Synthesis and X-Ray Diffraction Analysis of Bis(phenylsulphonyl)semibullvalenes. Lifting of the Degeneracy of Semibullvalenes in the Crystal Lattice[1]

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The bicyclo[3.3.0]octanediones **4** and **9a,b** and the [n.3.3]-propellanediones **9c,d,f,h** react with thiophenol in the presence of titanium(IV) chloride and triethylamine to afford high yields of the vinyl sulphides **5** and mixtures of the vinyl sulphides **10/11**. Sodium perborate oxidizes the vinyl sulphides **5** and **10/11** to the corresponding vinyl sulphones **6** and **12/13**. *N*-Bromosuccinimide converts **6** into the dibromodisulfones **7**. The exo,exo configuration of **7b** is established by X-ray crystallography. The mixtures of disulphones **12/13** are brominated by *N*-bromosuccinimide to yield complex mixtures of uncharacterized dibromodisulphones **14**. Debromination of the dibromodisulphones **7**, and the mixtures of **14** as well, by the zinc-copper couple results in the formation of crystalline semibullvalenes **8** and **15** in moderate to high yields. – X-ray diffraction analyses of **8a,b** and **15a–d** reveal large variations of the apparent atomic distances in the cyclopropane rings (C2–C8) and at the open ends of the molecules (C4···C6). This result is interpreted in terms of equilibrating, non-degenerate valence tautomers resulting in averaged atomic distances. The equilibrium constants are calculated from the atomic distances on the basis of a limiting value of 157.8 pm for the C2–C8 bonds of the non-rearranging valence tautomers. The results are compared to those obtained from X-ray diffraction analyses of other substituted semibullvalenes. The lifting of the degeneracy of semibullvalenes in the solid state is attributed to subtle intermolecular interactions.

The extremely fast degenerate Cope rearrangement renders semibullvalene (**1a**) one of the most fascinating members of the $(CH)_8$ hydrocarbon series[2]. After Hoffmann's[3] and Dewar's[4] predictions regarding the influence of substituents on the energy barrier to this rearrangement, substituted semibullvalenes became the targets of numerous synthetic endeavours[5]. While the predicted acceleration of the Cope rearrangement by electron-withdrawing groups at the *allylic part* of the molecule has been confirmed[6,7], the effect of substituents at the *bridgeheads* has received less attention. Günther et al. found recently, that methyl groups at the bridgeheads, as in **1b**, lowered the enthalpy of activation by no fewer than 3.3 $kJmol^{-1}$ [8]. Grohmann et al. eventually reported a dramatic effect when the bridgeheads of the semibullvalene tetraester **2b**[9] were connected by hydrocarbon chains of different length: The size of the annulated ring, formed in this way, determined the fundamental nature of the system. Thus, while **2c–e** and **g** exhibited all the characteristics of a normal semibullvalene, possessing a degenerate double minimum on the energy hypersurface, the hexamethylene-bridged semibullvalene tetraester **2f** was claimed to exist in the symmetric, delocalized structure **3** corresponding to the transition state considered for the degenerate Cope rearrangement[10].

In order to assess the influence of bridgehead substituents and, in particular, of the size of 1,5-annulated rings we embarked on a systematic study involving X-ray diffraction analysis and ^{13}C-NMR spectroscopy of semibullvalenes which differed only in the bridgehead substitution pattern. The existing series of such semibullvalenes, viz. **1**[2,11,12] and **2**[9,10,13], appeared less suitable for this purpose, however, because the series **1** is comprised of sensitive liquids, while the Cope barriers of the crystalline tetraesters **2** are apparently too low for the determination by ^{13}C-NMR spectroscopy. Furthermore, the interaction between the ester groups at the cyclopropane ring of **2**, rendering **2b**[9] and **d**[13] unsymmetrical in the crystalline state, may give rise to conformational changes that may be difficult to distinguish experimentally from a degenerate Cope rearrangement. Therefore, we devised a novel series of semibullvalenes similar to **1** and **2**, but devoid of their drawbacks. We report here on the synthesis and structures of bis(phenylsulphonyl)semibullvalenes **8** and **15**, which are crystalline, stable solids. As expected on the basis of the only moderate electronic effect of the phenylsulphonyl group[14], the Cope barriers of **8** and **15** were still high enough to allow a determination by ^{13}C-NMR spectroscopy[15].

A second feature, besides the hoped-for favourable influence on the properties of the semibullvalenes, made the phenylsulphonyl groups the substituents of choice: They are easily attached when the bicyclo[3.3.0]octane-2,6- **4** and the -3,7-diones **9** are employed as starting materials. The former

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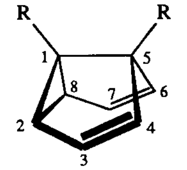

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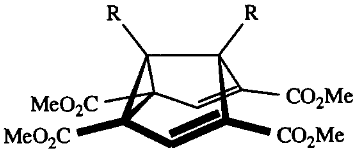

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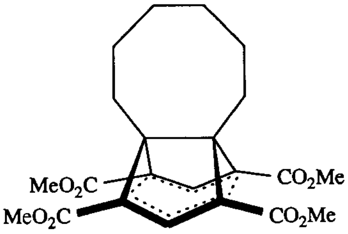
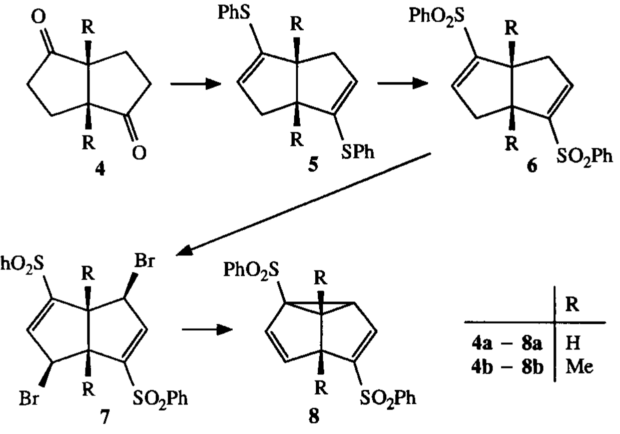


3

		R
1a[2]		H
1b[11]	2b[9]	CH_3

		R-R
	2c[9]	$(CH_2)_3$
1d[11]	2d[13]	$(CH_2)_4$
1e[12]	2e[13]	$(CH_2)_5$
1f[12]	2f[10,13]	$(CH_2)_6$
1g[12]	2g[13]	$(CH_2)_8$
1h[12]		$(CH_2)_{10}$

