Acta Cryst. (1987). C43, 1764–1766

Structure of 3-(4,4-Dimethyl-6-thiochromanyl)-2-butenyltriphenylphosphonium Bromide

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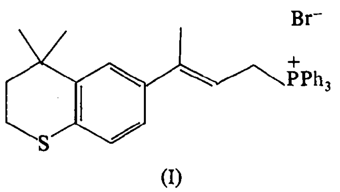
(*Received* 11 *December* 1986; *accepted* 22 *April* 1987)

Abstract. $C_{33}H_{34}PS^+.Br^-$, $M_r = 573{\cdot}6$, triclinic, $P\bar{1}$, $a = 11{\cdot}768\ (14)$, $b = 12{\cdot}702\ (11)$, $c = 11{\cdot}558\ (10)$ Å, $\alpha = 113{\cdot}66\ (5)$, $\beta = 100{\cdot}30\ (9)$, $\gamma = 63{\cdot}90\ (7)°$, $V = 1421{\cdot}1$ Å³, $Z = 2$, $D_x = 1{\cdot}340$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 15{\cdot}3$ cm^{-1}, $F(000) = 596$, $T = 138$ K, $R = 0{\cdot}045$ for 4187 observed reflections. In the thiochroman ring system, the heterocyclic thiopyran ring assumes a sofa conformation. The double bond in the vinyl chain has an *anti* arrangement of the larger groups and the conformation of the rest of the chain is such that the triphenylphosphonium system is folded back towards the thiochroman ring. There are two short C—H···Br⁻ contacts of 3·643 and 3·684 Å.

Introduction. Retinoids, derivatives of retinoic acid, have recently received considerable attention as agents which may be useful for cancer prevention and treatment (Orfanoes, 1981; Sporn, Roberts & Goodman, 1984; Nugent & Clark, 1985; Saurat, 1985). Heteroarotinoids are a group of synthetic retinoids containing in the system an aryl ring fused to a partially saturated ring with a heteroatom. The title compound (I) is a key intermediate required in the syntheses of a group of heteroaratinoids (Spruce, Rajadhyaksha, Berlin, Gale, Miranda, Ford, Blossey, Verma, Hossain, van der Helm & Breitman, 1987). The crystal-structure determination of the compound was carried out primarily to confirm the *anti* arrangement of groups around the double bond in the vinyl chain, establishing (I) as the *E* isomer.



(I)

Table 1. *Atomic parameters*

E.s.d.'s are within parentheses.

