

***anti*-1',1',2,2-Tetrachloro-3,3-dimethyl-1a',6b'-dihydrospiro[cyclopropane-1,2'-[1H]cycloprop[a]indene]**

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**Abstract.** C<sub>14</sub>H<sub>12</sub>Cl<sub>4</sub>,  $M_r = 322.1$ , monoclinic,  $C2/c$ ,  $a = 22.329$  (5),  $b = 9.798$  (4),  $c = 15.200$  (5) Å,  $\beta = 123.66$  (5)°,  $V = 2767.91$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.551$ ,  $D_m = 1.54_3$  Mg m<sup>-3</sup>,  $F(000) = 1312$ .  $R = 0.054$  for 1410 reflexions collected with an automatic four-circle diffractometer. The structure was solved by the direct multiresolution method *SHELX 76*. The six-membered benzene ring and the five-membered cyclopentene ring are planar and inclined at an angle of 1.1 (4)°.

**Introduction.** Colourless prisms of *anti*-1',1',2,2-tetrachloro-3,3-dimethyl-1a',6b'-dihydrospiro[cyclopropane-1,2'-[1H]cycloprop[a]indene] were kindly supplied by Dr Jan Kapuściński. Preliminary Weissenberg photographs showed the crystal system to be monoclinic with systematic extinctions consistent with space groups  $Ic$  or  $I2/c$ . A crystal shaped to a sphere, approximately 0.3 mm in diameter, was used for intensity measurements on a Syntex P2<sub>1</sub> automated four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. The cell used was the conventional one, *i.e.*  $C2/c$  or  $Cc$ .

1713 reflections were measured at room temperature within the range  $0^\circ \leq 2\theta \leq 55^\circ$ ; of these, 1410 had  $I \geq 2\sigma(I)$  and were classified as significant. The data were corrected for Lorentz and polarization effects but not for absorption:  $\mu(\text{Mo } K\alpha) = 0.760$  mm<sup>-1</sup>. The maximum  $hkl = 18,10,16$ . Cell dimensions obtained with space group  $Cc$  or  $C2/c$  are in the *Abstract*; for the non-conventional cell (space group  $Ic$  or  $I2/c$ ):  $a = 18.794$  (5),  $b = 9.798$  (4),  $c = 15.200$  (5) Å,  $\beta = 98.72$  (5)°. The distribution of  $E$  values calculated during the data reduction indicated  $C2/c$  as the space group. All subsequent calculations were performed for the centrosymmetric space group.

The phase problem was solved by the automatic centrosymmetric direct-methods program incorporated in the *SHELX 76* system (Sheldrick, 1976). The structure was refined by standard least-squares

methods and difference electron density syntheses. Three cycles of full-matrix least-squares refinement using isotropic temperature factors resulted in an  $R$  value of 0.127. Introduction of anisotropic temperature factors required the application of a blocked-full-matrix technique owing to the low core-memory capacity of our computer, and  $R$  decreased to 0.083 in two cycles. In two further cycles with all non-hydrogen atoms treated anisotropically  $R$  decreased to 0.079. In a subsequent weighted difference Fourier synthesis based on reflexions with  $\sin \theta/\lambda \leq 0.3$  Å<sup>-1</sup> to optimize the location of the H atoms, all H atoms, except those belonging to methyl groups, could be located. Therefore, the methyl H atoms were generated with the methyl groups assumed to be staggered (C–H constrained to 1.08 Å) and refined as rigid groups. The positional and isotropic thermal parameters of the H atoms, taken initially as for their parent C atoms, were refined. Final refinements converged with a conventional  $R = 0.0535$ ,  $R_w = 0.0544$  and  $R_e = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.0662$  for the observed reflexions. The weights were  $w = k/[\sigma^2(F_o) + gF_o^2]$  where  $k$  and  $g$  refined to 1.7604 and 0.00081 respectively. In the final difference map no significant density was observed. During the last cycle of refinement, parameter shifts of non-hydrogen atoms were all lower than 0.001 Å. Complex neutral scattering factors for C and Cl (Cromer & Mann, 1968) and the exponential series for spherical bonded H atoms (Stewart, Davidson & Simpson, 1965) were used.†

All calculations were performed on an Odra 1305 computer using the *SHELX 76* system of programs.