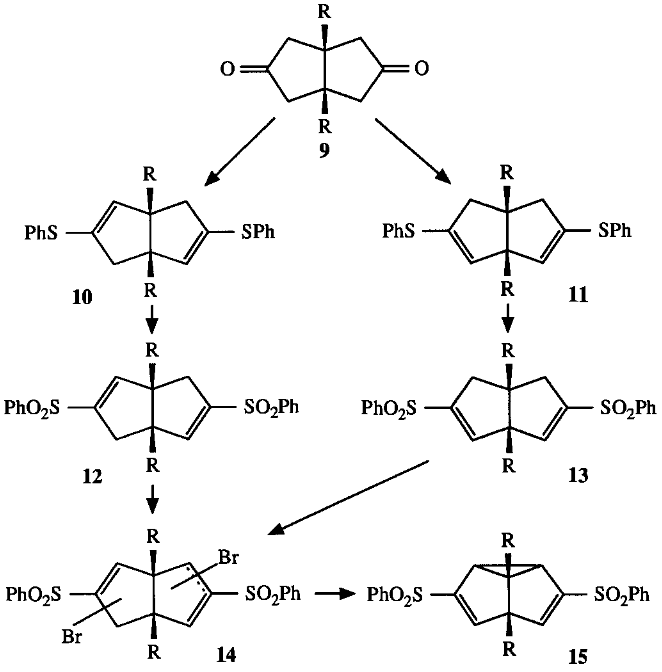
diketones are available by short syntheses involving the Kolbe electrolysis as the key step[16,17] while the latter result from the Weiss reaction[18–21]. The diketones **9b** and **d** have already been converted into mixtures of vinyl phenyl sulphones, viz. **12b**/**13b**[22] and **12d**/**13d**[7], and the corresponding vinyl 4-chlorophenyl sulphones have been obtained from **9c**[23]. The established procedures were now applied to the diketones **4a,b** and **9a,c,f,h**. The excellent method of Mukaiyama and Saigo[24], involving the reaction of a ketone with thiophenol in the presence of titanium(IV) chloride and triethylamine, afforded high yields of the vinyl sulphides **5** and mixtures of the vinyl sulphides **10**/**11**, provided that thiophenol and triethylamine were added very slowly to the solution of the diketone and titanium(IV) chloride in tetrahydrofuran. The vinyl sulphides are colourless low-melting crystals or oils (Table 1), which were purified by flash chromatography on silica gel.



	R
4a – 8a	H
4b – 8b	Me

The oxidation of the vinyl sulphides **5** and **10**/**11** was performed conveniently with sodium perborate in acidic acid[25], giving rise to excellent yields of the sulphones **6** and **12**/**13**, resp., which were isolated as high-melting, colourless crystals (Table 1).

As in the case of the diketones **9b**[22],**c**[21] and **d**[7], the Mukaiyama-Saigo method afforded equal amounts of the regioisomeric vinyl sulphides from the 3,7-diketones **9a,f,h**. The isomeric ratio of **10**/**11** remained unchanged after the oxidation to the sulphones **12**/**13**. Although the regioisomeric vinyl sulphides **10**/**11** and vinyl sulphones **12**/**13** can be separated by medium-pressure liquid chromatography on silica gel[26] or crystallization (**10a**/**11a**), the separation was carried out only on small samples and only to an extent that allowed the assignment of NMR signals in spectra of mixtures to individual isomers (Tables 11–14).



	R
9a – 15a	H
9b – 15b	Me

	R-R
9c – 15c	$(CH_2)_3$
9d – 15d	$(CH_2)_4$
9f – 15f	$(CH_2)_6$
9h – 15h	$(CH_2)_{10}$

Bromination with *N*-bromosuccinimide in dichloromethane of both 2,6-disulphones **6** furnished high yields of dibromides as single stereoisomers for which the gross structure **7** was proved by NMR spectroscopy (Tables 11 and 13). Because the configuration of the brominated carbon atoms could not be inferred by analogy[27], an X-ray diffraction analysis was performed (Tables 2 and 4, Figure 1), which established the *exo,exo* configuration for the bromination product of the disulphone **6b**. The twofold symmetry of **7b** in solution is retained in the crystal. The similarity of the NMR spectra of **7a** and **b** supports the assumption that **7a** also possesses the *exo,exo* configuration.

Bromination by *N*-bromosuccinimide of 3,7-substituted bicyclo[3.3.0]octa-2,6- and -2,7-dienes has inevitably given rise to the formation of hardly separable mixtures of regio- and stereoisomeric mono-, di-, and higher brominated

Table 1. Yields, melting points, and spectroscopic data of the bicyclo[3.3.0]octadiene derivatives **5**–**7**, **10**–**14**, and the semibullvalenes **8** and **15**. The data given for **14** refer to mixtures of isomeric dibromodisulphones. Except for the vinyl sulphones **6** and **12**/**13**, the reported yields were obtained after flash chromatography

Cpd.	Yield [%]	M.p. [°C]	IR (KBr) [cm^{-1}] C=C	IR (KBr) [cm^{-1}] SO$_2$
Vinyl sulphides				
5a	87	oil	1579[a]	
5b	74	60–61	1580	
10a/11a	97	oil	1581[a]	
10c/11c	93	45–46	1581	
10f/11f	89	oil	1579[a]	
10h/11h	87	oil	1580[a]	
Vinyl sulphones				
6a	98	161–162	1619	1303, 1148
6b	91	118–121	1604	1310, 1145
12a/13a	84	195–201	1617, 1582	1303, 1145
12c/13c	96	190–194	1616, 1580	1307, 1154
12f/13f	88	221–228	1621, 1581	1311, 1156
12h/13h	90	211–215	1618, 1582	1315, 1146
7a	86	176–177	1617, 1581	1321, 1145
7b	98	149–151	1612, 1581	1316, 1147
14a	77	185–195		
14b	96	150 (dec.)		
14c	95	230–250		
14d	75	235–250		
14f	53	230–245		
14h	39	225–240		
Semibullvalenes				
8a	92	168–169	1572	1304, 1147
8b	96	160–161	1582	1308, 1150
15a	49	150–152	1578	1309, 1150
15b	70	195 (dec.)	1585	1320, 1150
15c	65	202–203	1580	1318, 1144
15d	80	167–168	1581	1314, 1146
15f	69	192–194	1579	1318, 1149
15h	65	186–187	1579	1303, 1148

	UV (acetonitrile) λ_{max} [nm] (log ε)	
8a	220 (4.285)	247 (4.045)
8b	219 (4.196)	252 (3.923)
15a	222 (4.237)	250 (4.016)
15b	224 (4.062)	258 (3.741)
15c	224 (4.308)	253 (3.968)
15d	224 (4.256)	255 (3.938)
15f	224 (4.189)	259 (3.920)
15h	226 (4.130)	261 (3.762)

[a] Neat liquid.

products[28]. When the bromination of the mixture of isomeric disulphones **12**/**13** was monitored by HPLC, groups of products were detected, for which the number of bromine atoms was inferred on the basis of the order of the appearance. The maximum amount of desired dibromo compounds was obtained when 2.4 equivalents of *N*-bromosuccinimide was employed. Flash chromatography separated the monobromodisulphones and the higher brominated disulphones from the mixtures of dibromodisulphones **14**, which were obtained as almost colourless crystals and converted to the semibullvalenes **15** without characterization.

