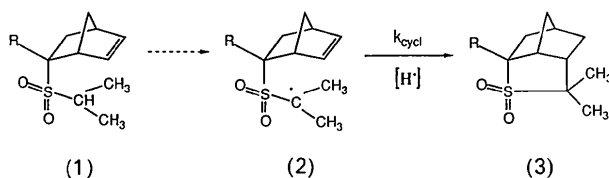
Fig. 1. Reaction scheme: from 2-norbornene radical-clock precursors to their tricyclononane derivatives.
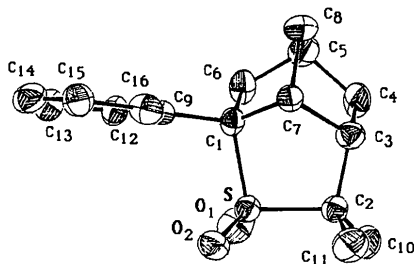
(*a*) R = CN, (*b*) R = C₆H₅

Fig. 2. Illustration of the molecular conformation. The thermal ellipsoids are drawn at the 50% probability level.

individual weights $w = 1/\sigma^2(F)$ for 972 observations with $I > 3\sigma(I)$. Final $R = 0.066$, $wR = 0.079$ and $S = 1.72$; $(\Delta/\sigma)_{max} = 0.01$ in final cycle; $\Delta\rho$ peak 0.48 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Comparing x, y, z and $-x$, $-y$, $-z$ refinements did not allow the absolute configuration to be fixed.

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

For (3a) the racemic solution gives a racemic compound in which the two enantiomers are present in equal quantities, but for the title compound (3b) we observe a crystallization in one of the most representative space groups devoid of inverse symmetry elements. The selection during the crystallization of identical conformations ending in a conglomerate, equivalent to a spontaneous resolution, is connected with the presence of phenyl groups involved in π–π interactions.

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), or as two interlocked five-membered rings. C(8) deviates 0.86 (1) and 0.84 (1) Å from the mean planes C(3)–C(4)–C(5)–C(7) and C(1)–C(6)–C(5)–C(7) respectively, thus constituting the common flap of the two envelopes. The corresponding distances in (3a), 0.834 (4) and 0.849 (4) Å, are not significantly different. A third five-membered heterocyclic ring also assumes an envelope conformation with C(7) as the flap 0.68 (1) Å away from the C(1)–S–C(2)–C(3) mean plane, compared to a distance of 0.699 (3) Å found in (3a). The mean lengthening of the C(3)—C(4) bond [0.13 (1) Å] and the mean reduction of the valence angle at C(3) and C(4), 5.6 (4)°, illustrate the major structural changes involved in the conversion of the norbornene moiety in (1a) and (1b) into a norbornane in (3a) and (3b).

The C(1)–S–C(2)–C(3)–C(4)–C(5)–C(6) seven-membered ring is similar to the basic chair conformation of cycloheptane with C_s symmetry, where the axial positions are occupied by O(1) and C(10) and the equatorial positions have the phenyl group, O(2) and C(11). The new bridging situation induces O(1) and O(2) to be eclipsed by C(10) and C(11) when viewed along the C(2)—S bond. In contrast, a naturally staggered conformation, as expected, is observed for these atoms in (1a) and (1b).

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* Lists of structure factors, anisotropic thermal parameters and positional parameters for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54526 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Replacement of the cyano group in (1a) by a phenyl in (1b) affects primarily the C(7)—C(1)—S bond angle and its reduction of about 9° is counterbalanced by the observed increase of all the bond angles at C(1) but mainly C(6)—C(1)—C(9). Consequently, upon cyclization the two structures (3a) and (3b) compare more closely than (1a) and (1b) and the only bond angle sensitive to the substitution is C(7)—C(1)—C(9), which is 4° greater in (3b) compared to (3a). Moreover the substitution of the cyano group induces a conformational change and so the isopropylsulfonyl group is placed in a favourable conformation for undergoing cyclization in (1a) but not in (1b), apparently in contradiction to the enhancement of the intramolecular radical cyclization in (2b) versus (2a). In fact, as shown by a conformational analysis with the means of a force-field calculation program (Pépe, Siri, Samat, Baldy & Estienne, 1991), the dihedral angles C(3)—C(1)—S—C(2) are 99 and 101° for (2a) and (2b) respectively [78 for (1a) and 166° for (1b)], and there is no privileged conformation induced by the phenyl group that is favourable for an intramolecular reaction. The acceleration of the addition in (2b) is due to the smaller distance between the reactive sites induced by the closing of the C(7)—C(1)—S angle when the 5-exo group is a phenyl substituent, as already observed in the parent compound (1b).

No intermolecular distances were below the sum of the van der Waals radii and so no particular effects due to packing forces need to be discussed.

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