for the two double bonds and 1·486 Å for the single bond.

Geometry of the molecule. The packing scheme of canadinium camphorsulfonate is shown in Fig. 3. The canadinium ion has a nearly flat shape. It extends in the y direction and is placed normal to the c axis. The ions are so arranged that they stack in the x direction forming a ribbon. Ring A of one ion in a ribbon at about $z = \frac{1}{4}$ is faced parallel to two D rings at $z = \frac{3}{4}$ and $-\frac{1}{4}$. These ions, each having the central part (rings B and C) at around $y = \frac{1}{4}$, thus make a layer perpendicular to the y axis. The shortest distance between canadinium and camphorsulfonate ions, 2·683 (11) Å, is found from atom N7 of the former to atom O(3) of the sulfonate group. The N atom is protonated as would be expected in an organic sulfonate salt and is the donor to the sulfonate group. The bulky negatively charged camphorsulfonate ions are tied to the planar ions by the hydrogen bonds and seem to toss about in the vacant trenches surrounded by the positive-ion layers.

Calculations were carried out on a FACOM-M380 computer at the Data Processing Center, Kyoto University. The values for the molecular geometry were calculated using a part of the program package *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

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4-Methylene-1,2,3,5-tetraphenylbicyclo[3.1.0]hex-2-ene (Tetraphenylhomofulvene)

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Abstract. $C_{31}H_{24}$, $M_r = 396·5$, monoclinic, $P2_1/c$, $a = 20·130$ (5), $b = 9·303$ (4), $c = 12·102$ (4) Å, $\beta = 93·60$ (4)°, $V = 2261·9$ (6) Å^3, $Z = 4$, $D_x = 1·163$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·33$ cm^{-1}, $F(000) = 840$, $T = 295$ K, $R = 0·074$ for 2350 observed reflexions. Only one of the four phenyl rings is slightly conjugated with the five-membered ring, the three others are nearly perpendicular. The distances in the cyclopropane part of the title compound are longer than those found in the 'normal' cyclopropane ring and consequently weaker. This probably explains why in homofulvenes the opening of the three-membered ring is preferred.

Introduction. In previous work the photochemical behaviour of the 4-methylenebicyclo[3.1.0]hex-2-ene system ['homofulvene' system (Rey, Huber & Dreiding, 1968)] with respect to singlet (Hüther & Brune, 1968; Jobst & Brune, 1979; Brune, Jobst & Lach, 1980; Brune, Lach & Schmidtberg, 1984; Brune, Lach & Schmidtberg, 1985a, b, c) and triplet (Jobst & Brune, 1979; Lach, 1984; Hofmann, 1984) excitation was studied. An unexpectedly strong influence of the substituents on the photo-stationary equilibrium and especially on the mechanisms of the photoreaction processes and their products was observed. To understand this influence, reliable information about the

bonding in the homofulvene system − especially in the cyclopropane part − was necessary; therefore a representative compound of this system had to be chosen for crystal-structure analysis. The unsubstituted homofulvene tends to polymerize and is therefore too unstable; the more stable polyalkylated derivatives crystallize only at relatively low temperature. Therefore the title compound was chosen because it forms stable crystals at room temperature and may be assumed to be typical for this class of compounds. This is the first X-ray analysis of a homofulvene.

Experimental. Crystals of the title compound crystallize as colourless needles with relatively well shaped faces (approx. $0.2 \times 0.2 \times 0.8$ mm). 3981 unique reflexions with $2 < \theta < 25°$, Philips PW 1100 four-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator, $\theta–2\theta$ scan, 2350 observed reflexions $[F > 1.5\sigma(F), -23 < h < 23, 0 < k < 10, 0 < l < 14]$; intensity of three standard reflexions did not vary during the period of measurement. Cell parameters from the refinement of 21 reflexions $(2 < \theta < 13°)$. No absorption correction. Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Structure refined by full-matrix least squares (on F) using unit weights (Sheldrick, 1977), first with isotropic then with anisotropic temperature parameters, until the parameter shifts are less than the corresponding standard deviations $(\Delta/\sigma < 0.02)$. A difference Fourier map showed the H atoms which were subsequently refined isotropically. Final $R = 0.074$ for all 2350 observed reflexions. The relatively high R value is due to the poor quality of the crystal. Maximum and minimum peak in final difference Fourier map 0.30, -0.30 e Å^{-3}. Scattering factors of Cromer & Mann (1968) and Doyle & Turner (1968). No correction for secondary extinction.