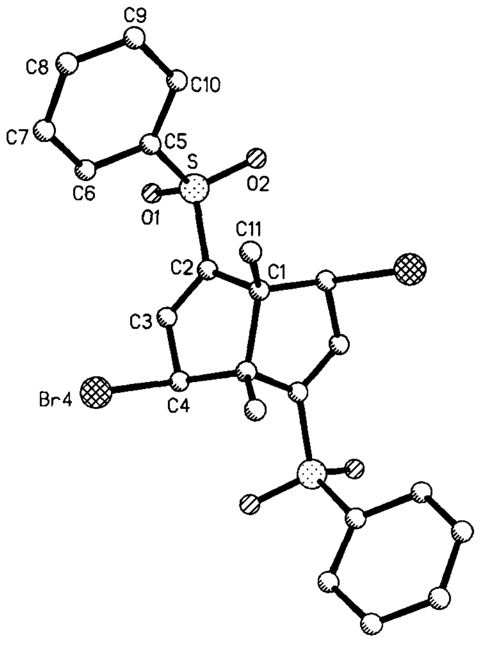


Figure 1. Perspective drawing of the dibromodisulphone **7b** with the labeling of the atoms corresponding to Table 4

The reductive cyclization to semibullvalenes of the dibromo-2,6-disulphones **7** and the mixtures of dibromo-3,7-disulphones **14** was achieved by the zinc-copper couple in tetrahydrofuran at elevated temperatures. Additional copper(I) chloride[29] and ultrasonic irradiation[30] greatly accelerated the reaction, which was monitored by HPLC. Workup of the reaction mixtures could be carried out without the exclusion of atmospheric oxygen, differently from the isolation procedure and handling of many semibullvalenes[6,7]. Thus, high yields of semibullvalenes were obtained in the 2,6-disulphone series **8**, while the yields of the 3,7-disulphonylsemibullvalenes **15** were somewhat lower (Table 1), most probably because of the difficulties encountered in the bromination step. Both types of semibullvalenes formed colourless, air-stable, high-melting crystals. While the bridgehead-substituted compounds **8b** and **15b**–**d**,**f**,**h** are perfectly stable in solution, the semibullvalenes **8a** and **15a**, devoid of a bridgehead substituent, decompose slowly in non-degassed solutions at ambient temperatures.

The structures of the new compounds can be anticipated on the basis of their methods of preparation and are confirmed by elemental analyses (Table 16) and spectroscopic techniques (Table 1, 11–15). ^{13}C-NMR spectra were especially useful for the distinction between bicyclo[3.3.0]octa-2,6-diene and -2,7-diene derivatives having the same substitution pattern, because the former exhibit four, the latter five ^{13}C signals for the bicyclo[3.3.0]octane ring system (Table 14). The different symmetry – on the NMR time scala – of the members of the 2,6- (**10**, **12**) and 2,7-diene series (**11**, **13**), viz. C_2 and C_S, is, of course, also reflected by the number of ^{13}C signals of the methylene bridges, but signal overlap may occur due to the narrowness of the chemical shift range. Be that as it may, the different numbers of ^{13}C signals allowed the assignment of the structure to the major and minor isomer in partially separated mixtures of **10**/**11** and **12**/**13**. With this knowledge at hand, we assigned the proton signals to a particular isomer (Table 12). From the NMR spectra of the bis(phenylsulphonyl)semibullvalenes **8** and **15** it could be immediately deduced that, in solution at ambient temperatures, the degenerate Cope rearrangement is fast on the ^{1}H and ^{13}C time scales. Lowering the temperature resulted in line broadening, coalescence phenomena, and eventually separation into the signals resulting from the ^{13}C atoms of the non-rearranging valence tautomers. In contrast, conformational motion involving the phenylsulphonyl groups remained rapid down to the lowest temperatures used in this study[15].

Anent the stunning report of delocalization in the hexamethylene-bridged semibullvalene tetraester **2f**, suggesting a unique influence of the attached eight-membered ring on the nature of the semibullvalene system[10], we note that the hexamethylene-bridged bis(phenylsulphonyl)semibullvalene **15f** does not show any extraordinary properties.

X-Ray Diffraction Analyses of Semibullvalenes

The solid-state structures of several degenerate semibullvalenes, e.g. **2b**,**d** and **16a**–**f**, have been investigated by X-ray diffraction analyses. Surprisingly, at first glance, the atomic distance C2–C8 in the cyclopropane ring and the distance C4···C6 at the open end of the molecules varied over a wide range (Table 3). It was of interest, therefore, to study the solid-state structures of the present series with a view to uncovering structural relationships and the preferred conformations of the phenylsulphonyl groups as well. Experimental details and results of the X-ray diffraction analyses are compiled in Table 2. The numbering of the atoms is shown in Figures 2–4. Atomic parameters are given in Tables 5–10.

