In sharp contrast to our findings in the preceding paper no irregularities of any kind can be observed in this structure. The conformation of rings A, B and C is a quite regular chair. The mean angles of puckering are 54·0, 55·1 and 55·0° respectively. Ring D is almost a C(13) envelope. The conformation of ring D is described by the phase angle $\Delta = 24\cdot3°$ and the angle of puckering $\varphi_m = 50\cdot4°$ (Altona, Geise & Romers, 1968). Some Newman projections at important points are shown in Fig. 3.

There is a striking resemblance between the geometry of rings C and D in AOT (preceding paper), EMT and the compound 2β-methyl-3-oxo-oestr-4-en-17β-ol p-bromobenzenesulphonate (Cody & Duax, 1972). A more detailed discussion of this phenomenon can be found in the preceding paper.

The packing of EMT is shown in Table 6. Each molecule is surrounded by 12 nearest neighbours. No remarkably short intermolecular distances were observed.

All calculations were carried out on the IBM 360/65 of the Central Computing Institute of the State University, Leiden.

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Table 6. *Packing of EMT*

I	x	y	z	VIII	$2-x$	$\frac{1}{2}+y$	$1-z$
II	x	y	$1-z$	IX	$2-x$	$\frac{1}{2}+y$	$-z$
III	x	y	$1+z$	X	$2-x$	$\frac{1}{2}-y$	$-z$
IV	$1+x$	y	$1-z$	XI	$2-x$	$\frac{1}{2}-y$	$1-z$
V	$1-x$	y	$1+z$	XII	$1-x$	$\frac{1}{2}-y$	$2-z$
VI	$1-x$	$\frac{1}{2}+y$	$2-z$	XIII	$1-x$	$\frac{1}{2}-y$	$1-z$
VII	$1-x$	$\frac{1}{2}+y$	$1-z$				

Crystal and Molecular Structure of a Dimer C42H28 from 1-Phenyl-3,3-biphenylene-allene

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A dimer from 1-phenyl-3,3-biphenylene-allene, chemical formula $C_{42}H_{28}$, was investigated by X-ray analysis. The space group is Cc with lattice parameters $a = 18\cdot546$, $b = 19\cdot924$, $c = 8\cdot688$ Å, $\beta = 110\cdot07°$ and $Z = 4$. The phase problem was solved by the multisolution method with two reflexions for origin definition and four unrestricted reflexions as variable. The final $R = 3\cdot6\%$, including an isotropic extinction factor in refinement. The compound was identified as 2-phenyl-3-fluorenylidene-4-benzylidene-spiro[cyclobutane-1,9'-fluorene] verifying a head-to-tail dimerization. The cyclobutane ring is nonplanar and shows a remarkable lengthening of one C–C bond to 1·61 Å. The orientation of the benzylidene group gives information about the mechanism of thermal allene dimerization.

## Introduction

The stereochemical course of the thermal dimerization of allenes has been the subject of several investigations during the last few years (Dehmlow & Ezimora, 1972; Jacobs, Byrn, Maverick, Muscio & Trueblood, 1971; Baldwin & Fleming, 1970, and references cited therein).

In this connexion the structures of several allene dimers have been determined. However, the understanding of the stereochemistry and mechanism of the allene dimerization is still incomplete. Further progress requires more definitive information about the structure of allene dimers. In particular, in the case of the dimers of highly substituted aryl-allenes, the conclusive deter-

mination of the structure by chemical methods is very difficult. After some chemical investigations on this subject (Kuhn & Rewicki, 1965; Rewicki, 1966), it was concluded that an X-ray diffraction study on the dimers of unsymmetrically substituted aryl-allenes would give more structural information.

Usually the thermal dimerization of unsymmetrically substituted allenes of formula (A) results in the formation of 1,2-dimethylene-cyclobutanes of the type (B) (head-to-head dimer) or (C) (head-to-tail dimer). It is not known in detail which structural features determine the formation of (B) or (C) type dimers and the stereochemistry at the cisoid butadiene system and at C(3)/C(4). The results obtained in the case of the formation of dimers (B) may be tentatively summarized in the following way: (1) of the different head-to-head dimers the one with the more highly substituted or conjugated allenyl carbon at the exocyclic position will be preferred. (2) The larger substituents at the cisoid butadiene system (R) are directed 'inward' as shown in (B). (3) The substituents X (and Y) are in *trans* positions.