**Discussion.** Kapuściński & Mąkosza (1977) have investigated the addition reaction of dichlorocarbene to  $\omega,\omega$ -dimethylbenzofulvene (1-isopropylidene[1H]in-

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34968 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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dene) (I). It was part of the investigation initiated by Mąkosza (1975, and references therein) on the preparation of carbenes in the catalytic two-phase system and its application to the preparation of polycyclic derivatives of indene. Dichlorocarbene, obtained by the reaction of chloroform and 50% aqueous NaOH in the presence of catalytic amounts of triethylbenzylammonium chloride (TEBA), reacts easily with (I) giving the crystalline compound (II) as the main product (70% yield). Kapuściński & Mąkosza (1977) have found from elemental analysis and PMR spectra that two molecules of dichlorocarbene joined (I) and the carbon skeleton of (I) was not rearranged. Formation of the two geometrical isomers *syn* and *anti* was theoretically possible as the result of dichlorocarbene addition to this conjugated, unsaturated system. However, the formation of the *syn* isomer was less probable, due to the high spatial overcrowding expected.

The molecular structure and atomic nomenclature are shown in Fig. 1. Final positional parameters and

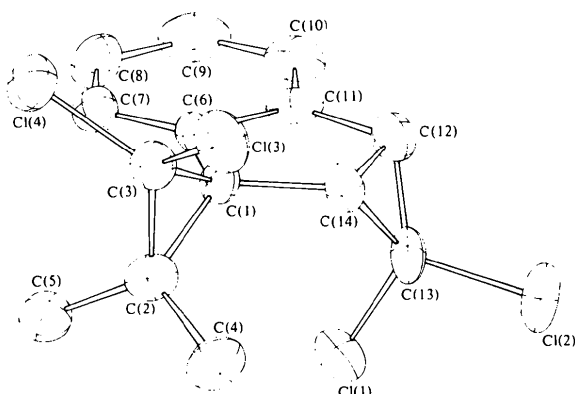


Fig. 1. ORTEP plot of the molecule, with 50% probability thermal ellipsoids and the atom labelling.

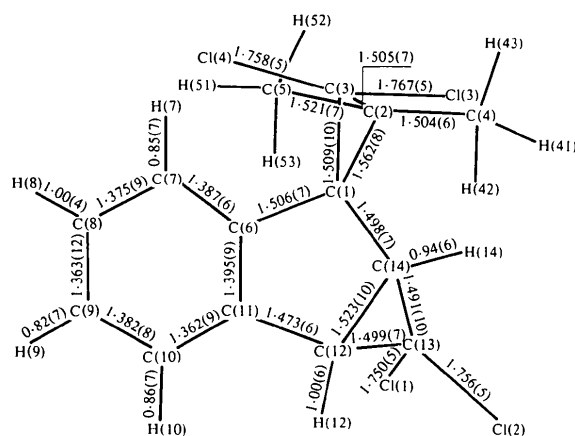


Fig. 2. Bond distances (Å) and the atom numbering. E.s.d.'s are given in parentheses and refer to the last significant digit.

isotropic thermal parameters are in Tables 1 and 2. The bond lengths and angles are given in Figs. 2 and 3 and Table 3. Table 4 lists the computed least-squares planes with the distances of various atoms from these planes, while in Table 5 selected intramolecular non-bonding distances and angles are given.