Discussion. Final atomic coordinates and thermal parameters are given in Table 1, main interatomic distances and angles in Table 2. The angles between the five-membered ring C(1)−C(2)−C(3)−C(4)−C(5) and C(3)−C(4)−C(6), C(8)−C(9)−C(10)−C(11)−C(12)−C(13), C(14)−C(15)−C(16)−C(17)−C(18)−C(19), C(20)−C(21)−C(22)−C(23)−C(24)−C(25), C(26)−C(27)−C(28)−C(29)−C(30)−C(31) are respectively 72·5 (5), 77·3 (4), 31·2 (5), 77·8 (5) and 70·6 (6)°.*

Fig. 1 shows the structure of a single molecule with the atomic numbering used (Motherwell & Clegg, 1978). The only phenyl ring which shows a slight coplanarity (31·2°) with the five-membered ring is the

one attached at C(2); its π electrons are stabilized by partial conjugation. The other phenyl rings are nearly perpendicular to the five-membered ring. This is probably due to stereochemical hindrance. Regarding the isomerization of the homofulvene system the

Table 1. *Atomic coordinates and mean anisotropic temperature factors with e.s.d.'s in parentheses*

$$\langle U \rangle = \tfrac{1}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$\langle U \rangle$(Å^2)
C(1)	0·7001 (2)	−0·0606 (5)	0·4947 (4)	0·043 (5)
C(2)	0·7071 (2)	0·0809 (5)	0·4618 (4)	0·041 (5)
C(3)	0·7601 (2)	0·0925 (5)	0·3782 (4)	0·043 (5)
C(4)	0·7845 (2)	−0·0680 (5)	0·3643 (4)	0·045 (5)
C(5)	0·7477 (2)	−0·1518 (5)	0·4437 (4)	0·043 (5)
C(6)	0·7421 (2)	0·0102 (5)	0·2729 (4)	0·048 (5)
C(7)	0·7553 (2)	−0·2937 (6)	0·4625 (4)	0·056 (6)
C(8)	0·6479 (2)	−0·1145 (5)	0·5650 (4)	0·043 (4)
C(9)	0·5815 (2)	−0·1184 (5)	0·5262 (4)	0·049 (5)
C(10)	0·5324 (2)	−0·1683 (6)	0·5901 (5)	0·059 (6)
C(11)	0·5492 (3)	−0·2255 (6)	0·6962 (5)	0·063 (6)
C(12)	0·6155 (3)	−0·2224 (6)	0·7336 (4)	0·058 (6)
C(13)	0·6639 (2)	−0·1740 (6)	0·6693 (4)	0·052 (5)
C(14)	0·6682 (2)	0·2065 (5)	0·4929 (4)	0·040 (4)
C(15)	0·6533 (2)	0·3144 (5)	0·4158 (4)	0·052 (5)
C(16)	0·6149 (3)	0·4300 (6)	0·4421 (5)	0·066 (6)
C(17)	0·5891 (3)	0·4417 (6)	0·5445 (5)	0·065 (6)
C(18)	0·6044 (3)	0·3361 (6)	0·6228 (5)	0·060 (6)
C(19)	0·6425 (2)	0·2185 (5)	0·5968 (4)	0·048 (5)
C(20)	0·8060 (2)	0·2171 (5)	0·3810 (4)	0·047 (5)
C(21)	0·8118 (3)	0·3052 (6)	0·2877 (5)	0·064 (6)
C(22)	0·8541 (4)	0·4215 (7)	0·2930 (6)	0·084 (8)
C(23)	0·8901 (3)	0·4581 (7)	0·3885 (7)	0·083 (9)
C(24)	0·8847 (3)	0·3733 (7)	0·4829 (6)	0·081 (8)
C(25)	0·8421 (3)	0·2538 (6)	0·4770 (5)	0·064 (6)
C(26)	0·8549 (2)	−0·1028 (5)	0·3446 (4)	0·048 (5)
C(27)	0·8751 (3)	−0·1392 (7)	0·2415 (5)	0·075 (7)
C(28)	0·9407 (4)	−0·1758 (9)	0·2258 (6)	0·101 (10)
C(29)	0·9862 (3)	−0·1825 (8)	0·3139 (7)	0·092 (9)
C(30)	0·9673 (3)	−0·1477 (7)	0·4171 (6)	0·075 (7)
C(31)	0·9023 (3)	−0·1119 (6)	0·4339 (5)	0·062 (6)

