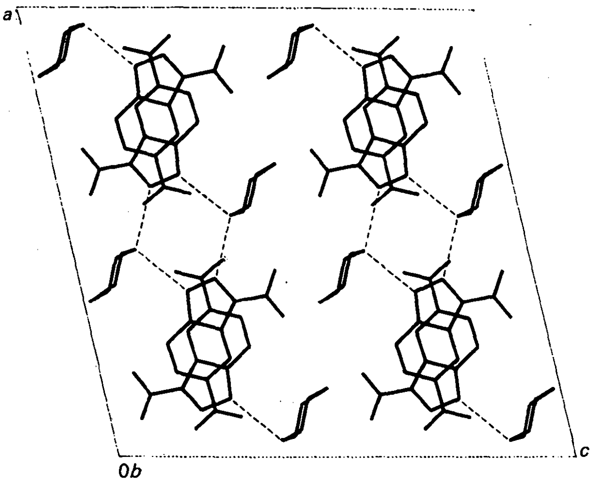

Fig. 3. Projection of the crystal structure along the *b* axis.

0·012 (3) Å. The thiomorpholinium cation has a chair conformation. The least-squares plane through it makes a dihedral angle of 91·3 (1)° with the plane of the indazole system.

The bond lengths and angles for the nitrobenzene part of 3,5-dinitroindazole (Table 2) are comparable with those found in (I), (II) and (III). The nitro group at C(5) lies in the plane of the indazole system. The plane of the —NO_2 group attached to the C(3) atom is inclined by 3·1 (1)° to the plane of the indazole system.

The negative charge of the N(1) atom of the pyrazole ring is presumably delocalized mainly through the bonds N(1)—N(2) [1·354 (3) Å] and N(2)—C(3) [1·339 (4) Å] for conjugation with the nitro group. The same bonds in (I) (molecule *B*), are 1·345 (3) and 1·321 (4) Å, respectively. Owing to the conjugation, the exocyclic bond C(3)—N(10) [1·417 (4) Å] is shorter than that [1·441 (4) Å] found in (I).

In the crystal lattice (Fig. 3), 3,5-dinitroindazole molecules are parallel and partly overlap, forming layers nearly perpendicular to **z**. However, there is no strong interaction between layers, the separation being *ca* 3·7 Å.

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Structures of Trimethylsulfonium Salts. I. Refinement of the Structure of the Iodide $(CH_3)_3SI$

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Abstract. Trimethylsulfonium iodide, $C_3H_9S^+.I^-$, $M_r = 204{\cdot}07$, monoclinic, $P2_1/m$, $a = 7{\cdot}201$ (2), $b = 7{\cdot}998$ (2), $c = 5{\cdot}930$ (2) Å, $\beta = 94{\cdot}87$ (5)°, $V = 340$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}991$, $D_m = 1{\cdot}98$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 4{\cdot}821$ mm^{-1}, $F(000) = 192$, $T = 293$ K, final $R = 0{\cdot}022$, $wR = 0{\cdot}025$ for 993 independent observed reflections. The structure consists of stacks of I^-

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters for* $(CH_3)_3SI$ *with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
I	0·74053 (4)	0·250	0·62678 (5)	3·726 (5)
S	0·3313 (2)	0·250	0·0263 (2)	3·72 (2)
C(11)	0·1424 (8)	0·250	0·2079 (8)	5·4 (1)
C(12)	0·2682 (5)	0·4232 (4)	−0·1539 (5)	4·16 (6)
C(12*)	0·2682 (5)	0·0768 (4)	−0·1539 (5)	4·16 (6)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $(CH_3)_3SI$

Trimethylsulfonium ion

S—C(1)	1·805 (6)	C(1)—S—C(2)	101·1 (2)
S—C(2)	1·785 (3)	C(2)—S—C(2)	101·8 (1)

Iodide coordination

I—S	4·690 (1)	4·547 (1)	4·426 (2)	3·935 (1)
I—C(1)	4·786 (5)	4·309 (6)	4·181 (1)	3·971 (6)
I—C(2)	4·148 (3)	4·080 (3)	3·992 (3)	3·831 (3)

anions and pyramidal $(CH_3)_3S^+$ cations, which have approximate 3*m* symmetry. The results agree fairly well with previous data.

Introduction. The cell parameters of the title compound have been given by Mussgnug (1941). The structure was first solved by Zuccaro & McCullough (1959), with poor accuracy; the C-atom thermal parameters were not refined and the H atoms were not located. We have begun a structural study of some trimethylsulfonium salts with the refinement of the iodide.

Experimental. Crystals obtained by recrystallization of the commercial product (Aldrich) in water. Prismatic colorless crystal; density measured by pycnometry in xylene.

Crystal size 0·17 × 0·19 × 0·22 mm. Enraf–Nonius CAD-4 diffractometer; graphite monochromator. Unit-cell parameters from least-squares refinement of 25 reflections with $5 < \theta < 13°$; systematic absences: $0k0$ ($k = 2n$); space group $P2_1/m$ (No. 11) or $P2_1$ (No. 4).

$\omega/2\theta$ scan, scan width 1·2°; $1 < \theta < 30°$. $-4 < h < 8$, $-11 < k < 11$, $-10 < l < 10$, four orientation reference reflections (207, 520, 064, 303) every 200 scans: no significant variation; same intensity reference reflections recorded every 2 h, fading of 10·7% during 50·0 h; decay correction. 2662 measured reflections, 2527 reflections with $I > 3\sigma(I)$. Lorentz and polarization corrections; absorption corrections from ψ scans: relative transmission factor between 0·878 and 0·999. 993 reflections after averaging, $R_{int} = 0·014$.