(A) (B) (C)
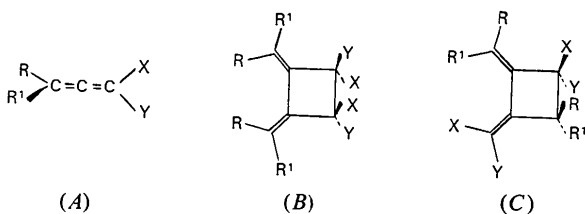
We became interested in the investigation of head-to-tail dimers of type (C). In order to prove the validity of the above-mentioned rules (2) and (3) for dimers of type (C) we started an X-ray analysis.

Head-to-tail dimers, presumably of type (C), are obtained by thermal dimerization of 1-phenyl (or halogeno)-3,3-biphenylene-allenes in high yields (Kuhn & Rewicki, 1965). Spectroscopic results show without doubt that the dimers obtained cannot have the structure (B) of 1,2-bisfluorenylidene-3,4-diphenyl (or dihalogeno)-cyclobutanes as supposed by several authors (Nagase, 1961; Kollmar & Fischer, 1968), but until now the structure of these dimers could not be established definitively. In this paper we report the structure of the yellow dimer obtained as the major product from the dimerization of 1-phenyl-3,3-biphenylene-allene (RR' = biphenylene, X = C_6H_5 and Y = H; formula A).

Experimental

Yellow, blade-like crystals (m.p. 184–186 °C) were obtained by crystallization from ethyl acetate/methanol (Kuhn & Rewicki, 1965). From oscillation and Weissenberg photographs the approximate lattice constants were determined. Systematically absent reflexions hkl for $h + k = 2n$ and $h0l$ for $l = 2n$ and monoclinic Laue symmetry indicated either the space group Cc or $C2/c$;

the cell volume and the experimentally measured density indicated four molecules per unit cell. This favoured the non-centrosymmetric space group because a centrosymmetric molecular conformation was not probable. With an automatic diffractometer (Siemens AED) the precise cell parameters were determined, and the intensities of 2615 reflexions were measured with Ni-filtered Cu $K\alpha$ radiation in a θ range between 4·5° and 70·0°. Of these, 123 had an intensity less than the statistical error and were considered unobserved. The most important crystallographic data are given in Table 1.

Table 1. *Crystallographic data*

Chemical formula	$C_{42}H_{28}$
Molecular weight	$M = 535·2$
Cell parameters	$a = 18·546$ (7) Å
	$b = 19·924$ (8)
	$c = 8·688$ (4)
	$\beta = 110·07$ (3)°
Cell volume	$V = 2997$ Å^3
Density	$D_{exp} = 1·20$ g cm^{-3}
	$D_{calc} = 1·18$ g cm^{-3}
Space group	Cc
Number of molecules per unit cell $Z = 4$	
Absorption coefficient $\mu = 5·2$ cm^{-1} (Cu $K\alpha$)	

Structure determination and refinement

The data reduction and normalization showed an acentric distribution of E values, verifying the space group Cc. This space group is extremely unsuitable for the application of direct methods because it is acentric, and it is centred and allows only two reflexions for origin fixing. In addition, the origin in the x and z directions is not restricted to any special values, and this implies an unfavourable seminvariant modulus. The condition $\left| \dfrac{h_1 l_1}{h_2 l_2} \right| = \pm 1$ [equivalent to the condition given by Karle & Hauptman (1961) for the primitive cell] is a more stringent restriction for the choice of origin-defining reflexions than is usually encountered.

Another difficulty is that space group Cc has very few special reflexions ($0k0$ only), so that the phases which are not used for defining the origin and the enantiomorph have to be varied over the whole 2π-range.

