DEFORMATION OF THE ADAMANTANE SKELETON BY SUBSTITUTION: CRYSTAL STRUCTURE OF 1-METHYLSULFONYLADAMANTANE

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The crystals of 1-methylsulfonyladamantane are monoclinic, space group $P2_1/a$, with a = 11.094(3), b = 7.668(2), c = 13.161(3) Å, β = 101.74(2)^0 , V = 1 096.1(5) Å^3, Z = 4, D_x = 1.29 g cm^{-3}, MoK$_\alpha$, λ = 0.71069 Å, μ = 2.65 cm^{-1}, $F(000)$ = 456, T = 291 K, the final R value is 0.036 for 1 834 observed reflections. For this compound and from literature data, the bond angles of adamantane derivatives are briefly discussed: the angle on the substituted C(1) atom depends clearly on the substituent but the available figures are still rather imprecise.

Dependence of bond angles on substitution was systematically studied on benzene derivatives[1,2]. In the alicyclic series, the derivatives of adamantane would be a convenient model but X-ray analysis of simple compounds has bee difficult due to disorder phenomena and phase transitions[3]. More promising are derivatives with strongly polar substituents[4,5]. In this note we report the structure of 1-methylsulfonyladamantane while our attempts to prepare well diffracting crystals of 1-adamantanecarboxylic acid, 1-nitroadamantane, 1-adamantanethiol and 1-phenyladamantane have failed. With reference to other reported structures[4 - 15], some evidence can be gained concerning the substituent effects on bond angles.

EXPERIMENTAL

Crystals of methylsulfonyladamantane[16], m.p. 104 °C, were obtained by evaporation from methanol. D_m was not measured. A parallelepiped crystal with dimensions 0.42 x 0.38 x 0.22 mm was selected. The unit cell parameters and their standard deviations were obtained by a least-squares best fit to the setting angles of 15 reflections in the range 5° ≤ 2θ ≤ 30° . 2 153 h k ± l independent reflections with sinθ/λ ≤ 0.62 Å^{-1} were collected on a Syntex P2$_1$ diffractometer using the scan mode and graphite monochromatized MoK$_\alpha$ radiation. Only 1 834 independent reflections with I ≥ 2.5 $\sigma(I)$ were conserved for the refinement of the structure. A standard reflection (5 −3 −4) was checked every 50 reflections, no significant deviation was observed.

The structure was solved by direct methods using[17] SHELXS 86 and refined by anisotropic least-squares on F values[18].

All hydrogen atoms were located from a difference Fourier synthesis. They were refined with an isotropic common temperature factor. Weighting: $w = 1/(\sigma^2 + 0.00009\,F^2)$. The final R indices are: $R = 0.036$, $R_W = 0.040$ for 1 834 observed reflections. Final maximum shift to error = 0.11 . $S = 2.56$. Maximum and minimum heights in the final difference Fourier synthesis = 0.26 and −0.22 e Å^{-3}. Atomic scaterring factors from International Tables[19].

The atomic parameters are given in Table I, bond distances and angles in Tables II and III. Further data are deposited at the Cambridge Structural Database. Figure 1 is a view showing the numbering of the atoms, Fig. 2 shows the packing in the unit cell.

DISCUSSION

According to the experience from benzene derivatives[1], the greatest and most regular substituent effects are expected on the angles at C(1). With unsymmetrical substituents even the symmetry of the adamantane skeleton is distorted and the three angless C(*j*)–C(1)–X = α_i are unequal. Therefore, we define the deformation parameter Δ as a mean value either from the angles α_i or from the intraskeletal angles β_i = C(*j*)–C(1)–C(*k*).

$$\Delta = -\sum_{i=1}^{3} \alpha_i/3 + 109.47 = \sum_{i=1}^{3} \beta_i/3 - 109.47$$

TABLE I
Atomic coordinates (. 10^4) and equivalent temperature factors (Å^2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}[a]
C(1)	2043(1)	3377(2)	7138(1)	2.49(2)
C(2)	2810(2)	4818(3)	6787(2)	4.06(4)
C(3)	3150(3)	6149(3)	7674(2)	5.56(5)
C(4)	1975(3)	6890(3)	7953(2)	6.23(5)
C(5)	1229(2)	5432(3)	8301(2)	4.95(4)
C(6)	1997(3)	4533(3)	9246(2)	5.02(4)
C(7)	3154(2)	3791(3)	8970(1)	4.08(3)
C(8)	2788(2)	2450(3)	8099(1)	3.33(3)
C(9)	3921(2)	5220(3)	8621(2)	5.28(5)
C(10)	873(2)	4122(3)	7412(2)	3.87(4)
S(11)	1664(0)	1716(1)	6149(0)	3.08(1)
O(12)	906(1)	435(2)	6514(1)	4.68(3)
O(13)	2790(1)	1126(2)	5883(1)	5.17(3)
C(14)	764(2)	2715(3)	5044(2)	3.94(4)

[a] $B_{eq} = (8/3)\pi^2 \sum_i \sum_j U_{ij}\, a_i^* a_j^* a_i a_j$.

For compound 1-methylsulfonyladamantane, Δ = 0.4 compared to 1.6 for methylsulfonylbenzene[1]. We have calculated several further values of Δ from the literature data, however, the simplest substituents, like those investigated in the benzene series[1], are not at disposal.

