cis,cis-1,3-Bis(styryl)azulene

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Abstract. $C_{26}H_{20}$; M.W. 332·45; monoclinic, space group $A2/a$; $a=15·155$ (3), $b=12·722$ (2), $c=12·539$ (2) Å, $\beta=104·49$ (1)°; $D_c=1·176$ g cm^{-3} for $Z=4$. Mo $K\alpha$ diffractometer data. Final $R=0·043$. The molecule lies on the twofold axis coincident with the C(2)–C(6) vector. Bond lengths in the C–C=C–C portions of the molecule have typical sp^2–sp^2 single and double bond values. The (C=C)–azulyl and (C=C)–phenyl twist angles are 25·9 and 43·3° respectively.

Introduction. A green platelet of (I), crystallized from n-heptane (Currie, 1970) and with approximate dimensions $0·4 \times 0·4 \times 0·1$ mm was mounted parallel to **b**. Precession and Weissenberg photographs established the space group. A Picker FACS-I diffractometer and Mo radiation (graphite monochromator, $K\alpha$, $\lambda=0·71069$ Å) were used for lattice parameter and intensity measurements. The final unit-cell parameters were obtained by a least-squares fit to the 2θ values of 12 reflections manually centered at $\pm 2\theta$.

(I)
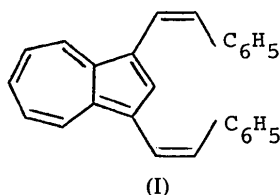
Intensities were measured by the 2θ–θ scan method with a 2θ rate of 0·5° min^{-1}, and with 40 s backgrounds. Three standard intensities were counted at 50-reflection intervals. 2968 reflections were measured to a maximum 2θ of 50° giving 1657 unique data (excluding 83 systematically absent); 1377 of these were 3σ above background and classified 'observed'. Absorption corrections were not made. The structure was solved by the routine application of direct methods using the X-RAY System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) subprogram *PHASE*. An E map computed with 289 phases ($147+$, $142-$) gave initial coordinates for the 14 unique C atoms. The structure refinement was by full-matrix least-squares, minimizing the function $\sum w(F_o-F_c)^2$, where $w=1$ for

$F_o \leq 20$ and $w=20/F_o$ for $F_o>20$ [Hughes (1941) scheme]. The calculations used anisotropic temperature factors for C and isotropic terms for H (initially located in a difference map), and included an isotropic secondary extinction correction [$r^*=0·00038$ (1), equation 22 in Larson (1970)]. Atomic scattering factors for C were obtained from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965). In the final least-squares cycle the average and maximum shifts were 0·3 and 1·5σ. The final $R(\sum|F_o-F_c|/\sum F_o)$ and weighted R ($\sum w(F_o-F_c)^2/\sum wF_o^2$) factors were 0·043 and 0·051.† The final atomic parameters are listed in Table 1.

Discussion. The compound was investigated to determine the extent of nonplanarity of the cis,cis-azulyl-C=C-phenyl structure for possible correlation with visible and n.m.r. spectral data. An *ORTEP*-II (Johnson, 1971) drawing with bond lengths and angles is given in Fig. 1. While the azulene, C–C=C–C and benzene moieties are individually planar within experimental error, the three groups are not coplanar with each other. The nonplanarity can be easily seen in Fig. 2, which has been drawn looking down the C_2 axis and which clearly illustrates the Z-shape of the molecule. The azulyl–C=C and C=C–phenyl twist angles are 25·9 and 43·3°, respectively, and the total azulene-benzene twist is 53·4°. These twists, which arise from steric interactions between the two phenyls and between the phenyls and the C(2)–H(2) portion of the azulene ring, are sufficiently large to make all of the phenyl···phenyl and azulyl···phenyl contacts larger than the corresponding van der Waals distances. The distance between the two phenyl rings planes is *ca.* 5·0 Å. The steric pressures are slightly reduced by the *ca.* 10° increase of the two C–C=C angles, C(9) and C(10), over the normal trigonal 120° value, and by the exocyclic bond angle differences at C(1) and C(11). C–C=C angles in the 130° range have been found in *trans*-stilbene (Robertson & Woodward, 1937), 1,2-dicyano-*trans*-stil-

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† A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30242 (20 pp., 1 microfiche). Copies of this table may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Table 1. *Fractional coordinates, temperature factors* ($Å^2$) *and e.s.d.'s* (*in parentheses*)