	x	y	z	U_{eq}(Å²)
Br(1)	0·46266 (4)	0·38951 (4)	0·18025 (4)	0·0253 (2)
S(1)	−0·06462 (9)	1·23926 (9)	0·63460 (9)	0·0267 (4)
C(2)	−0·1915 (4)	1·3436 (4)	0·5682 (4)	0·037 (2)
C(3)	−0·2233 (4)	1·2741 (4)	0·4362 (4)	0·031 (2)
C(4)	−0·1190 (3)	1·2156 (3)	0·3385 (4)	0·026 (2)
C(4a)	0·0061 (3)	1·1264 (3)	0·3773 (3)	0·019 (2)
C(5)	0·1003 (3)	1·0373 (3)	0·2868 (3)	0·018 (2)
C(6)	0·2163 (3)	0·9530 (3)	0·3133 (3)	0·017 (2)
C(7)	0·2394 (4)	0·9603 (3)	0·4385 (3)	0·019 (2)
C(8)	0·1508 (3)	1·0468 (3)	0·5303 (3)	0·022 (2)
C(8a)	0·0341 (3)	1·1322 (3)	0·5030 (3)	0·019 (2)
C(9)	−0·0981 (4)	1·3198 (4)	0·3231 (5)	0·040 (2)
C(10)	−0·1657 (5)	1·1435 (6)	0·2129 (5)	0·050 (3)
C(11)	0·3142 (3)	0·8590 (3)	0·2147 (3)	0·017 (2)
C(12)	0·3224 (4)	0·8961 (4)	0·1083 (4)	0·025 (2)
C(13)	0·3902 (3)	0·7476 (3)	0·2246 (3)	0·017 (2)
C(14)	0·5016 (3)	0·6440 (4)	0·1445 (3)	0·018 (2)
P(15)	0·64565 (8)	0·66196 (8)	0·21346 (8)	0·0163 (4)
C(16)	0·6601 (3)	0·6712 (3)	0·3739 (3)	0·018 (2)
C(17)	0·7390 (3)	0·7227 (4)	0·4578 (3)	0·023 (2)
C(18)	0·7554 (4)	0·7235 (4)	0·5804 (4)	0·027 (2)
C(19)	0·6920 (4)	0·6727 (4)	0·6184 (4)	0·026 (2)
C(20)	0·6139 (3)	0·6212 (3)	0·5362 (3)	0·021 (2)
C(21)	0·5987 (3)	0·6175 (3)	0·4121 (3)	0·018 (2)
C(22)	0·7829 (3)	0·5309 (3)	0·1282 (3)	0·019 (2)
C(23)	0·7724 (4)	0·4268 (4)	0·0304 (4)	0·027 (2)
C(24)	0·8796 (4)	0·3245 (4)	−0·0290 (4)	0·031 (2)
C(25)	0·9974 (4)	0·3256 (4)	0·0072 (4)	0·030 (2)
C(26)	1·0085 (4)	0·4288 (4)	0·1033 (4)	0·033 (2)
C(27)	0·9020 (4)	0·5311 (4)	0·1634 (4)	0·027 (2)
C(28)	0·6352 (3)	0·8059 (3)	0·2089 (3)	0·019 (2)
C(29)	0·5791 (4)	0·9196 (4)	0·3068 (4)	0·026 (2)
C(30)	0·5550 (4)	1·0322 (4)	0·2944 (4)	0·033 (2)
C(31)	0·5869 (4)	1·0292 (4)	0·1836 (5)	0·037 (2)
C(32)	0·6433 (4)	0·9158 (4)	0·0848 (4)	0·034 (2)
C(33)	0·6676 (3)	0·8033 (4)	0·0966 (4)	0·025 (2)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Experimental. Plate-shaped crystal, 0·21 × 0·17 × 0·08 mm, from methanol–ether, Enraf–Nonius CAD-4 single-crystal X-ray diffractometer with a liquid-N_2 low-temperature set-up, Mo $K\alpha$ radiation (graphite monochromator), lattice parameters from setting of 24 reflections with $11 < \theta < 18°$. 5646 unique reflections with $2\theta \le 53°$; $-14 \le h \le 14$, $0 \le k \le 15$, $-14 \le l \le 14$; θ–2θ scan, scan width $(0{\cdot}70 + 0{\cdot}20\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(3{\cdot}0 + 0{\cdot}86\tan\theta)$ mm, vertical aperture 4 mm; three standard reflections measured every 7200 s of X-ray exposure, maximum variation 4%; 4187 observed reflections on the basis $I \ge 2\sigma(I)$; Lorentz and polarization corrections, no absorption correction. Structure solved by heavy-atom technique, refined by full-matrix least squares with minimization of $\sum w(|F_o| - |F_c|)^2$ (Sheldrick, 1976), $w = 1/\sigma^2(F)$; all

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H atoms located from difference map and refined with isotropic temperature factors; final $R = 0{\cdot}045$, $wR = 0{\cdot}043$ for 4187 observed reflections; $(\Delta/\sigma)_{\max} = 0{\cdot}07$; $S = 1{\cdot}3$ for 461 variables; highest peak in the final difference map $0{\cdot}6\ \mathrm{e\ Å^{-3}}$ around the Br atom. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are listed in Table 1.*

Discussion. A stereoview of a single molecule is shown in the *ORTEP* plot (Johnson, 1976) in Fig. 1. Bond distances and the atom-numbering scheme are given in Fig. 2. Bond angles are listed in Table 2. In Table 3, selected bond distances, bond angles, endocyclic torsion angles and asymmetry parameters [as defined by Duax & Norton (1975)] for the thiochroman ring system in the present structure are compared with the corresponding values observed in other related structures.

In the present structure, the conformation of the heterocyclic thiopyran ring is intermediate between the 3α-sofa and 2β,3α-half-chair. The asymmetry parameters for the thiopyran ring [$\Delta C_s(3) = 12{\cdot}0°$ and $\Delta C_2(2\text{–}3) = 16{\cdot}5°$] indicate that the conformation is closer to a 3α-sofa. Atoms C(2), S(1), C(8a), C(4a) and C(4) lie approximately in a plane (r.m.s. deviation of the mean plane, 0·053 Å) and atom C(3) deviates from the plane by 0·658 Å. In three of the four related compounds listed in Table 3, the heterocyclic ring conformation is closer to a half-chair, whereas in the fourth [4-(*p*-hydroxyphenyl)-2,2,4,7-tetramethylthiochroman], the ring is closer to a boat conformation. The two S—C distances, S(1)—C(2) = 1·800 (4) Å and S(1)—C(8a) = 1·759 (3) Å, in the present structure are significantly different from each other. This is in general true for all thiochroman systems with an unsubstituted S atom. In most compounds where the S atom is

Table 2. *Bond angles* (°)

E.s.d.'s are within parentheses.