All bonds and valency angles have typical values within their e.s.d.'s. The aromatic benzene ring as well as the five-membered cyclopentene ring are both planar and form an angle of 1.1 (4)°. The spiro cyclopropane ring [C(1), C(2) and C(3)] makes an angle of 89.0 (5)° with the plane of the five-membered ring. C(2) and C(3) are at approximately equal distances from the plane of

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^3$ ) of the non-hydrogen atoms

The estimated standard deviations in parentheses refer to the last significant digit.

	x	y	z	U (Å <sup>2</sup> )
C(1)	3909 (2)	2297 (5)	4429 (3)	26 (2)
C(2)	3495 (3)	3484 (5)	4555 (4)	35 (3)
C(3)	3499 (3)	2067 (5)	4939 (4)	38 (3)
C(4)	2815 (3)	3967 (6)	3564 (4)	46 (3)
C(5)	3912 (3)	4618 (5)	5351 (4)	42 (3)
C(6)	4715 (2)	2193 (4)	4998 (3)	27 (2)
C(7)	5267 (3)	2588 (5)	6007 (4)	33 (3)
C(8)	5970 (3)	2375 (6)	6333 (4)	42 (3)
C(9)	6135 (4)	1830 (6)	5667 (5)	53 (3)
C(10)	5590 (3)	1432 (6)	4660 (5)	44 (3)
C(11)	4890 (3)	1613 (5)	4331 (4)	33 (3)
C(12)	4243 (3)	1295 (5)	3284 (4)	37 (3)
C(13)	3772 (3)	2469 (5)	2639 (4)	39 (3)
C(14)	3612 (3)	1735 (5)	3345 (4)	32 (3)
Cl(1)	4099 (1)	4143 (1)	2910 (1)	48 (1)
Cl(2)	3168 (1)	2192 (2)	1277 (1)	54 (1)
Cl(3)	2704 (1)	1081 (1)	4279 (1)	51 (1)
Cl(4)	3970 (1)	1732 (1)	6302 (1)	46 (1)

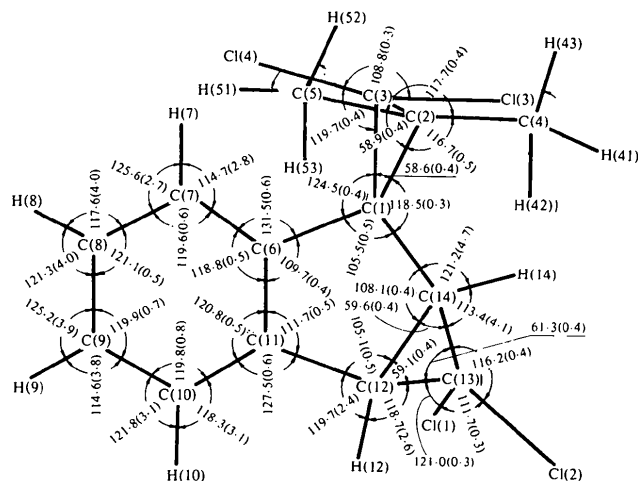


Fig. 3. Schematic drawing showing bond angles (°). E.s.d.'s are given in parentheses. The omitted angles are given in Table 4.

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) and isotropic thermal parameters ( $\times 10^3$ ) of the hydrogen atoms

The estimated standard deviations are given in parentheses.

	x	y	z	U ( $\text{\AA}^2$ )
H(41)	254	328	289	96
H(42)	299	485	335	88
H(43)	245	428	378	80
H(51)	434	415	608	58
H(52)	357	520	551	116
H(53)	414	529	506	107
H(7)	513 (3)	292 (5)	639 (4)	26
H(8)	636 (3)	267 (5)	706 (4)	41
H(9)	654 (3)	163 (5)	583 (4)	44
H(10)	568 (3)	110 (5)	422 (4)	24
H(12)	423 (3)	44 (6)	291 (4)	47
H(14)	318 (3)	126 (5)	298 (4)	34

Table 3. Bond angles ( $^\circ$ ) not included in Fig. 3

The e.s.d.'s in parentheses refer to the last significant digit.