The form of the anisotropic temperature factors is $\exp\left[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{23}klb^*c^*)\right]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·1539 (2)	0·7780 (2)	0·9583 (2)	0·044 (1)	0·049 (1)	0·047 (1)	0·0007 (9)	0·0039 (9)	−0·0012 (9)
C(2)	0·250	0·7157 (3)	1·000	0·052 (2)	0·042 (2)	0·052 (2)	0·000	0·002 (1)	0·000
C(6)	0·250	1·1240 (3)	1·000	0·086 (3)	0·045 (2)	0·075 (2)	0·000	0·013 (2)	0·000
C(7)	0·1470 (2)	1·0774 (2)	0·9520 (2)	0·077 (2)	0·050 (1)	0·067 (2)	0·014 (1)	0·012 (1)	0·004 (1)
C(8)	0·1189 (2)	0·9713 (2)	0·9410 (2)	0·056 (1)	0·053 (1)	0·051 (1)	0·008 (1)	0·008 (1)	−0·001 (1)
C(8A)	0·1884 (2)	0·8844 (2)	0·9733 (2)	0·047 (1)	0·047 (1)	0·042 (1)	0·0020 (9)	0·0070 (9)	−0·0008 (9)
C(9)	0·0355 (2)	0·7445 (2)	0·9151 (2)	0·044 (1)	0·059 (1)	0·061 (1)	−0·001 (1)	0·002 (1)	−0·002 (1)
C(10)	−0·0061 (2)	0·6511 (2)	0·8727 (2)	0·046 (1)	0·058 (1)	0·064 (1)	−0·003 (1)	0·005 (1)	−0·004 (1)
C(11)	0·0534 (2)	0·5588 (2)	0·8441 (2)	0·047 (1)	0·056 (1)	0·046 (1)	−0·004 (1)	−0·0022 (9)	−0·003 (1)
C(12)	0·1427 (2)	0·5672 (2)	0·7931 (2)	0·053 (1)	0·072 (2)	0·054 (1)	−0·004 (1)	0·004 (1)	−0·006 (1)
C(13)	0·1907 (3)	0·4778 (3)	0·7608 (3)	0·064 (2)	0·103 (3)	0·067 (2)	0·009 (2)	0·007 (1)	−0·021 (2)
C(14)	0·1511 (3)	0·3796 (3)	0·7791 (3)	0·094 (2)	0·079 (2)	0·091 (2)	0·022 (2)	−0·003 (2)	−0·026 (2)
C(15)	0·0637 (3)	0·3710 (3)	0·8296 (3)	0·104 (3)	0·057 (2)	0·091 (2)	−0·002 (2)	0·003 (2)	−0·006 (2)
C(16)	0·0143 (2)	0·4590 (2)	0·8605 (2)	0·071 (2)	0·060 (2)	0·062 (1)	−0·011 (1)	0·006 (1)	−0·003 (1)

Table 1 (*cont.*)

	x	y	z	U
H(2)	0·250	0·639 (3)	1·000	0·050 (8)
H(6)	0·250	1·205 (3)	1·000	0·07 (1)
H(7)	0·081 (2)	1·124 (2)	0·920 (2)	0·077 (8)
H(8)	0·033 (2)	0·955 (2)	0·902 (2)	0·064 (7)
H(9)	−0·024 (1)	0·801 (1)	0·919 (1)	0·086 (5)
H(10)	−0·094 (1)	0·643 (1)	0·860 (1)	0·092 (5)
H(12)	0·169 (2)	0·643 (2)	0·779 (2)	0·072 (8)
H(13)	0·254 (3)	0·485 (3)	0·720 (3)	0·11 (1)
H(14)	0·186 (3)	0·314 (3)	0·753 (3)	0·13 (1)
H(15)	0·032 (3)	0·306 (3)	0·841 (3)	0·11 (1)
H(16)	−0·042 (2)	0·454 (2)	0·902 (2)	0·069 (8)