Table 2. *Starting set reflexions*

h	k	l	E	Initial phases (°)	Final phases (°)
5	1	1	2·05	0	35
9	11	2	1·99	0	7
−2	14	4	3·18	45, 135, 225, 315	254
16	0	4	2·90	45, 135, 225, 315	279
0	14	4	2·87	45, 135, 225, 315	1
0	4	1	2·27	45, 135	102

The phase determination was carried out with the program system *MULTAN* (Germain, Main & Woolfson,

1971). The starting reflexions defined by the *CON-VERGE* part of *MULTAN* are listed in Table 2. It was decided to use four variable reflexions in addition to those defining the origin in order to obtain sufficient starting reflexions for the tangent refinement. Therefore it was necessary to carry out 128 trials of phase determination with the *FASTAN* program of *MULTAN*. Unfortunately, no trial led to an R_E value (Karle & Karle, 1966) better than 37%. After this, six attempts with best R_E values were refined with the *TANGEN* link of the X-RAY 70 program system (Hall, 1970). One of these attempts including 327 reflexions with $E > 1.45$ had a significantly better residual (16%) than the rest. In the E map calculated with the phases of this set the 42 highest maxima corresponded to 41 atoms of the molecule, maximum number 40 being incorrect. The first isotropic refinement by the method of least squares (*ORFLS* link of the X-RAY

70 system) led to $R = 14.7\%$ and showed the missing atom.

After introducing anisotropic temperature parameters, R decreased to 7.4%. By means of several difference syntheses, all hydrogen atoms were located and included in refinements with isotropic temperature factors. Because of the remarkable influence of secondary extinction on some strong reflexions, further refinements were carried out with the program *LINUS* (Hamilton & Coppens, 1969) including an isotropic extinction parameter and unit weights. The transmission coefficients and mean path lengths were computed with a modified absorption correction program (Burnham, 1966). The final residual $R = \sum ||F_o| - |e \cdot F_c|| / \sum |F_o|$, where e is the individual extinction coefficient, was 3.6% for the observed reflexions and 3.8% including unobserved reflexions, with an extinction parameter $g = (0.087 \pm 0.01) \times 10^4$ (Zachariasen, 1967).

