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THE CRYSTAL AND MOLECULAR STRUCTURE OF 10,10-DIMETHYL-10-GERMA-9-THIO-9,10-DIHYDROANTHRACENE

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Summary

The X-ray analysis of 10,10-dimethyl-10-germa-9-thio-9,10-dihydroantracene has been carried out. The crystals are orthorhombic: a 11.130(3), b 7.556(2), c 30.795(5) Å; $Z = 4$; space group *Pbca*. The structure was solved by a combination of Patterson and Fourier methods and refined to $R = 0.047$ ($R_w = 0.050$, $w = 1/\sigma^2(F_0)$). The molecule is not planar and the dihedral angle formed by the two benzene rings is 143.6°. The central ring has the boat conformation. The ^{13}C NMR chemical shifts associated with benzene carbon atoms correlate well with bond angles obtained by X-ray methods.

Introduction

Attempts to correlate the changes in the geometry of compounds having an anthracene-like skeleton and containing heteroatoms in positions 9 and 10 with chemical and spectroscopic behaviour require a detailed knowledge of the structural parameters.

The oxidation rates, the ^{13}C NMR and photoelectron (He(I)) spectra of a series of this type of compounds having as one of the two heteroatoms an element of the IVB group were recently studied [1]. These data suggest that the sulphur lone pair and the external benzene rings are involved in some conjugative interactions which decrease on going towards the Sn derivatives and that this effect is related to the changes in the geometry of the non-benzenoid ring. In order to contribute to knowledge about the influence of a conjugation chain along the central ring on the structural parameters the X-ray structure analysis of 10,10-dimethyl-10-germa-9-thio-9,10-dihydroanthracene was undertaken.

Experimental

Collection and reduction of X-Ray data

A prismatic colourless crystal, recrystallized from ethanol, and bounded by

TABLE 1

CRYSTAL DATA FOR $C_{14}H_{14}GeS$

a 11.130(3) Å	Orthorhombic	D_c 1.36 gcm^{-3}
b 7.556(2) Å	Space group $Pbca$	$Z = 4$
c 30.795(5) Å	Mo-K_α radiation	$W = 286.9$
V 2589.8 Å^3	μ 24.1 cm^{-1}	

the forms {100}, {001}, {103}, {110} was used for data collection. The volume of the crystal was 0.020 mm^3. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least-squares fit to 13 $(\vartheta, \chi, \varphi)_{hkl}$ carefully measured on a Siemens AED single crystal diffractometer. Cell dimensions and crystal data are given in Table 1. A total of 6324 $(\pm h, k, l)$ reflections were measured at room temperature using the $\omega - 2\vartheta$ scanning technique and Zr-filtered Mo-K_α radiation. Data were corrected for absorption effects and the subsequent merging of equivalent reflections gave a total of 1771 reflections with $I > 2\sigma(I)$ ($\sigma(I)$ from counting statistics) which were used for the structure analysis.

Structure determination and refinement

The structure was solved by a combination of Patterson and Fourier methods, from which all the non hydrogen atoms were located. After a few cycles of anisotropic full-matrix least-squares, $R = 0.065$, a difference synthesis revealed all the hydrogen atoms. Further cycles of refinement including the hydrogens with isotropic thermal parameters lowered the R factor to 0.047 and R_w to 0.049 ($w = 1/\sigma^2(F_0)$). The scattering factors used throughout the analysis were those reported in the International Tables [2]. A list of observed and calculated structure factor amplitudes is available from the authors on request.

The atomic coordinates and thermal parameters with their e.s.d.s are given in Table 2.

All the calculations were carried out on the CYBER 76 computer of the Centro di Calcolo InterUniversitario dell'Italia NordOrientale, Casalecchio (Bologna) using the SHELX system of programs [3] and with financial support from the University of Parma.

Results and discussion

A drawing of the molecule with the arbitrary numbering schem used in the analysis is shown in Fig. 1. Bond distances and angles are given in Table 3 and Tables 4 and 5 present some mean planes of the molecule.