TABLE II
Bond distances (Å)

Bond	Distance	Bond	Distance
C2–C1	1.522(2)	C8–C1	1.537(2)
C10–C1	1.527(2)	S11–C1	1.809(2)
C3–C2	1.540(3)	C4–C3	1.533(4)
C9–C3	1.535(3)	C5–C4	1.516(4)
C6–C5	1.522(3)	C10–C5	1.531(3)
C7–C6	1.514(3)	C8–C7	1.532(3)
C9–C7	1.515(3)	O12–S11	1.438(1)
O13–S11	1.437(1)	C14–S11	1.763(2)

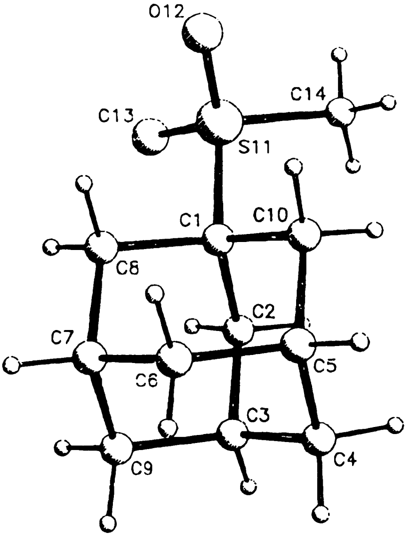


FIG. 1
View of the molecule of 1-methylsulfonyladamantane showing the atom numbering[20]

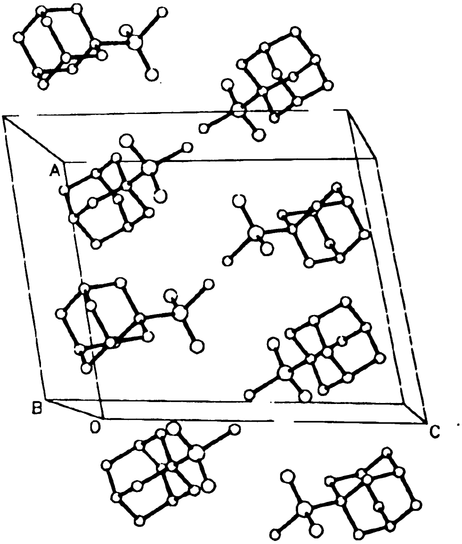
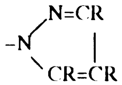


FIG. 2
Stereoscopic view of the packing in the unitcell[20]

TABLE III
Bond angles (in °)

Bond angle		Bond angle	
C8–C1–C2	110.2(1)	C10–C1–C2	110.7(2)
C10–C1–C8	108.6(1)	S11–C1–C2	110.8(1)
S11–C1–C8	105.9(1)	S11–C1–C10	110.4(1)
C3–C2–C1	108.5(2)	C4–C3–C2	109.8(2)
C9–C3–C2	108.5(2)	C9–C3–C4	109.8(2)
C5–C4–C3	110.0(2)	C6–C5–C4	109.3(2)
C10–C5–C4	109.0(2)	C10–C5–C6	110.0(2)
C7–C6–C5	109.6(2)	C8–C7–C6	108.9(2)
C9–C7–C6	110.9(2)	C9–C7–C8	109.7(2)
C7–C8–C1	108.7(1)	C7–C9–C3	109.1(2)
C5–C10–C1	109.1(2)	O12–S11–C1	107.9(1)
O13–S11–C1	108.1(1)	O13–S11–O12	117.6(1)
C14–S11–C1	107.3(1)	C14–S11–O12	107.5(1)
C14–S11–O13	108.1(1)		

TABLE IV
Angular substituent parameters (°) for adamantane 1-derivatives compared with similar derivatives of benzene

X	1-X-$C_{10}H_{15}$	X-C_6H_5 (ref.[1])	X
$-CH(C_2H_5)NHCOCH_3$	−1.9 (ref.[10])	−1.9	$-CH_3$
$-CCl=CHCHO$	−1.0 (ref.[11])	−1.8	$-CH=CHR$
$-CON(CH_3)_2$	−1.3 (ref.[12])	−0.6	$-COOR$
	−0.9[a] (refs[8,9])	−0.1	$-N=NC_6H_5$
$-COOH$	−0.1 (ref.[13])	0.1	$-COOH$
$-H$	+0.3 (ref.[14])	0	$-H$
$-OH$	−0.2 (ref.[6])	+0.2	$-OH$
$-OCONHC(CH_3)_2COOH$	+1.2 (ref.[7])	+1.5	$-OCOCH_3$
$-SO_2CH_3$	+0.4 (this work)	+1.6	$-SO_2CH_3$
$-NH_3^+$	+1.1[b] (refs[4,5])	+1.8	$-NH_3^+$
$-NH=C(NH_2)NHC_6H_4I\text{-}2$	+0.2 (ref.[15])		

[a] Mean from three differently methylated pyrazole derivatives. [b] Mean from two salts with different counterions.

In Table IV, the available values are compared with those pertinent to similar substituents on benzene[1]. Since the angle deformation depends mainly on the first atom of the substituent, some similarity is observed between the two series. The agreement appears to be merely qualitative but is not so bad considering that the two groups compared are sometimes rather different. It is evident that the bond angles in adamantane derivatives depend on substitution in a similar way as in the derivatives of benzene, although the sensitivity might be smaller in a more rigid system. First of all the accuracy of the presently available values is lower for adamantane than for benzene derivatives, so that an exact comparison is not yet possible.

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