C(2)—C(1)—C(6)	125.4 (4)	C(11)—C(12)—C(13)	117.2 (4)
C(3)—C(1)—C(14)	119.0 (4)	H(12)—C(12)—C(14)	122 (4)
C(1)—C(2)—C(5)	119.9 (4)	Cl(2)—C(13)—C(12)	117.0 (4)
C(4)—C(2)—C(5)	113.6 (4)	C(1)—C(14)—C(13)	118.5 (4)
C(1)—C(3)—C(2)	62.4 (4)	C(12)—C(14)—H(14)	121 (4)
C(2)—C(3)—Cl(3)	119.8 (3)		

the five-membered ring, *i.e.* 0.746 and  $-0.757 \text{ \AA}$  respectively. The other cyclopropane ring [C(12), C(13) and C(14)] forms angles of  $67.2 (5)^\circ$  and  $68.2 (5)^\circ$  with the mean planes of the six- and five-membered rings respectively.

There are a number of rather close intramolecular non-bonded contacts in the molecule (Table 5). As the molecule is heavily substituted, it is undoubtedly subject to steric strain and these short distances can be attributed to repulsive forces.

On heating above 373 K the title compound decomposes with the elimination of HCl, giving a derivative of naphthalene in quantitative yield. Kapuściński & Mąkosza (1977) have explained this isomerization as a concerted reaction between the *endo* Cl and the eliminated proton of methyl group C(4). They assumed that as a result of the free rotation of the methyl group, this distance can be as short as  $3.6 \text{ \AA}$ . We have found this distance to be  $2.97 \text{ \AA}$  (Table 5); this strongly supports the proposed mechanism of isomerization.

We thank Professor M. Mąkosza and Dr Jan Kapuściński, Warsaw, for a sample of the compound.

Table 4. Deviations of atoms ( $\text{\AA} \times 10^3$ ) from the least-squares planes

E.s.d.'s refer to the last significant digit and are given in parentheses.

(a) Plane through C(6), C(7), C(8), C(9), C(10) and C(11)

$$5.3115x + 8.9175y - 6.2956z = 1.3146$$

C(1)	23 (5)	C(10)	1 (6)
C(6)	-1 (4)	C(11)	-2 (5)
C(7)	7 (5)	C(12)	25 (5)
C(8)	-8 (6)	C(13)	1228 (5)
C(9)	4 (6)	C(14)	44 (5)

The e.s.d. of the atoms defining the plane from the plane is  $\sigma = 5$ ;  $\chi^2 = 2.25$ .

(b) Plane through C(6), C(11), C(12), C(14) and C(1)

$$5.6054x + 8.9349y - 6.2223z = 1.4910$$

C(1)	-2 (5)	C(10)	26 (6)
C(2)	746 (5)	C(11)	-1 (5)
C(3)	-757 (5)	C(12)	-1 (5)
C(6)	1 (4)	C(14)	2 (5)
C(7)	34 (5)		
C(8)	41 (6)		
C(9)	53 (6)		

The e.s.d. of the atoms defining the plane from the plane is  $\sigma = 1$ ;  $\chi^2 = 0.20$ .

(c) Plane through C(12), C(13) and C(14)

$$5.0566x + 6.1464y + 7.5175z = 5.4090$$

(d) Plane through C(1), C(2) and C(3)

$$8.7850x + 2.2240y + 7.9546z = 7.4691$$

The angle between the planes (a) and (b) is  $1.1 (4)^\circ$ . Plane (c) makes angles of  $67.2 (5)^\circ$  and  $68.2 (5)^\circ$  with planes (a) and (b) respectively. The angles between plane (d) and the normals to planes (b) and (a) are  $89.1 (5)^\circ$  and  $89.9 (5)^\circ$  respectively. Bond C(2)—C(3) makes angles of  $1.9 (5)^\circ$ ,  $2.5 (5)^\circ$  and  $67.6 (5)^\circ$  with the normals to planes (a), (b) and (c) respectively.