C(2)–S(1)–C(8a)	102·0 (1)	C(7)–C(6)–C(11)	120·3 (3)
C(14)–P(15)–C(16)	109·9 (1)	C(6)–C(7)–C(8)	120·9 (3)
C(14)–P(15)–C(22)	111·3 (2)	C(7)–C(8)–C(8a)	121·6 (2)
C(14)–P(15)–C(28)	107·4 (2)	S(1)–C(8a)–C(4a)	126·0 (3)
C(16)–P(15)–C(22)	108·2 (1)	C(4a)–C(8a)–C(8)	119·2 (3)
C(16)–P(15)–C(28)	109·7 (2)	S(1)–C(8a)–C(8)	114·7 (1)
C(22)–P(15)–C(28)	110·2 (2)	C(6)–C(11)–C(12)	117·4 (4)
S(1)–C(2)–C(3)	111·8 (4)	C(6)–C(11)–C(13)	119·0 (2)
C(2)–C(3)–C(4)	114·9 (4)	C(12)–C(11)–C(13)	123·6 (3)
C(3)–C(4)–C(4a)	111·7 (2)	C(11)–C(13)–C(14)	128·5 (2)
C(3)–C(4)–C(9)	109·6 (4)	C(13)–C(14)–P(15)	110·1 (3)
C(3)–C(4)–C(10)	107·1 (4)	P(15)–C(16)–C(17)	120·4 (2)
C(4a)–C(4)–C(9)	109·3 (3)	P(15)–C(16)–C(21)	119·5 (3)
C(4a)–C(4)–C(10)	110·3 (4)	C(17)–C(16)–C(21)	120·0 (2)
C(9)–C(4)–C(10)	108·8 (3)	P(15)–C(22)–C(23)	121·1 (3)
C(4)–C(4a)–C(5)	120·0 (2)	P(15)–C(22)–C(27)	119·6 (4)
C(4)–C(4a)–C(8a)	122·9 (3)	C(23)–C(22)–C(27)	119·2 (4)
C(5)–C(4a)–C(8a)	117·1 (3)	P(15)–C(28)–C(29)	120·7 (2)
C(4a)–C(5)–C(6)	123·9 (2)	P(15)–C(28)–C(33)	118·3 (4)
C(5)–C(6)–C(7)	117·2 (3)	C(29)–C(28)–C(33)	120·3 (4)
C(5)–C(6)–C(11)	122·5 (2)		

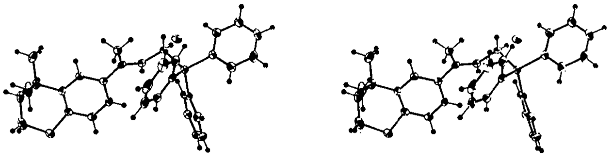

Fig. 1. A stereoview of a single molecule.

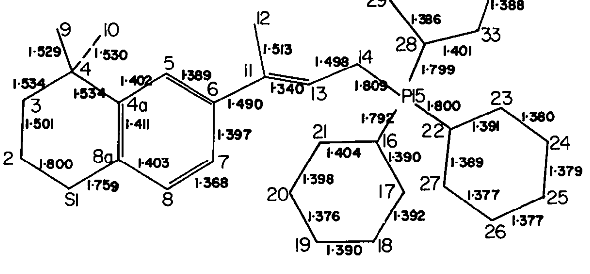

Fig. 2. Bond distances (Å). E.s.d.'s are 0·004 Å for S—C and P—C bonds and range from 0·005 to 0·007 Å for C—C bonds.