While a planar conformation is best for conjugation, in this case the molecule is not planar but shows a "butterfly" conformation bent along the Ge...S direction with an angle of 143.6°. Similar deviations from planarity were previously found in 9,9,10,10-tetramethyl-9,10-disiladihydroanthracene (155.5°) [4], in 9,10-dihydroanthracene (145°) [5], in 9-t-butyl-9,10-dihydroanthracene (146.6°) [6], in *cis*-9-methyl-thioxanthene 10-oxide (127.2°) [7], and in *trans*-thioxanten-9-ol-10-oxide (132.4°) [8]. In all these compounds the $p(\pi)$—$d(\pi)$ interactions were found to be insignificant or completely absent.

TABLE 2

FRACTIONAL COORDINATES AND THERMAL PARAMETERS

Fractional coordinates (X 10^4) and thermal parameters (in 10^{-4} Å^2) with standard deviations in parentheses for non hydrogen atoms

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	−741(1)	178(1)	8839(1)	408(3)	424(3)	480(3)	28(2)	29(3)	5(2)
S	1346(1)	2843(3)	8412(1)	399(7)	1052(14)	617(9)	53(9)	99(7)	−147(8)
C(1)	1039(5)	2926(8)	8978(2)	384(24)	491(31)	587(31)	6(24)	−73(23)	37(21)
C(2)	1752(6)	4075(9)	9215(3)	524(33)	554(38)	921(52)	−8(35)	−156(34)	−29(29)
C(3)	1627(7)	4150(12)	9652(3)	728(47)	817(52)	876(58)	−195(42)	−311(44)	51(41)
C(4)	795(7)	3135(12)	9865(2)	885(49)	917(54)	550(38)	−112(35)	−188(38)	102(46)
C(5)	90(7)	1967(9)	9626(2)	757(44)	569(38)	522(37)	15(27)	−27(31)	62(33)
C(6)	203(5)	1820(7)	9179(2)	466(26)	376(26)	468(28)	41(22)	−32(22)	82(22)
C(7)	−2279(6)	−240(9)	9110(2)	542(34)	494(36)	762(41)	75(29)	120(30)	−86(29)
C(8)	104(7)	−2019(10)	8750(3)	665(42)	571(38)	767(50)	0(32)	72(35)	117(31)
C(9)	−947(4)	1424(7)	8296(2)	378(25)	471(27)	434(26)	9(21)	4(20)	64(21)
C(10)	−1962(5)	1250(8)	8042(2)	489(30)	541(34)	590(34)	−73(27)	−55(27)	33(25)
C(11)	−2070(7)	2074(10)	7644(2)	660(37)	783(47)	556(36)	−57(32)	−179(31)	147(37)
C(12)	−1181(7)	3118(9)	7504(2)	749(42)	695(43)	471(31)	73(30)	−40(30)	201(35)
C(13)	−117(6)	3418(10)	7754(2)	623(36)	693(41)	557(34)	56(31)	164(31)	51(33)
C(14)	−52(4)	1545(7)	8147(2)	421(25)	501(30)	462(28)	13(24)	72(22)	13(24)

Fractional coordinates (X 10^3) and isotropic thermal parameters (in 10^{-3} Å^2) for hydrogen atoms

	x/a	y/b	z/c	U		x/a	y/b	z/c	U
H(2)	229(8)	494(9)	906(3)	66(8)	H(81)	79(9)	−181(14)	855(3)	112(14)
H(3)	219(7)	490(9)	978(3)	66(8)	H(82)	−31(9)	−270(13)	858(3)	112(14)
H(4)	70(6)	301(10)	1018(3)	66(8)	H(83)	20(9)	−264(13)	903(4)	112(14)
H(5)	−46(7)	153(11)	979(3)	66(8)	H(10)	−250(8)	52(12)	814(3)	66(8)
H(71)	−277(8)	109(13)	915(3)	112(14)	H(11)	−274(7)	185(10)	748(2)	66(8)
H(72)	−224(9)	−96(14)	928(3)	112(14)	H(12)	−124(6)	376(10)	723(2)	66(8)
H(73)	−286(9)	−103(14)	893(3)	112(14)	H(13)	44(6)	408(10)	767(3)	66(8)