Table 2. Experimental details and results of the X-ray diffraction analyses of the dibromodisulphone **7b** and the bis(phenylsulphonyl)-semibullvalenes **8a**,**b** and **15a**–**d**. For atomic parameters see Tables 4–10

Cpd.	7b	8a	8b	15a	15b	15c	15d
Molecular formula	$C_{22}H_{20}Br_2O_4S_2$	$C_{20}H_{16}O_4S_2$	$C_{22}H_{20}O_4S_2$	$C_{20}H_{16}O_4S_2$	$C_{22}H_{20}O_4S_2$	$C_{23}H_{20}O_4S_2$	$C_{24}H_{22}O_4S_2$
Molecular mass	572.34	384.46	412.52	384.46	412.52	424.53	438.56
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/a$	$P2_1/n$	$P2_1$
a [pm]	2041.7(5)	2699.8(6)	1357.8(4)	2022.8(5)	2373.6(8)	2406.1(7)	1209.3(5)
b [pm]	1158.4(3)	866.1(2)	1338.5(3)	817.8(1)	782.4(4)	775.0(2)	783.7(5)
c [pm]	1036.2(2)	786.2(2)	1109.6(2)	1097.8(3)	1117.9(4)	1117.1(2)	1141.9(9)
β [°]	112.28(2)	94.10(2)	97.25(2)	97.75(2)	103.46(3)	102.09(2)	93.13(5)
V [pm^3] • 10^{-6}	2267.7(9)	1833.8(7)	2000.1(8)	1799.5(7)	2019(2)	2037.7(8)	1081(1)
Z	4	4	4	4	4	4	2
d(calcd) [g cm^{-3}]	1.676	1.392	1.370	1.419	1.357	1.384	1.347
Size of crystal [mm]	0.4x0.55x0.2	0.4x0.8x0.3	0.75x0.8x0.7	0.2x0.8x0.15	0.75x0.75x0.15	0.5x0.75x0.15	0.6x0.6x0.05
Range (h)	0 – 26	0 – 35	0 – 17	0 – 26	0 – 30	0 – 31	0 – 15
(k)	0 – 15	0 – 11	0 – 17	0 – 10	0 – 10	0 – 10	0 – 10
(l)	–13 – 12	–10 – 10	–14 – 14	–14 – 14	–14 – 14	–14 – 14	–14 – 14
No. of measured reflections	2939	4620	5179	4570	5110	5166	2764
Symmetry-independent reflections	2622	4246	4631	4164	4662	4834	2661
Observed reflections $F>3\sigma(F)$	1731	3589	4084	2770	3355	3474	2244
Linear absorpt. coeff. [mm^{-1}]	3.74	0.30	0.28	0.30	0.28	0.28	0.26
Absorption correction	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan
Ratio $F_{obs.}$/parameters	12.64	15.21	16.08	11.74	13.21	13.26	8.31
R	0.070	0.046	0.051	0.066	0.086	0.055	0.082
R_w	0.057	0.044	0.050	0.054	0.080	0.051	0.072
Diff. Four. $\Delta\rho_{max}$[*] [eÅ^{-3}]	0.73	0.25	0.28	0.30	2.48	0.64	0.55
$\Delta\rho_{min}$[**]	–0.47	–0.27	–0.26	–0.30	–0.35	–0.31	–0.51

[*] Maximum and [**] minimum of the remaining electron density in the final differential Fourier synthesis.

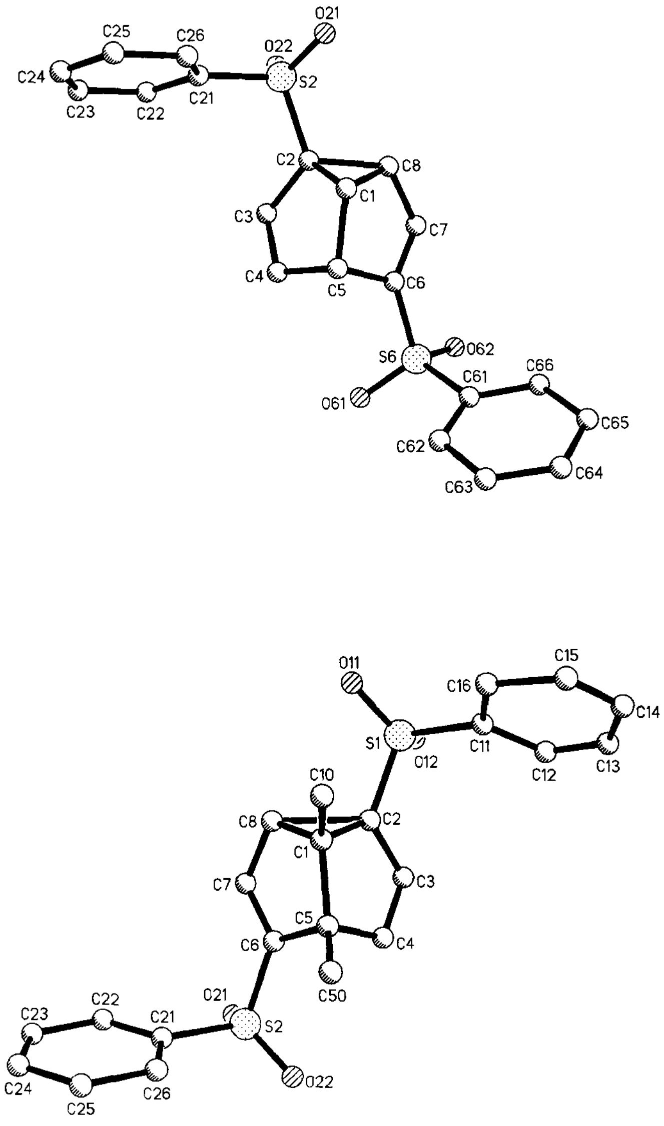


Figure 2. Perspective drawings of the 2,6-bis(phenylsulphonyl)-semibullvalenes **8a** (above) and **8b** (below) showing the numbering of the atoms