Table 3. *Selected structural parameters of the heterocyclic ring in the thiochroman ring system*

	(I)	(II)	(III)	(IV)	(V)
Bond distances (Å)					
S(1)–C(2)	1·800 (4)	1·818	1·818	1·761	1·843
S(1)–C(8a)	1·759 (4)	1·770	1·712	1·760	1·762
Bond angles (°)					
C(2)–S(1)–C(8a)	102·0 (1)	101·5	103·6	102·6	103·6
S(1)–C(8a)–C(4a)	126·0 (3)	123·2	128·5	121·5	121·0
C(8a)–C(4a)–C(4)	122·9 (3)	124·0	120·5	124·8	119·4
Endocyclic torsion angles (°)					
S(1)–C(2)–C(3)–C(4)	−66·2 (5)	69·2	62·0	66·5	23·8
C(2)–C(3)–C(4)–C(4a)	56·2 (6)	−51·7	−52·4	−47·1	−63·5
C(3)–C(4)–C(4a)–C(8a)	−20·8 (7)	14·4	21·8	16·1	46·8
C(4)–C(4a)–C(8a)–S(1)	−0·5 (8)	2·5	−9·3	−7·7	5·1
C(4a)–C(8a)–S(1)–C(2)	−7·0 (5)	12·9	17·8	24·5	−40·5
C(8a)–S(1)–C(2)–C(3)	37·4 (5)	−47·0	−39·7	−51·2	24·0
Asymmetry parameters (°)*					
$\Delta C_s(3)$	12·0	22·2	12·7	25·1	—
$\Delta C_2(2\text{–}3)$	16·5	3·6	9·4	6·7	—

(I) Present work. (II) 2,4-Diphenyl-2,3-dihydrobenzo[*h*]thiochroman (Kharchenko, Krivenko, Fedotova, Evtushenko, Shcherbakov, Aleksandrov & Struchkov, 1980). (III) 4-(*p*-Hydroxyphenyl)-2,2,4-trimethylthiochroman (MacNicol, Mills & Wilson, 1969). (IV) 4-Bromothiochroman 1,1-dioxide (Andreetti, Bocelli & Sgarabotto, 1978). (V) 4-(*p*-Hydroxyphenyl)-2,2,4,7-tetramethylthiochroman (Hardy, McKendrick & MacNicol, 1977).

* As defined by Duax & Norton (1975); $\Delta C_s = 0°$ for ideal sofa, $\Delta C_2 = 0°$ for ideal half-chair.

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* Lists of structure factors, anisotropic thermal parameters, phenyl bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43994 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

substituted, there is no noticeable difference between the two types of S—C distances (Ealick, van der Helm, Ramalingam, Thyvelikakath & Berlin, 1977; Ealick, van der Helm, Baker & Berlin, 1979; Andreetti, Bocelli & Sgarabotto, 1978). The endocyclic C—S—C angle of 102·0 (2)° is close in value to that observed in the other compounds and seems to be independent of the substitution pattern in the heterocyclic ring.

The vinyl chain is twisted out of the plane of the thiochroman ring system by more than 30° [torsion angle, C(7)—C(6)—C(11)—C(13) = 33·1 (7)°] and has nearly ideal *anti* conformation for its double bond, C(11)—C(13) [torsion angle, C(6)—C(11)—C(13)—C(14) = −174·1 (4)°]. This places the methyl carbon, C(12), in a *syn* position with respect to C(14). The resulting steric strain is reflected in the angles C(12)—C(11)—C(13) of 123·6 (3)° and C(11)—C(13)—C(14) of 128·5 (2)°, both of which are significantly larger than 120°. The conformation about the C(13)—C(14) bond is skewed [torsion angle C(11)—C(13)—C(14)—P(15) = 92·6 (4)°] and as a result the triphenylphosphonium system is folded back towards the thiochroman ring system. The geometry around the P atom is nearly tetrahedral with an average P—C(sp^2) distance of 1·797 (4) Å and a slightly longer P—C(sp^3) distance of 1·809 (4) Å.

The Br^- anion has a number of short contacts with C atoms [$Br^-\cdots C(20) = 3{\cdot}618$, $Br^-\cdots C(14) = 3{\cdot}643$, $Br^-\cdots C(14') = 3{\cdot}684$, $Br^-\cdots C(19) = 3{\cdot}689$, $Br^-\cdots C(33) = 3{\cdot}721$, $Br^-\cdots C(21) = 3{\cdot}800$, $Br^-\cdots C(23) = 3{\cdot}937$, $Br^-\cdots C(12) = 3{\cdot}989$ Å]. Of these, the contacts with C(14) and C(14′)($1-x$, $1-y$, $-z$) with $H\cdots Br^-$ distances of 2·75 and 2·76 Å and $C—H\cdots Br^-$ angles of 157 and 177°, indicate possible $C—H\cdots Br^-$ hydrogen bonding. Similar $C—H\cdots Br^-$ hydrogen bonds have been observed in a related structure {$[(C_6H_5)_3PCH(COC_6H_5)_2]Br.C_2H_5OH$; Antipin, Kalinin, Struchkov, Aladzheva, Mastryukova & Kabachnik (1980)} and in 2-amino-4-phenylthiazole hydrobromide (Form, Raper & Downie, 1974).