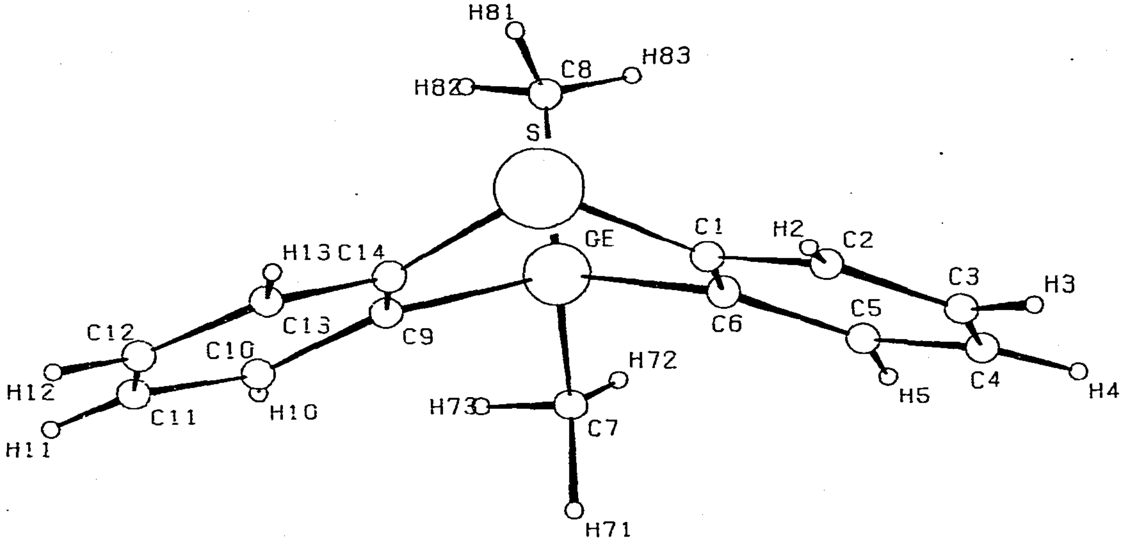

Fig. 1. Projection of the molecule 10,10-dimethyl-10-germa-9-thio-9,10-dihydroanthracene.

A more planar conformation was observed in 10,10-dichloro-10-germa-9-oxa-9,10-dihydroanthracene [9], with a butterfly angle of 170.5°. In this last compound other structural parameters significantly different from that observed in the compound under study are the endocyclic Ge—C bond lengths (1.90(1),

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°)

Ge—C(6)	1.934(6)	C(1)—C(2)	1.384(10)	C(9)—C(10)	1.380(8)
Ge—C(9)	1.933(7)	C(1)—C(6)	1.396(8)	C(9)—C(14)	1.385(7)
Ge—C(7)	1.930(7)	C(2)—C(3)	1.354(13)	C(10)—C(11)	1.380(9)
Ge—C(8)	1.928(8)	C(3)—C(4)	1.370(12)	C(11)—C(12)	1.337(11)
S—C(1)	1.777(7)	C(4)—C(5)	1.392(11)	C(12)—C(13)	1.376(10)
S—C(14)	1.770(5)	C(5)—C(6)	1.387(9)	C(13)—C(14)	1.388(9)
C(2)—H(2)	1.01(8)	C(7)—H(72)	0.75(10)	C(10)—H(10)	0.87(8)
C(3)—H(3)	0.93(8)	C(7)—H(73)	1.30(10)	C(11)—H(11)	0.91(8)
C(4)—H(4)	0.98(8)	C(8)—H(81)	0.99(10)	C(12)—H(12)	0.99(7)
C(5)—H(5)	0.86(8)	C(8)—H(82)	0.87(10)	C(13)—H(13)	0.89(6)
C(7)—H(71)	1.15(9)	C(8)—H(83)	0.98(10)		