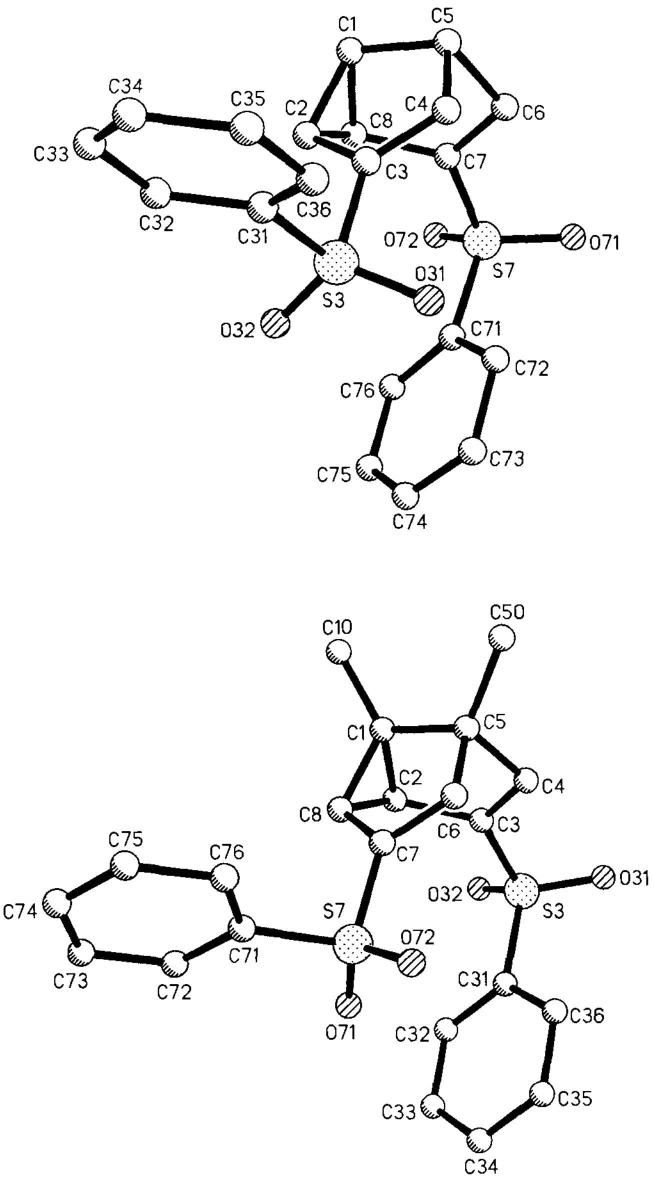


Figure 3. Perspective drawings of the 3,7-bis(phenylsulphonyl)semibullvalenes **15a** (above) and **15b** (below) showing the numbering of the atoms

Conformations of the Phenylsulphonyl Groups

Of the two drawings of 2,6-bis(phenylsulphonyl)semibullvalenes **8** shown in Figure 2, only that of **8a** represents a realistic picture of an isolated molecule; that of **8b** is the averaged representation of two non-equivalent valence tautomers (see below) and, therefore, inappropriate for the discussion of the conformations of the phenylsulphonyl groups. As shown by the perspective drawings of the 3,7-bis(phenylsulphonyl)semibullvalenes **15a**–**d** (Figures 3, 4), the substituents at the bridgeheads hardly influence the conformations of the phenylsulphonyl groups, if at all. In the semibullvalenes **8a** and **15a**–**d**, and the dibromodisulphone **7b** as well, the phenylsulphonyl groups that are attached to a carbon-carbon double bond adopt conformations in which the formal p-orbital at the planar carbon atom is more or less eclipsing the sulphur-phenyl bond and bisecting the angle between the oxygen atoms. In the 3,7-bis(phenylsulphonyl)semibullvalene series **15a**–**d**, these conformations are realized in two ways, which result in unsymmetrical structures with one phenyl group pointing to the *exo*, the other to the *endo* face of the molecule. Apparently, minimization of the repulsion between the sulphonyl groups is mainly responsible for the observed unsymmetry of **15a**–**d** in the solid state.

Atomic Distances of Semibullvalenes and Equilibria Between Non-Equivalent Valence Tautomers in the Solid State

The atomic distances C2–C8 and C4···C6 of semibullvalenes that undergo a degenerate Cope rearrangement in solution are interesting because they are more than others changed during the rearrangement. While these distances are found in narrow ranges in the 3,7-series **15a**–**d**, they differ dramatically in the 2,6-bis(phenylsulphonyl)semibull-

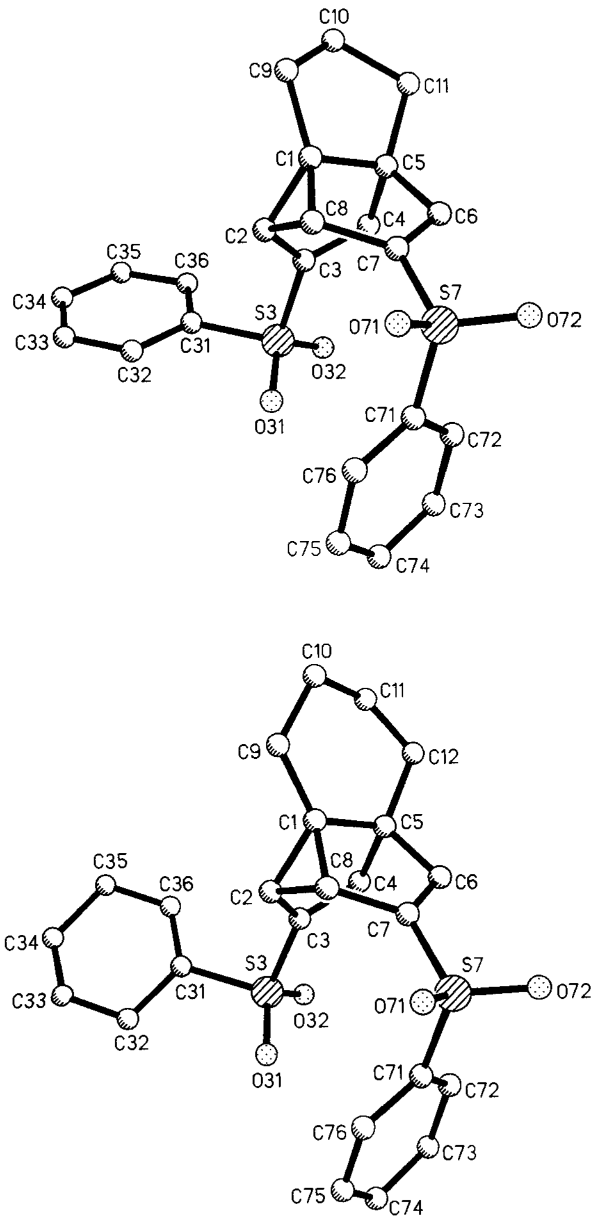


Figure 4. Perspective drawings of the 1,5-bridged 3,7-bis(phenylsulphonyl)semibullvalenes **15c** (above) and **15d** (below) showing the numbering of the atoms

valenes **8a** and **b**. A similarly broad range of bonding distances C2–C8 and non-bonding distances C4···C6 has been found already by X-ray crystallography of other substituted semibullvalenes (Table 3). Only recently, however, the true cause of the enormous variation of apparent geometric parameters was recognized for the semibullvalene dicarbonitriles **16a** and **b** by means of solid-state ^{13}C-NMR spectroscopy: The atomic distances, as observed by X-ray crystallography, are in fact average values originating from *non-equivalent* valence tautomers, which are interconverted by a fast (non-degenerate) Cope rearrangement. Thus, the degeneracy, as observed in solution, is lifted by intermolecular forces in the crystal lattice[31]. Though unequivocal evidence has been offered hitherto only for **16a** and **b**, it seems reasonable to rationalize unusual atomic distances of other semibullvalenes in the same way. On this basis, atomic distances that obviously are average values may be used to estimate the ratio of the non-equivalent valence tautomers A $\rightleftharpoons$ B in the solid state. Let p be the mole fraction of B, and $(\mathrm{C2-C8})_{\mathrm{A}}$, $(\mathrm{C4\cdots C6})_{\mathrm{B}}$ the limiting distances of the non-rearranging valence tautomers A and B, then the average distance $(\mathrm{C2-C8})_{\mathrm{aver.}}$ and the equilibrium constant K are given by the equations (1) and (2).