This work was supported by a grant (CA 17562) to DvdH from the National Cancer Institute, Department of Health and Human Services.

References

ANDREETTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1978). *Cryst. Struct. Commun.* **7**, 543–546.

ANTIPIN, M. YU., KALININ, A. E., STRUCHKOV, YU. T., ALADZHEVA, I. M., MASTRYUKOVA, T. A. & KABACHNIK, M. I. (1980). *Zh. Strukt. Khim.* **21**(4), 175–182.

DUAX, W. L. & NORTON, D. (1975). *Atlas of Steroid Structures*, Vol. I, pp. 18–19. New York: Plenum Press.

EALICK, S. E., VAN DER HELM, D., BAKER, J. R. & BERLIN, K. D. (1979). *Acta Cryst.* B**35**, 495–497.

EALICK, S. E., VAN DER HELM, D., RAMALINGAM, K., THYVELIKAKATH, G. X. & BERLIN, K. D. (1977). *J. Heterocycl. Chem.* **14**, 387–390.

FORM, G. R., RAPER, E. S. & DOWNIE, T. C. (1974). *Acta Cryst.* B**30**, 342–348.

HARDY, A. D. U., MCKENDRICK, J. J. & MACNICOL, D. D. (1977). *J. Chem. Soc. Perkin Trans.* pp. 1145–1147.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KHARCHENKO, V. A., KRIVENKO, A. P., FEDOTOVA, O. V., EVTUSHENKO, I. YA., SHCHERBAKOV, A. A., ALEKSANDROV, G. G. & STRUCHKOV, YU. T. (1980). *Khim. Geterotsikl. Soedin. Latv. SSSR*, pp. 1337–1342.

MACNICOL, D. D., MILLS, H. H. & WILSON, F. B. (1969). *Chem. Commun.* pp. 1332–1333.

NUGENT, J. & CLARK, S. (1985). Editors. In *Retinoids, Diffraction and Disease.* Ciba Foundation Symposium 113. London: Pitman Publishing Co.

ORFANOES, C. E. (1981). In *Retinoids: Advances in Basic Research and Therapy.* Berlin: Springer Verlag.

SAURAT, J. H. (1985). In *Retinoids: New Trends in Research and Therapy.* Basel: Karger.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SPORN, M. B., ROBERTS, A. B. & GOODMAN, D. S. (1984). In *The Retinoids*, Vols. 1 and 2. Orlando, FL: Academic Press.

SPRUCE, L. W., RAJADHYAKSHA, S. N., BERLIN, K. D., GALE, J. B., MIRANDA, E. T., FORD, W. T., BLOSSEY, E. C., VERMA, A. K., HOSSAIN, M. B., VAN DER HELM, D. & BREITMAN, T. R. (1987). *J. Med. Chem.* In the press.

Acta Cryst. (1987). C**43**, 1766–1769

Structure of the 1:1 Complex of 3-Pyridinecarbonitrile with Pentachlorophenol

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(*Received* 7 *October* 1986; *accepted* 2 *April* 1987)

Abstract. $C_6HCl_5O.C_6H_4N_2$, $M_r = 370{\cdot}45$, triclinic, $P\bar{1}$, $a = 7{\cdot}713$ (5), $b = 8{\cdot}679$ (5), $c = 13{\cdot}914$ (9) Å, $\alpha = 117{\cdot}08$ (5), $\beta = 94{\cdot}13$ (6), $\gamma = 115{\cdot}07$ (5)°, $V = 709{\cdot}5$ (8) Å^3, $Z = 2$, $D_m = 1{\cdot}72$, $D_x = 1{\cdot}73$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = 1·01 mm^{-1}, $F(000) = 368$, $T = 301$ (1) K, final $R = 0{\cdot}032$ for 1736 non-zero

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