C(6)—Ge—C(9)	102.7(2)	C(1)—C(6)—C(5)	116.9(6)
C(6)—Ge—C(7)	110.7(3)	C(1)—C(6)—Ge	120.4(5)
C(6)—Ge—C(8)	111.4(4)	C(5)—C(6)—Ge	122.7(8)
C(7)—Ge—C(8)	110.7(3)	Ge—C(9)—C(10)	122.7(5)
C(7)—Ge—C(9)	110.4(2)	Ge—C(9)—C(14)	119.8(4)
C(8)—Ge—C(9)	110.8(3)	C(10)—C(9)—C(14)	117.4(5)
C(1)—S—C(14)	106.6(3)	C(9)—C(10)—C(11)	122.1(6)
S—C(1)—C(2)	115.4(5)	C(10)—C(11)—C(12)	119.2(7)
S—C(1)—C(6)	122.8(5)	C(11)—C(12)—C(13)	121.2(6)
C(2)—C(1)—C(6)	121.6(6)	C(12)—C(13)—C(14)	119.5(6)
C(1)—C(2)—C(3)	119.4(7)	C(13)—C(14)—S	115.4(4)
C(2)—C(3)—C(4)	121.5(8)	C(9)—C(14)—C(13)	120.4(5)
C(3)—C(4)—C(5)	118.9(6)	S—C(14)—C(9)	124.0(5)
C(4)—C(5)—C(6)	121.7(6)		

TABLE 4

DISTANCES (Å) OF RELEVANT ATOMS FROM MEAN PLANES THROUGH THE MOLECULE

Plane 1: C(1)—C(6)	C(1) 0.010, C(2) −0.002, C(3) −0.013, C(4) 0.010, C(5) 0.005, C(6) −0.009, Ge −0.050, S −0.080
Plane 2: C(9)—C(14)	C(9) 0.015, C(10) −0.019, C(11) 0.005, C(12) 0.020, C(13) −0.020, C(14) −0.001, Ge 0.083, S 0.132
Plane 3: C(1), C(6), C(9), C(14)	C(1) 0.0004, C(6) −0.0003, C(9) 0.0003, C(14) −0.0003, Ge 0.562, S 0.578
Plane 4: Ge, C(7), C(8)	

1.89(1) Å as compared with 1.934(6), 1.933(7) Å), the endocyclic C—Ge—C angle (105(1)° compared with 102.7(2)°), the C—C—Ge bond angles within the heterocyclic ring (116(1), 116(1)° compared with 120.4(5) and 119.8(4)°) and the C—C—C bond angles in the external ring *ipso* to the germanium (119(1), 121(1)° instead of 116.9(6) and 117.4(5)). The S—C bond distances are comparable with those found in several phenothiazines, but the variation of S—C bond lengths with the amount of conjugation is always very small and at the limit of significance. So it seems that conjugative interactions significantly modify the whole bonding in the molecule and that to correlate the photoelectron spectral data with geometrical parameters the crystal structures of all compounds of the series are required.

The heterocyclic ring has a boat conformation, with the sulphur and the germanium atoms displaced by 0.578 and 0.562 Å, respectively, from the mean plane. The plane formed by the germanium and the two methyl carbon atoms is perpendicular to the plane of the central ring.

The ^{13}C NMR chemical shifts associated with the carbon atoms of the benzene rings [1] are a useful tool for the investigation of charge density differences in the ground state within homogeneous series [10] and concomitant changes in hybridisation, and correlate quite well with bond angles at C(1), C(6), C(9) and C(14). In fact the changes from the sp^2 hybridisation observed for these atoms is quite remarkable and, while the carbons adjacent to the germanium show a narrowing of the internal angles of the benzene rings (C(10)—C(9)—C(14) 117.4(5)°, C(1)—C(6)—C(5) 116.9(6)°), the carbons adjacent to the sulphur show normal angles within the benzene rings (C(9)—C(14)—C(13) 120.4(5)°, C(2)—C(1)—C(6) 121.6(6)°) but enlarged angles in the hetero-

TABLE 5

NORMAL EQUATIONS OF PLANES IN THE FORM: $lX + mY + nZ = p$ (X, Y and Z are in Å, referred to orthogonal axes x, y and z^*)

Plane	*l*	*n*	*m*	*p*
1	−0.6929	0.7126	−0.1100	−2.2776
2	0.4356	−0.7761	−0.4559	−12.9569
3	0.5844	−0.7893	−0.1884	−6.2795
4	0.4228	0.0907	0.9017	24.2062

cyclic ring (C(9)—C(14)—S 124.0(5)°, C(6)—C(1)—S 122.8(5)°).

The packing is consistent with Van der Waals interactions.

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