$$(\mathrm{C2-C8})_{\mathrm{aver.}} = p(\mathrm{C4\cdots C6})_{\mathrm{B}} + (1-p)(\mathrm{C2-C8})_{\mathrm{A}} \qquad (1)$$

$$\begin{aligned} K[\mathrm{B}]/[\mathrm{A}] &= p/(1-p) \qquad (2)\\ &= [(\mathrm{C2-C8})_{\mathrm{aver.}} - (\mathrm{C2-C8})_{\mathrm{A}}]/\\ &\quad [(\mathrm{C4\cdots C6})_{\mathrm{B}} - (\mathrm{C2-C8})_{\mathrm{aver.}}] \end{aligned}$$

The limiting values $(\mathrm{C2-C8})_{\mathrm{A}}$ and $(\mathrm{C4\cdots C6})_{\mathrm{B}}$ may be estimated with the help of the non-degenerate semibullvalenes **17**[6] and **18**[32] which exist virtually as single valence tautomers. Though their substitution pattern is totally different, **17** and **18** possess equal cyclopropane bond lengths C2–C8. Precisely the same size of this bond length is now found for the degenerate semibullvalene **8a** (Table 3). On the other hand, the non-bonding distances C4···C6 of **17** [229.9(6) pm][6], **18** [235.2(3) pm][32], and **8a** [234.8(4) pm] differ significantly. Apparently, the substitution pattern mainly influences the length of the non-bonding distance C4···C6 at the open end of the molecules rather than the cyclopropane bond C2–C8 which hence may be assumed constant at 157.8 pm. It goes without saying that the atomic distances are averaged properties of molecules in the particular crystal lattice. The *sum of the atomic distances* C2–C8 + C4···C6, however, may be regarded as a property of a single molecule. This sum, therefore, has the same value for each of the non-equivalent valence tautomers A and B, and, of course, for their average representation as well (Table 3) [equation (3)].

$$\begin{aligned} (\mathrm{C2-C8})_{\mathrm{aver.}} + (\mathrm{C4\cdots C6})_{\mathrm{aver.}} &= (\mathrm{C2-C8})_{\mathrm{A}} + (\mathrm{C4\cdots C6})_{\mathrm{A}}\\ &= (\mathrm{C2-C8})_{\mathrm{B}} + (\mathrm{C4\cdots C6})_{\mathrm{B}} \qquad (3) \end{aligned}$$

From (2) and (3) follows

$$K \approx [(\mathrm{C2-C8})_{\mathrm{aver.}} - 157.8]/[(\mathrm{C4\cdots C6})_{\mathrm{aver.}} - 157.8] \qquad (4)$$

The equilibrium constants $K = [\mathrm{B}]/[\mathrm{A}]$ calculated from the average distances by equation (4) are given in Table 3.

The majority of limiting non-bonding distances C4···C6, which are based on the assumption of a constant length of the cyclopropane bond C2–C8 (157.8 pm), is found in the range of 227–235 pm. Only for the tetraesters **2b** and **16f**, and both forms of the 2,6-dicarbonitrile **16a** as well, limiting non-bonding distances around 240 pm are calculated. These values are probably somewhat too high because the influence of strong electron acceptor groups that are attached to the cyclopropane ring[35] in fact lengthens the cyclopropane bond C2–C8 beyond 157.8 pm. According to equation (3), this would lead to a shorter limiting non-bonding distance C4···C6 and, according to equation (4), to a somewhat smaller equilibrium constant.

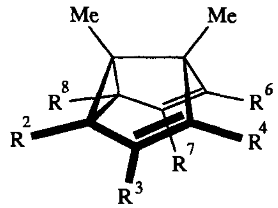
Table 3. Experimental atomic distances $(C2-C8)_{aver.}$ and $(C4\cdots C6)_{aver.}$, their sum [equation (3)], limiting distances C4···C6, calculated for the non-equivalent valence tautomers A and B (see text), and equilibrium constant $K = [B]/[A]$ for non-equivalent valence tautomers in the crystal, estimated by means of equation (4)

Cpd.	$(C2-C8)_{aver.}$	$(C4\cdots C6)_{aver.}$	C2–C8 + C4···C6	C4···C6[a]	B : A	Ref.
2b	178.2(5)	221	399	241	24 : 76[b]	[9]
2d	182.8					[13]
8a	157.8(3)	234.8(4)	393	234.8	<1 :>99	this work
8b	185.4(4)	206.6(5)	392	234.2	36 : 64	this work
15a	159.8(6)	225.6(8)	385	227.6	3 : 97	this work
15b	159.7(7)	225.3(9)	385	227.2	3 : 97	this work
15c	161.7(4)	228.5(5)	390	232.4	5 : 95	this work
15d	159.4(12)	226.4(14)	386	228.0	2 : 98	this work
16a (α-form)	172.2(3)	224.9(4)	397	239.3	18 : 82[b]	[6]
16a (β-form)	199.0(4)	199.6(4)	399	240.8	50 : 50	[31]
16b	183.5(3)	204.8	388	230.5	35 : 65	[33]
16b (173 K)	170.6(7)	218.6	389	231.4	17 : 83	[33]
16c	159.6(3)	227.7	387	229.5	3 : 97	[33]
16d	161.0(7)	227.8	389	231.0	4 : 96	[28]
16e	186.5(10)	186.5(10)	373	215	50 : 50	[28]
16f	164.4	234.7	399	241.3	8 : 92[b]	[34]

[a] Limiting values for the non-equivalent valence tautomers A and B as calculated by equation (3) on the basis of the approximation $(C2-C8)_A \approx (C2-C8)_B \approx 157.8$ pm. – [b] The equilibrium constant is probably somewhat too high, because electron acceptor substituents at the cyclopropane ring extend the length of the C2–C8 bond beyond the assumed limiting value of 157.8 pm. For example, a limiting value of 160.0 pm yields $K = 16:84$ for the α-form of **16a**.