Table 5. Selected intramolecular non-bonding distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

E.s.d.'s of the distances are  $0.05 \text{ \AA}$  and of the angles  $1-2^\circ$ .

Cl(1)—H(42)	2.97	Cl(4)—H(42)—C(4)	112
Cl(2)—H(12)	2.86	Cl(2)—H(12)—C(12)	75
Cl(2)—H(14)	2.74	Cl(2)—H(14)—C(14)	82
Cl(3)—H(41)	2.89	Cl(3)—H(41)—C(4)	90
Cl(3)—H(14)	2.71	Cl(3)—H(14)—C(14)	107
Cl(4)—H(51)	2.59	Cl(4)—H(51)—C(5)	111
Cl(4)—H(7)	2.77	Cl(4)—H(7)—C(7)	119

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## Low-Temperature Structure of 3-(*p*-Bromophenyl)thiazolo[3,2-*a*]pyridinium Tetrafluoroborate

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**Abstract.** C<sub>13</sub>H<sub>9</sub>BrNS<sup>+</sup>.BF<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 377.99, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 12.200 (2), *b* = 7.633 (1), *c* = 14.664 (2) Å, β = 97.84 (1)°; *d<sub>x</sub>* = 1.855 Mg m<sup>-3</sup>, *Z* = 4, λ(Mo *K*α<sub>1</sub>) = 0.70926 Å, μ = 340.5 mm<sup>-1</sup>, m.p. = 489 K. Diffraction data were collected at about 123 K and the structure was refined to *R* = 0.052. The fused thiazole and pyridine rings are quite regular.

**Introduction.** During an extensive study of the reactions and syntheses of azolium systems (Messmer & Gelléri, 1965; Gelléri & Messmer, 1973), the geometry and aromaticity of the thiazolo skeleton became of interest. A quantum-chemical approach to the behaviour of the title compound led to the X-ray study. The compound was synthesized by a modification of the method of Bradsher & Boliek (1967) from 2-mercaptopyridine and *p*-bromophenacyl bromide. The condensation of the intermediate product [α-(2-pyridylthio)-4-bromoacetophenone] yielded the title compound which was crystallized as the tetrafluoroborate salt.

Unit-cell parameters and their e.s.d.'s were calculated from diffractometer data using the least-squares technique. 3945 independent reflexions were collected at low temperature (about 123 K) on a Syntex *P*2<sub>1</sub> automatic four-circle diffractometer with monochromated Mo *K*α<sub>1</sub> radiation. 416 reflexions [*I* ≤ 2σ(*I*)] were taken as unobserved. No absorption correction was made. The fractional coordinates of Br and S were determined by the Patterson method. Other non-hydrogen atoms were located in a subsequent

Fourier map. The structure was refined by anisotropic least squares using the program *SHELX* (Sheldrick, 1976). H atoms were located from the assumed geometry of the *sp*<sup>2</sup> C atoms and were refined in one isotropic cycle. The final *R* values are 0.052 and 0.058 for the observed and all reflexions, respectively. No sign of disorder in the BF<sub>4</sub> group could be detected in the difference maps. The final atomic coordinates are listed in Tables 1 and 2.\*

**Discussion.** A view of the molecule with the atomic numbering is shown in Fig. 1. Bond lengths and angles are given in Tables 3 and 4.

The fused thiazole and pyridine rings are coplanar (the dihedral angle is 4°). The phenyl ring is twisted with respect to the thiazole ring about C(5)–C(10) by 52.0°, which is very close to the value (49.2°) found in 3-phenyltetrazolo[4,5-*a*]pyridinium tetrafluoroborate (PTPTF; Sasvári, Czugler, Gelléri, Náray-Szabó, Hess & Schwarz, 1979). The main difference between the two structures lies in the endocyclic bond angles of the pyridine rings. These are quite close to 120° in the title compound while two extreme values were observed for PTPTF. The 117.8° at C(9) is, however, the same as in PTPTF (117.3°). The thiazole ring resembles a

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35119 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.