bene (Wallwork, 1961), 1,2-difluoro-*trans*-(4'-bromo-stilbene) (Chetkina & Gol'der, 1967) and 1,2-difluoro-*trans*-(4'-methylstilbene) (Chetkina & Gol'der, 1968). The 122° phenyl–C=C angle in diethylstilbestrol [1,2-diethyl-*trans*-(4',4''-dihydroxystilbene)] (Weeks, Cooper & Norton, 1970) is presumably due to the steric bulk of the ethyl group which limits the opening of this angle. The phenyl–C=C twist angles in the stilbenes range from 63° in diethylstilbestrol down to 3° in *trans*-stilbene itself. In molecules in which the steric crowding is greater than in *trans*-stilbene, both the C–C=C angle
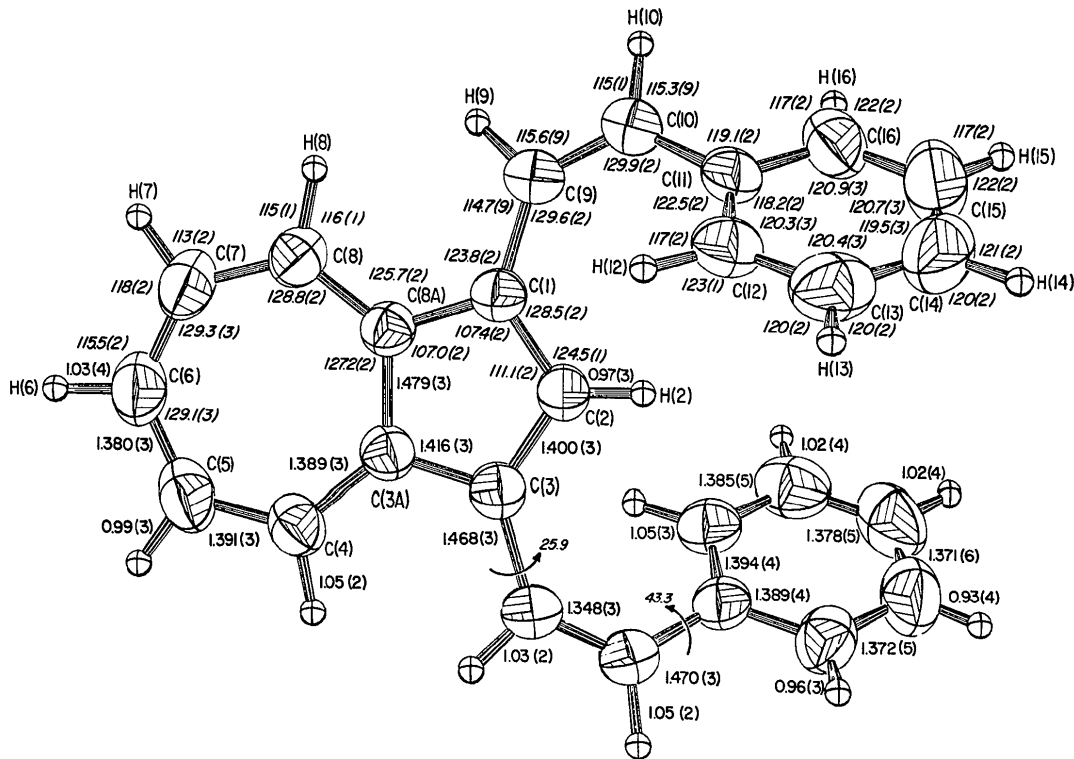
Fig. 1. *ORTEP* drawing with the C atoms represented as 50 % ellipsoids and with 0·1 Å spheres for H. Bond lengths (Å) and angles (°) are superimposed.
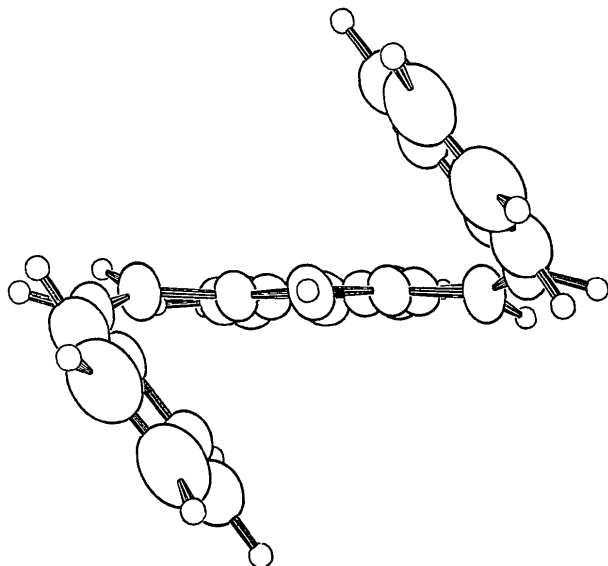
Fig. 2. *ORTEP* view approximately parallel to the twofold axis.

and phenyl–C=C twist distortions are required for strain relief (Harnick, Herbstein, Schmidt & Hirshfield, 1954).

Bond lengths in the azulene ring are normal and in good agreement with other azulenes: *e.g.* azulene–*sym*-trinitrobenzene complex (Hanson, 1965), azulene–1,3-dipropionic acid (Ammon & Sundaralingam, 1966) and azulene [electron diffraction, Bastiansen & Derissen (1966)]. The benzene distances show the typical decrease going from the point of connection, C(11), to the opposite side of the ring, C(14), caused by (uncorrected) thermal-motion effects. The C–C=C–C distances, 1·468–1·348–1·470 Å, have normal values for Csp^2–Csp^2 single and double bonds and are reminiscent of the corresponding lengths in butadiene, 1·463 and 1·341 Å (Kuchitsu, Fukuyama & Morino, 1968). Assuming that *trans,trans*-1,3-bis(styryl)azulene would be almost totally planar and similar to *trans*-stilbene, and that the *cis,trans* isomer would have one planar and one twisted azulyl–C=C–phenyl portion, the structures of the *trans,trans*, *cis,trans* and *cis,cis* compounds agree well with structural ideas deduced from the visible absorption maxima of 693, 673 and 653 nm, respectively. The decrease in azulene···benzene conjugation from the most planar *trans,trans* to the least planar *cis,cis* coincides with 693···653 nm decrease in the visible maxima. The values of δ 8·28 (*trans,trans*),

8·08 (*cis,trans*), and 7·75 ppm (*cis,cis*) assigned to the H(2) chemical shifts in the n.m.r. spectra (LaBar, 1971) also are in agreement with the results of the present study.

None of the intra- or intermolecular contacts are shorter than the corresponding van der Waals distances.

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