Table 3. *Fractional atomic coordinates and anisotropic thermal parameters*

The temperature factor expression used was exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The estimated standard deviations are in parentheses. All values for nonhydrogen atoms are $\times 10^4$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−1738 (2)	−7665 (2)	4685 (4)	28 (1)	18 (1)	119 (5)	−1 (1)	17 (2)	−3 (2)
C(2)	−2158 (2)	−7154 (2)	5523 (4)	27 (1)	23 (1)	133 (5)	−1 (1)	20 (2)	−8 (2)
C(3)	−1394 (2)	−6772 (2)	6191 (4)	28 (1)	19 (1)	128 (5)	−2 (1)	13 (2)	−4 (2)
C(4)	−1092 (2)	−7142 (2)	5102 (4)	29 (1)	17 (1)	127 (5)	−2 (1)	14 (2)	−3 (2)
C(5)	−556 (2)	−7003 (2)	4424 (4)	31 (1)	24 (1)	145 (6)	−6 (1)	20 (2)	−2 (2)
C(6)	−301 (2)	−7420 (2)	3337 (4)	28 (1)	28 (1)	127 (5)	−1 (1)	19 (2)	3 (2)
C(7)	70 (3)	−7113 (2)	2373 (6)	49 (2)	40 (2)	183 (7)	−1 (1)	48 (3)	16 (3)
C(8)	352 (3)	−7496 (3)	1389 (6)	57 (2)	51 (2)	185 (7)	1 (2)	63 (3)	11 (3)
C(9)	293 (3)	−8175 (3)	1363 (5)	48 (2)	55 (2)	164 (7)	4 (2)	42 (3)	−14 (3)
C(10)	−61 (3)	−8501 (2)	2329 (6)	49 (2)	35 (2)	214 (8)	−2 (1)	45 (3)	−21 (3)
C(11)	−360 (2)	−8117 (2)	3298 (5)	38 (1)	29 (1)	174 (6)	−4 (1)	34 (2)	−3 (3)
C(12)	−1110 (2)	−6359 (2)	7498 (4)	30 (1)	19 (1)	130 (5)	−0 (1)	14 (2)	0 (2)
C(13)	−315 (2)	−6109 (2)	8327 (4)	32 (1)	19 (1)	143 (5)	−2 (1)	6 (2)	3 (2)
C(14)	372 (2)	−6223 (2)	8046 (5)	30 (1)	24 (1)	203 (7)	−2 (1)	12 (2)	1 (2)
C(15)	1056 (2)	−5946 (2)	9102 (6)	34 (1)	30 (1)	246 (8)	−5 (1)	10 (3)	2 (3)
C(16)	1071 (3)	−5555 (3)	10446 (6)	41 (2)	35 (2)	232 (9)	−13 (1)	−3 (3)	0 (3)
C(17)	397 (3)	−5440 (2)	10739 (5)	56 (2)	28 (1)	173 (7)	−10 (1)	8 (3)	−12 (3)
C(18)	−289 (2)	−5718 (2)	9698 (4)	40 (1)	20 (1)	140 (6)	−2 (1)	8 (2)	2 (2)
C(19)	−1061 (2)	−5713 (2)	9786 (4)	47 (2)	18 (1)	141 (6)	−0 (1)	19 (2)	−4 (2)
C(20)	−1321 (3)	−5410 (2)	10932 (5)	66 (2)	27 (1)	166 (7)	−4 (1)	37 (3)	−13 (3)
C(21)	−2095 (3)	−5492 (2)	10752 (5)	71 (2)	26 (1)	208 (8)	5 (1)	63 (4)	−2 (3)
C(22)	−2589 (2)	−5862 (2)	9458 (5)	52 (2)	28 (1)	200 (7)	6 (1)	52 (3)	3 (3)
C(23)	−2333 (2)	−6163 (2)	8301 (4)	40 (1)	23 (1)	162 (6)	2 (1)	29 (2)	−1 (2)
C(24)	−1555 (2)	−6092 (2)	8482 (4)	38 (1)	18 (1)	132 (5)	2 (1)	18 (2)	1 (2)
C(25)	−2853 (2)	−6785 (2)	4364 (4)	28 (1)	25 (1)	139 (5)	0 (1)	22 (2)	−10 (2)
C(26)	−3547 (2)	−7131 (2)	3663 (5)	29 (1)	29 (1)	188 (6)	−3 (1)	25 (2)	−10 (2)
C(27)	−4193 (2)	−6818 (3)	2615 (5)	28 (1)	40 (2)	214 (8)	−2 (1)	16 (3)	−14 (3)
C(28)	−4163 (2)	−6152 (3)	2245 (5)	36 (2)	39 (2)	197 (8)	8 (1)	1 (3)	1 (3)
C(29)	−3486 (2)	−5799 (2)	2925 (5)	41 (2)	28 (1)	232 (8)	3 (1)	17 (3)	3 (3)
C(30)	−2830 (2)	−6117 (2)	3980 (5)	34 (1)	24 (1)	192 (7)	−2 (1)	13 (2)	−5 (2)
C(31)	−2149 (2)	−7877 (2)	2904 (4)	29 (1)	21 (1)	121 (5)	0 (1)	19 (2)	−4 (2)
C(32)	−2402 (2)	−7481 (2)	1520 (4)	43 (2)	26 (1)	137 (5)	2 (1)	17 (2)	1 (2)
C(33)	−2785 (3)	−7784 (2)	−0 (5)	61 (2)	37 (2)	131 (6)	2 (2)	9 (3)	0 (3)
C(34)	−2898 (3)	−8479 (3)	−104 (5)	63 (2)	34 (2)	151 (7)	−4 (1)	7 (3)	−16 (3)
C(35)	−2631 (2)	−8873 (2)	1287 (5)	49 (2)	26 (1)	167 (6)	−6 (1)	21 (3)	−18 (3)
C(36)	−2251 (2)	−8569 (2)	2796 (4)	29 (1)	22 (1)	144 (5)	−1 (1)	19 (2)	−6 (2)
C(37)	−1884 (2)	−8859 (2)	4456 (4)	28 (1)	20 (1)	155 (6)	−1 (1)	29 (2)	−3 (2)
C(38)	−1808 (2)	−9518 (2)	4982 (5)	40 (1)	21 (1)	195 (7)	−1 (1)	40 (3)	3 (2)
C(39)	−1403 (2)	−9648 (2)	6660 (5)	49 (2)	22 (1)	223 (7)	1 (1)	46 (3)	19 (2)
C(40)	−1110 (2)	−9126 (2)	7758 (5)	43 (2)	34 (1)	167 (7)	−0 (1)	21 (3)	15 (3)
C(41)	−1193 (2)	−8462 (2)	7227 (4)	35 (1)	28 (1)	145 (6)	−4 (1)	19 (2)	3 (2)
C(42)	−1572 (2)	−8340 (2)	5566 (4)	24 (1)	21 (1)	140 (5)	−1 (1)	20 (2)	0 (2)