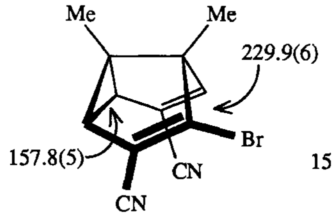
Early attempts to correlate atomic distances of semibullvalenes with the barriers to the degenerate Cope rearrangement in solution have met with failure, because the average nature of the atomic distances had not been recognized[36]. However, as pointed out above, the sum of the cyclopropane bond length C2–C8 and the non-bonded distance C4···C6 can be regarded as a molecular property. It comes to no surprise, therefore, that for the semibullvalene tetraesters **2b**, **16f** and the dicarbonitrile **16a**, which rearrange most rapidly, this sum attains significantly higher values (397–399 pm) than for the slower rearranging semibullvalenes (385–393 pm).

The semibullvalenes **8a, 15a–d, 16c,d** and **f**, which have quite different substitution patterns, exist in the crystal by more than 90% as single valence tautomers because the degeneracy of the Cope rearrangement, observed in solution, is lifted by intermolecular forces, resulting in a considerable free enthalpy difference between the interconverting valence tautomers. This free enthalpy difference is smaller for **2b**, **8b, 16b** and the α-form of **16a** and eventually approaches zero for **16e** and the β-form of **16b** which, at ambient temperature, are degenerate also in the solid state. Because the intermolecular forces that lift the degeneracy depend on the particular geometrical arrangement of several molecules in the crystal, correlations with molecular properties such as substitution pattern cannot be expected. On the other hand, X-ray crystallography and solid-state ^{13}C-NMR spectroscopy of semibullvalenes, both at variable temperatures and combined with computer-based methods of displaying crystal lattices[37], may be used to probe the subtle nature of such intermolecular forces.

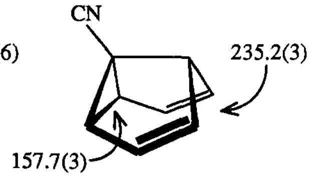


16

	R^2	R^4	R^6	R^8	R^3, R^7
16a	CN	H	CN	H	H
16b	H	H	H	H	CN
16c	H	H	H	H	CO_2Me
16d	Br	Br	H	H	CN
16e	Br	H	Br	H	CN
16f	CO_2Me	CO_2Me	CO_2Me	CO_2Me	OAc



17[6]



18[32]

Unfortunately, we were unable to obtain crystals suitable for X-ray crystallography of the hexamethylene-bridged semibullvalene **15f**, which is related to the hexamethylene-bridged semibullvalene tetraester **2f**, allegedly existing as the delocalized species **3**[10]. The semibullvalene **15f**, however, behaved in every respect exactly as the other members **15a–d** and **h** of this series.

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Experimental

Yields, melting points, and spectroscopic data: Table 1; ^{1}H NMR: Tables 11 and 12; ^{13}C NMR: Tables 13 and 14. – Melting points: Sealed capillary tubes, apparatus from Büchi, Flawil, Switzerland. – IR: Perkin-Elmer 1420 spectrometer. – ^{1}H NMR : Bruker AC 200

(0.153 Hz/pt.), AC 250 (0.305 Hz/pt.), and WM 400 (0.215 Hz/pt.) spectrometer. In order to resolve close signals and small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation[38]. Spectra of higher order were analysed by standard methods[39] and simulated with the help of the PANIC programme. – ^{13}C NMR: Bruker AC 200 and AC 250 spectrometer. – Low-resolution 70-eV MS: Spectrometer 8200 of Finnigan MAT. – UV: Hitachi U 3200 spectrometer.

High performance liquid chromatography (HPLC): Bruker LC 21 chromatograph equipped with a Knauer (Berlin) UV/Vis detector No. 87.00 (λ = 254 nm) and a (250 × 4.6) mm stainless steel column packed with Nucleosil 100, 3 μm (Bischoff, Leonberg); 2 ml/min petroleum ether (50–70°C) (PE)/ethyl acetate (EA) (70:30), retention times t_R [min] = 2.6 (**7a**), 4.6/5.5/6.3 (**14a**), 7.0 (**8a**), 8.9 (**6a**), 13.3 (**12a**), 15.0 (**13a**), 16.3 (**15a**); PE/EA (80:20), t_R = 6.9 (**7b**), 7.3/8.0/9.9 (**14b**), 9.4/10.8/11.8 (**14d**), 10.4 (**8b**), 13.5 (**6b**), 14.5/15.0/16.5 (**14c**), 14.9 (**12d**), 15.2 (**15d**), 16.0 (**13d**), 16.3 (**12b**), 17.5 (**15b**), 17.6 (**13b**), 18.2 (**12c**), 18.3 (**15c**), 19.0 (**13c**); PE/EA (85:15), t_R = 8.0/8.4/11.2/12.8 (**14h**), 13.8 (**12h**), 14.2 (**15h**), 14.6 (**13h**), 14.7/15.2/17.6 (**14f**), 21.6 (**15f**), 21.8 (**12f**), 22.6 (**13f**). – Preparative medium-pressure liquid chromatography: (260 × 28) mm glass column packed with reversed-phase material Europrep 60 C18, 60 Å, 20–45 μm (Knauer), equipped with a Knauer UV/Vis detector No. 87.00 (λ = 254 nm), 50 ml/min methanol/water (85:15), 13 bar, t_R = 6.1–11.0 (**15h**). – Flash chromatography: (45 × 4) cm glass column packed with silica gel 32–63 μm (ICN-Biomedicals), PE/EA, 1.8 bar, Knauer UV/Vis detector No. 87.00 (λ = 254 nm).

Tetrahydrofuran was distilled under Ar from sodium/potassium alloy, triethylamine under N_2 from $LiAlH_4$. The following compounds were prepared according to procedures reported in the literature: *Bicyclo[3.3.0]octane-2,6-dione* (**4a**)[17]; *1,5-dimethylbicyclo[3.3.0]octane-2,6-dione* (**4b**)[16]; *bicyclo[3.3.0]octane-3,7-dione* (**9a**)[20]; *tricyclo[3.3.3.0^{1,5}]undecane-3,7-dione* (**9c**)[23]; *tricyclo[6.3.3.0^{1,8}]tetradecane-10,13-dione* (**9f**) and *tricyclo[10.3.3.0^{1,12}]octadecane-14,17-dione* (**9h**)[40]; *1,5-dimethyl-3,7-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene* (**12b**) and *1,5-dimethyl-3,7-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,7-diene* (**13b**)[22]; *8,11-bis(phenylsulphonyl)tricyclo[4.3.3.0^{1,6}]dodeca-7,10-diene* (**12d**) and *8,11-bis(phenylsulphonyl)tricyclo[4.3.3.0^{1,6}]dodeca-7,11-diene* (**13d**)[7].