Table 2. *Main interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)−C(2)	1·384 (7)	C(1)−C(8)	1·480 (7)
C(2)−C(3)	1·519 (6)	C(8)−C(9)	1·388 (6)
C(3)−C(4)	1·584 (6)	C(9)−C(10)	1·373 (7)
C(4)−C(5)	1·474 (7)	C(10)−C(11)	1·410 (8)
C(5)−C(1)	1·447 (6)	C(11)−C(12)	1·383 (8)
C(3)−C(6)	1·511 (6)	C(12)−C(13)	1·361 (7)
C(4)−C(6)	1·537 (6)	C(13)−C(8)	1·397 (7)
C(5)−C(7)	1·348 (6)	C(3)−C(20)	1·482 (6)
C(2)−C(14)	1·469 (6)	C(20)−C(21)	1·405 (7)
C(14)−C(15)	1·390 (7)	C(21)−C(22)	1·376 (9)
C(15)−C(16)	1·373 (7)	C(22)−C(23)	1·376 (8)
C(16)−C(17)	1·378 (8)	C(23)−C(24)	1·399 (11)
C(17)−C(18)	1·386 (8)	C(24)−C(25)	1·403 (8)
C(18)−C(19)	1·385 (7)	C(25)−C(26)	1·374 (7)
C(19)−C(14)	1·393 (7)	C(6)−H(1)	1·04 (4)
C(4)−C(26)	1·487 (6)	C(6)−H(2)	0·96 (4)
C(26)−C(27)	1·379 (8)	C(7)−H(3)	0·94 (5)
C(27)−C(28)	1·388 (9)	C(7)−H(4)	0·99 (4)
C(28)−C(29)	1·367 (10)		
C(29)−C(30)	1·367 (11)		
C(30)−C(31)	1·376 (8)		
C(31)−C(26)	1·399 (7)		
C(5)−C(1)−C(2)	110·6 (4)	C(14)−C(2)−C(3)	121·4 (4)
C(3)−C(2)−C(1)	110·4 (4)	C(20)−C(3)−C(2)	120·3 (4)
C(4)−C(3)−C(2)	103·9 (4)	C(20)−C(3)−C(4)	122·8 (4)
C(5)−C(4)−C(3)	104·9 (4)	C(26)−C(4)−C(3)	121·9 (4)
C(4)−C(5)−C(1)	110·0 (4)	C(26)−C(4)−C(5)	120·8 (4)
C(6)−C(3)−C(4)	59·5 (5)	C(7)−C(5)−C(4)	124·9 (4)
C(6)−C(4)−C(3)	62·6 (3)	C(7)−C(5)−C(1)	125·0 (4)
C(6)−C(4)−C(3)	57·9 (3)	H(2)−C(6)−H(1)	127 (3)
C(8)−C(1)−C(5)	124·0 (4)	H(4)−C(7)−H(3)	132 (4)
C(8)−C(1)−C(2)	125·2 (2)		
C(14)−C(2)−C(1)	128·1 (4)		

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 42871 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
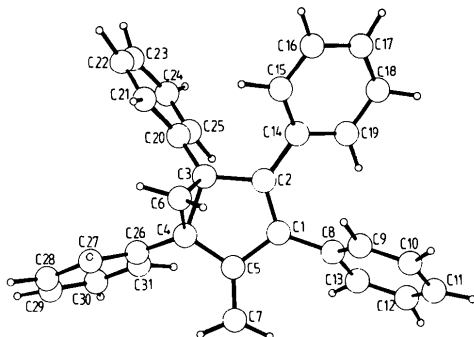
Fig. 1. Structure of a single molecule with atomic numbering, projected on the five-membered ring.

distances in the cyclopropane part of the molecule are interesting: the C(3)—C(4) distance of 1·584 (6) Å is unusually long compared with the one found in the normal cyclopropane ring [1·52 Å (Dunitz, Feldmann & Schomaker, 1952)]. This may be caused by the repulsion between the phenyl rings at C(3) and C(4). C(4)—C(6), 1·537 (6) Å, is also somewhat longer than expected, whereas the C(3)—C(6) distance, 1·511 (6) Å, agrees with the expected value. At present the reason for these different distances is not clear. The distances obtained make it clear why the opening of the enlarged and consequently weakened bonds of the three-membered ring, C(4)—C(6) (Brune, Lach & Schmidtberg, 1985a,b), C(3)—C(4) (Brune, Lach & Schmidtberg, 1985c), form the primary step in the photo-isomerization. The C(5)—C(7) double bond, 1·348 (6) Å, corresponds, within experimental errors, to the value found for a bond at the end of a conjugated system, whereas the C(1)—C(2) double bond, 1·384 (7) Å, clearly shows the additional partial conjugation with the phenyl ring at C(2). The spatial orientations of the phenyl rings at C(3) and C(4) do not allow conjugated interactions with the Walsh π orbitals of the cyclopropane ring.

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3-Benzylidene-4-chromanone

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Abstract. $C_{16}H_{12}O_2$, $M_r = 236·1$, triclinic, $P\bar{1}$, $a = 8·620$ (1), $b = 9·212$ (2), $c = 7·980$ (1) Å, $\alpha = 95·64$ (1), $\beta = 107·64$ (1), $\gamma = 89·90$ (1)°, $V = 600·7$ (2) Å^3, $Z = 2$, $D_x = 1·305$ (1) g cm^{-3}, λ(Cu $K\alpha$) $= 1·54178$ Å, $\mu = 6·01$ cm^{-1}, $F(000) = 248$, $T = 292$ K, $R = 0·0411$ for 1380 unique observed reflec-