Table 3 *(cont.)*

	x	y	z	B
H(2)	−0·224 (2)	−0·738 (2)	0·649 (4)	1·1 (6)
H(5)	−0·027 (2)	−0·660 (2)	0·472 (4)	2·5 (8)
H(7)	0·019 (2)	−0·659 (2)	0·245 (5)	4·9 (11)
H(8)	0·053 (2)	−0·722 (2)	0·063 (5)	4·2 (10)
H(9)	0·043 (3)	−0·849 (3)	0·055 (6)	7·2 (15)
H(10)	−0·016 (2)	−0·899 (2)	0·223 (5)	3·6 (9)
H(11)	−0·054 (2)	−0·834 (2)	0·407 (4)	2·1 (8)
H(14)	0·038 (2)	−0·656 (2)	0·708 (4)	2·8 (9)
H(15)	0·152 (3)	−0·610 (3)	0·895 (6)	6·5 (13)
H(16)	0·159 (2)	−0·542 (3)	1·130 (5)	5·2 (12)
H(17)	0·039 (2)	−0·525 (3)	1·159 (5)	4·4 (10)
H(20)	−0·095 (3)	−0·516 (3)	1·197 (5)	5·2 (11)
H(21)	−0·233 (3)	−0·522 (3)	1·152 (6)	6·6 (13)
H(22)	−0·313 (2)	−0·589 (2)	0·925 (4)	3·5 (9)
H(23)	−0·272 (2)	−0·636 (2)	0·730 (4)	2·2 (8)
H(26)	−0·358 (2)	−0·759 (2)	0·383 (4)	2·4 (8)
H(27)	−0·470 (2)	−0·712 (2)	0·120 (4)	2·8 (8)
H(28)	−0·458 (2)	−0·593 (2)	0·153 (5)	4·2 (10)
H(29)	−0·348 (2)	−0·535 (2)	0·268 (4)	3·1 (9)
H(30)	−0·237 (2)	−0·587 (2)	0·455 (4)	2·8 (8)
H(32)	−0·235 (2)	−0·696 (2)	0·156 (4)	2·4 (8)
H(33)	−0·315 (2)	−0·755 (3)	0·890 (5)	4·4 (10)
H(34)	−0·328 (2)	−0·872 (2)	0·874 (5)	4·4 (10)
H(35)	−0·273 (2)	−0·934 (2)	0·121 (4)	1·6 (7)
H(38)	−0·218 (2)	−0·981 (3)	0·402 (5)	5·4 (11)
H(39)	−0·135 (2)	−0·010 (2)	0·702 (5)	4·4 (11)
H(40)	−0·072 (3)	−0·919 (2)	0·893 (5)	5·1 (11)
H(41)	−0·095 (2)	−0·809 (2)	0·800 (4)	2·3 (8)

The form factors used for carbon were taken from *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms from Stewart, Davidson & Simpson (1965). The atom parameters are listed in Table 3.*

Discussion

A stereoscopic plot of the molecule is shown in Fig. 1. The final bond lengths with atom numbering are given in Fig. 2(a), the bond angles between carbon atoms in Fig. 2(b). The mean value of 36 C–C bond distances in the benzenoid rings is 1·388 (11) Å; the value given in parentheses is calculated from the equation $\sigma = |[\sum(\bar{x}-x_i)^2/n]$.

For the 26 C–H bond lengths and the C–C–C bond angles the average values are 1·00 (7) Å and 120 (1)°.

As assumed, the dimer has the head-to-tail form (C), with the two fluorene substituents on opposite sides of the cyclobutane system, one fluorene being connected by a double bond and the other forming a

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30453 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Least-squares planes*