Crystal structure solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) in space group $P2_1/m$. H atoms located by difference Fourier synthesis. Anisotropic least-squares full-matrix refinement (on F) for non-H atoms; isotropic for H atoms; extinction coefficient refined: $g = 3·2181 \times 10^{-6}$ (Stout & Jensen, 1968). 48 variables. Final refinement with 993 reflections; final $R = 0·022$ ($wR = 0·025$). Unit weights. Maximum and minimum peak heights in final Fourier synthesis: 0·723 and −0·472 e Å^{-3}. $S = 0·475$. $(\Delta/\sigma)_{max} = 0·29$. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius *SDP* (Enraf–Nonius, 1979) used for all calculations; computer used: VAX 730.

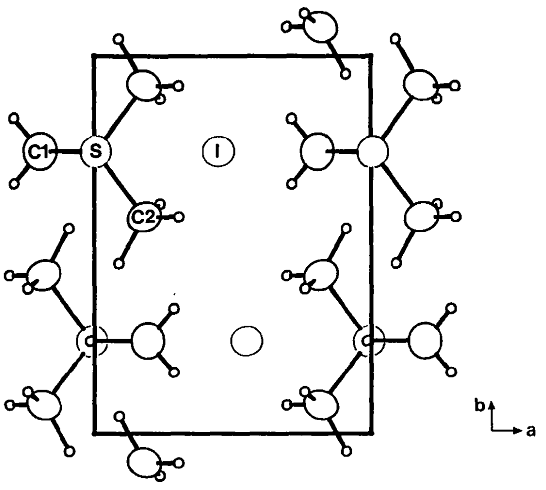

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(CH_3)_3SI$.

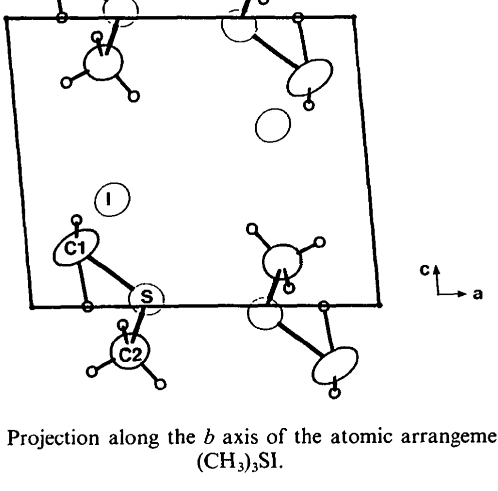

Fig. 2. Projection along the *b* axis of the atomic arrangement of $(CH_3)_3SI$.

Discussion. The final atomic coordinates are reported in Table 1. Our results agree fairly well with the previous work.* The main bond distances and angles are listed in Table 2. The clearly defined thiocation is pyramidal, suggesting sp^3 hybridization of the sulfur. Although containing only one symmetry plane (for $y = 0{\cdot}25$ or $0{\cdot}75$), in which are located I, S and C(1) atoms, the thiocation approximates very well to the $3m$ symmetry assigned to the free ion: the C—S—C bond angles are equal, 101·4° (4), and the bond distances differ by very little, 1·785 and 1·805 Å. The structure (shown in Figs. 1 and 2) may be approximately described as a distorted NaCl structure, each ion being surrounded by six of the opposite charge (Zuccaro & McCullough, 1959).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53395 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (±)-(2*S*,1′*S*)-2-[Hydroxy(phenyl)methyl]-2-methylcyclohexanone, $C_{14}H_{18}O_2$

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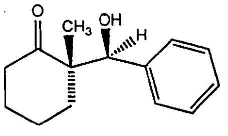
Abstract. $M_r = 281{\cdot}30$, monoclinic, $P2_1/n$, $a = 10{\cdot}966\,(4)$, $b = 7{\cdot}170\,(3)$, $c = 15{\cdot}976\,(4)$ Å, $\beta = 93{\cdot}14\,(2)°$, $V = 1254{\cdot}3\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}16$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}706$ cm^{-1}, $F(000) = 472$, $T = 295$ K, final $R = 0{\cdot}057$ for 1212 unique observed reflections. The compound was prepared by reaction of the trichlorotitanium-$\Delta^{1(2)}$-enolate of 2-methylcyclohexanone with benzaldehyde.

Introduction. The stereochemistry of the major aldol isomer formed in the reaction of the trichlorotitanium-$\Delta^{1(2)}$-enolate of 2-methylcyclohexanone and benzaldehyde is depicted below. This compound has played a pivotal role in the recent re-evaluation of the boat transition state of aldol reactions in general (Nakamura & Kuwajima, 1983; Hoffmann, Ditrich & Froch, 1985). The nature of (I) does not permit the application of ^{1}H NMR spectroscopy (Heathcock, 1983) for the determination of its relative stereochemistry since it is fully substituted at the α-carbon. Hence, the proton on C(8) does not provide any stereochemical information although it is noted that in the NMR spectrum, taken in CCl_4, the C(8) proton signal appears at a higher field than that of the diastereomeric adduct.



(I)

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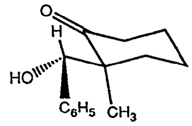

(II)

A crystal structure analysis of (I), prepared according to the procedure of Nakamura & Kuwajima (1983), was undertaken to determine unambiguously all aspects of the stereochemistry of this compound.

Experimental. Clear, colorless crystal of the aldol, (I), 0·25 × 0·27 × 0·30 mm, m.p. 337·5–339 K, aligned on Nicolet *R*3*m*/*E* diffractometer with an Mo target, normal focus tube, graphite monochromator

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