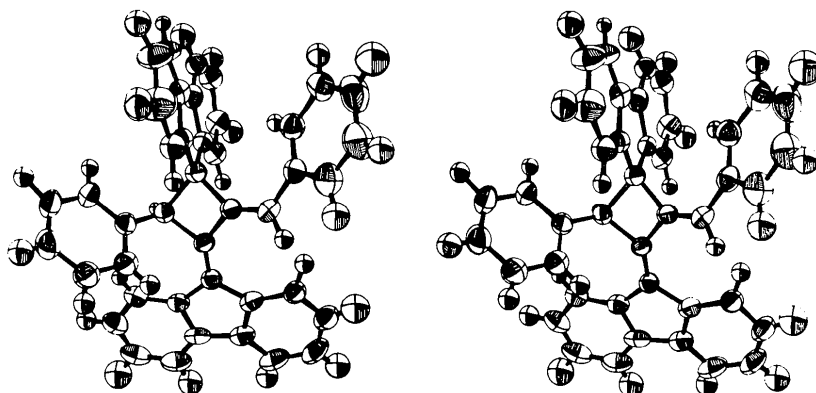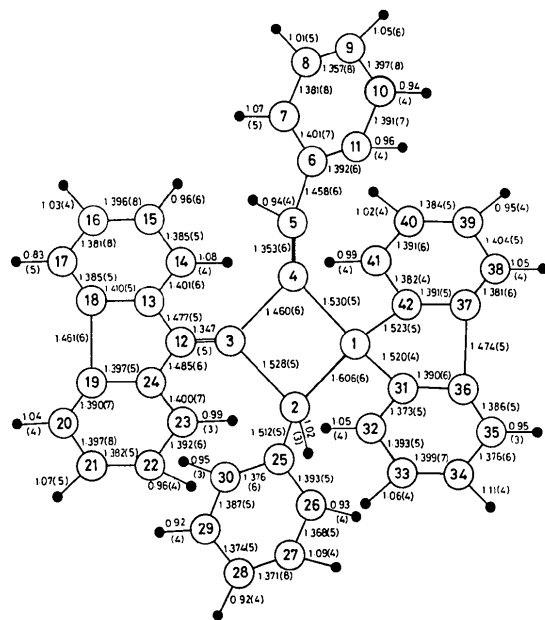| Plane	Defining atoms	Mean deviation from the plane (Å)	Angle with other planes Plane	Angle (°)	Distance to atoms not in plane Atom	Distance (Å)
1	C(1)—C(4)	0·1			C(12)	0·502
					C(5)	0·532
2	C(6)—C(11)	0·007			C(5)	0·082
3	C(13)–C(18)	0·003				
4	C(12), C(13), C(18)	0·002	3	3·3		
	C(19), C(24)		5	1·1		
5	C(19)–C(24)	0·005	3	4·1		
6	C(12)–C(24)	0·04	1	21·9		
7	C(25)–C(30)	0·002			C(2)	0·013
8	C(31)–C(36)	0·006				
9	C(1), C(31), C(36)	0·017	8	2·3		
	C(37), C(42)		10	1·2		
10	C(37)–C(42)	0·009	8	3·4		
11	C(1), C(31)–C(42)	0·035	1	86·6		

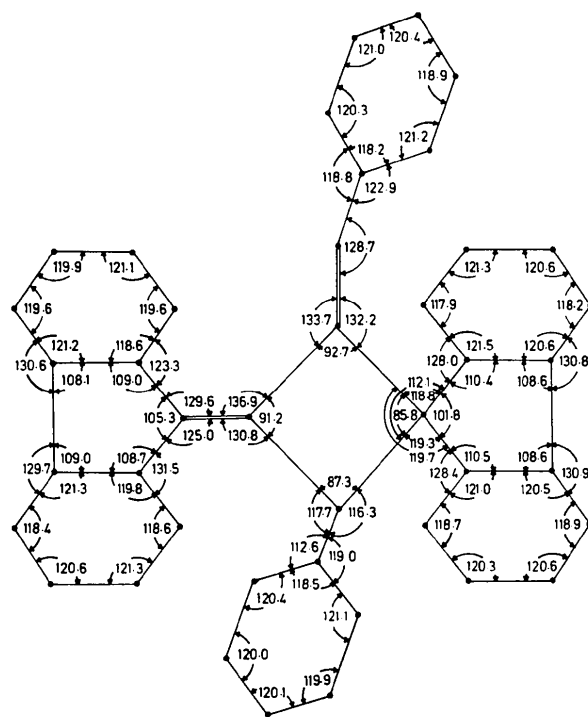

Fig. 1. Stereoscopic plot of the molecule.

spiro[fluorene-cyclobutane] system. The substitution of four relatively large aromatic groups on the cyclobutane ring causes remarkable deformations of the 1,2-dimethylenecyclobutane system. The most significant result is the lengthening of the bond C(1)–C(2) to

(a)

(b)

Fig. 2. (a) Bond lengths and (b) angles (standard deviations in parentheses).

1·61 Å. In agreement with this extreme value even for a cyclobutane single bond, the dimer shows some reactions, e.g. thermal rearrangement and catalytic hydrogenation, including a fission of this weak bond (Rewicki, unpublished).

The cyclobutane ring is not planar (Table 4); the planes defined by C(1), C(2), C(4) and C(2), C(3), C(4) form a roof-like arrangement with an angle of 162°. The cisoid butadiene system also shows significant deviations from the normal geometry. The torsional angle C(5)–C(4)–C(3)–C(12) about the central single bond of the butadiene system has a value of −38°, the torsional angle C(1)–C(4)–C(3)–C(2) is −13·5°. The torsional angles related to the double bonds also differ distinctly from zero (Table 5).

Table 5. Torsional angles

C(1)–C(2)–C(3)–C(4)	12·9°
C(2)–C(3)–C(4)–C(1)	−13·5
C(3)–C(4)–C(1)–C(2)	12·9
C(4)–C(1)–C(2)–C(3)	−12·3
C(5)–C(4)–C(3)–C(12)	−38·2
C(1)–C(4)–C(5)–C(6)	−17·4
C(3)–C(4)–C(5)–C(6)	180·0
C(4)–C(5)–C(6)–C(11)	−24·6
C(2)–C(3)–C(12)–C(24)	−10·2

The large aromatic substituents are arranged in the following way. The fluorenylidene group is turned from the plane defined by the atoms C(2)–C(3)–C(4)–C(12) by about 10° away from the phenyl group at C(2). Both fluorene groups show a slight deviation from planarity caused by an equal-directed inclination of the phenyl rings against the central five-membered ring. The fluorene group at C(1) is not exactly normal to the least-squares plane defined by the cyclobutane ring atoms. The angle on the side of C(2) is enlarged to 94°. This causes a slight twist away from the bulky phenyl group at C(2). The phenyl ring of the benzylidene group is turned by 22·5° from the plane C(4)–C(5)–C(6)–H(5). The phenyl substituent at C(3) is twisted by 53° from the plane defined by the atoms C(2)–C(4)–C(25).

Regarding the mechanism of allene dimerization, the determination of the stereochemistry at the exocyclic benzylidene group is the most important result of this study. The stereochemistry at the cisoid butadiene system is described using the notation of Baldwin & Fleming (1970). The anti orientation obtained for the bulky phenyl group at C(5) is preferred not only in the 1,1-biphenylene-3-phenylallene dimer but also in the corresponding 3-halogenoallene dimers, the structure of which was also determined by X-ray diffraction (Wendling, unpublished). The stereoselective formation of these dimers as the predominant or even exclusive products is incompatible with stereochemical predictions derived through application of the common concept of allene dimerization.

According to this concept the thermal dimerization of allenes is a two-step process with intermediate for-

mation of a perpendicular 2,2'-biallylene biradical (formula D) which distorts subsequently through twisting around the central single bond to form finally the 1,2-bismethylenecyclobutane products by a conrotatory ring closure between two terminal allylic carbons. The stereochemistry observed at the cisoid butadiene system and at the saturated cyclobutane carbons has been rationalized by postulating preferential occupation of the inner positions at both ends of each allylic system in the intermediate (D) by the most bulky substituents (R, X). Consequently, after ring closure the larger substituents should be accommodated in the *syn,syn* configuration at the exocyclic carbons and in the *trans* positions at the saturated cyclobutane carbons.
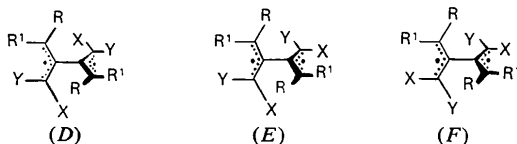
Consideration of our results indicates that the inward orientation assumed for the larger substituents in the 2,2'-biallylene intermediate (formula D) cannot be sustained generally. The exclusive and stereoselective formation of dimers (C) with a bulky phenyl or halogen substituent at the *anti* position on the exocyclic carbon is most plausibly interpreted in terms of intermediates bearing one or two of the larger groups in an outward position of the perpendicular 2,2'-biallylene (formulae E, F). Some recent studies on allene dimers confirm this conclusion (Dehmlow & Ezimora, 1972).

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