Vinyl Sulphides **5** *and* **10/11**. *General Procedure:* Under N_2, titanium(IV) chloride (40 g, 0.21 mol) was added dropwise within 20 min to a stirred, cooled (0–10°C) solution of the diketone **4** or **9** (0.1 mol) in tetrahydrofuran (250 ml). The brick-red suspension was vigorously stirred and kept at 20–25°C while a solution of triethylamine (42.5 ml, 0.42 mol) and thiophenol (23 ml, 0.21 mol) in tetrahydrofuran (35 ml) was added very slowly (within 24 h) from a dropping funnel which was equipped with a needle valve. When a drop hit the surface, a deep red colour appeared which faded rapidly. Stirring was continued for 36 h. The reaction mixture was cooled with ice/water and a saturated aqueous solution of potassium carbonate (400 ml) was added, followed by cyclohexane (400 ml). The organic layer was decanted from the white slimy residue, which was washed and extracted with cyclohexane (3 × 200 ml). The combined organic solutions were extracted with saturated aqueous solutions of potassium carbonate (2 × 0.5 l) and potassium dihydrogen phosphate (3 × 0.5 l), 0.5 M aqueous sodium hydroxide (0.5 l), and water (3 × 0.5 l) and dried with sodium sulphate. The solvent was distilled under vacuum, and the residue was purified by flash chromatography on silica gel with PE/EA (99:1).

2,6-Bis(phenylthio)bicyclo[3.3.0]octa-2,6-diene (**5a**) was obtained from **4a** as a colourless oil (28.1 g, 87%).

1,5-Dimethyl-2,6-bis(phenylthio)bicyclo[3.3.0]octa-2,6-diene (**5b**), obtained from **4b**, formed colourless crystals (25.8 g, 74%), m.p. 60–61°C.

3,7-Bis(phenylthio)bicyclo[3.3.0]octa-2,6-diene (**10a**) and *3,7-Bis(phenylthio)bicyclo[3.3.0]octa-2,7-diene* (**11a**) were obtained from **9a** as a 1:1 mixture which formed a colourless oil (31.2 g, 97%).

3,7-Bis(phenylthio)tricyclo[3.3.3.0^{1,5}]undeca-2,6-diene (**10c**) and *3,7-Bis(phenylthio)tricyclo[3.3.3.0^{1,5}]undeca-2,7-diene* (**11c**) were obtained from **9c** as a 1:1 mixture which formed colourless crystals (33.6 g, 93%), m.p. 45–46°C.

10,13-Bis(phenylthio)tricyclo[6.3.3.0^{1,8}]tetradeca-9,12-diene (**10f**) and *10,13-Bis(phenylthio)tricyclo[6.3.3.0^{1,8}]tetradeca-9,13-diene* (**11f**) were obtained from **9f** as a 1:1 mixture which formed a colourless oil (36.0 g, 89%).

14,17-Bis(phenylthio)tricyclo[10.3.3.0^{1,12}]octadeca-13,16-diene (**10h**) and *14,17-Bis(phenylthio)tricyclo[10.3.3.0^{1,12}]octadeca-13,17-*

Table 4. Atomic parameters (× 10^4) and equivalent isotropic thermal displacement parameters U_{equiv} (× 10^{-1}) [pm^2] for the dibromodisulphone **7b**. The parameters U_{equiv} are defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
S	-870(1)	3737(2)	-545(2)	62(1)
Br(4)	-1479(1)	1966(1)	-5192(1)	100(1)
O(1)	-1356(2)	4688(3)	-1078(5)	79(2)
O(2)	-256(2)	3892(4)	731(4)	83(2)
C(1)	-2(3)	2439(4)	-1735(5)	44(2)
C(2)	-591(3)	3288(4)	-1883(5)	46(2)
C(3)	-937(3)	3634(5)	-3188(6)	58(3)
C(4)	-705(3)	3059(5)	-4182(5)	54(2)
C(5)	-1356(3)	2552(5)	-310(6)	58(3)
C(6)	-1933(3)	2136(6)	-1418(7)	71(3)
C(7)	-2325(4)	1249(7)	-1218(9)	86(4)
C(8)	-2165(4)	778(7)	48(10)	93(5)
C(9)	-1596(5)	1172(7)	1167(8)	93(4)
C(10)	-1178(4)	2082(6)	999(7)	74(3)
C(11)	-148(3)	1267(5)	-1210(6)	67(3)

Table 5. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, for 2,6-bis(phenylsulphonyl)semibullvalene (**8a**)

	x	y	z	U(eq)
S(2)	273(1)	1889(1)	7558(1)	53(1)
S(6)	1840(1)	-3379(1)	6266(1)	66(1)
C(1)	1186(1)	911(3)	6287(3)	60(1)
C(2)	774(1)	599(3)	7425(3)	53(1)
C(3)	989(1)	-177(3)	8970(3)	58(1)
C(4)	1463(1)	-514(3)	8822(3)	61(1)
C(5)	1607(1)	-180(3)	7032(3)	60(1)
C(6)	1468(1)	-1720(3)	6148(3)	63(1)
C(7)	1003(1)	-1708(3)	5485(3)	74(1)
C(8)	788(1)	-141(3)	5595(3)	72(1)
O(21)	198(1)	2687(2)	5957(2)	70(1)
O(22)	-134(1)	1018(2)	8154(2)	66(1)
C(21)	479(1)	3220(3)	9147(3)	50(1)
C(22)	411(1)	2896(3)	10849(3)	65(1)
C(23)	573(1)	3954(4)	12070(3)	79(1)
C(24)	796(1)	5295(4)	11598(4)	84(1)
C(25)	861(1)	5605(3)	9926(4)	85(1)
C(26)	702(1)	4563(3)	8671(3)	65(1)
O(61)	2088(1)	-3460(2)	7941(2)	87(1)
O(62)	1543(1)	-4665(2)	5634(3)	90(1)
C(61)	2295(1)	-3007(3)	4827(3)	57(1)
C(62)	2730(1)	-2287(3)	5392(3)	68(1)
C(63)	3087(1)	-2041(4)	4257(5)	91(1)
C(64)	3005(1)	-2480(4)	2599(5)	102(2)
C(65)	2570(1)	-3175(4)	2034(4)	104(2)
C(66)	2210(1)	-3447(4)	3147(3)	82(1)

diene (**11h**) were obtained from **9h** as a 1:1 mixture which formed a colourless oil (40.0 g, 87%).

Vinyl Sulphones **6** *and* **12/13**. *General Procedure:* A stirred solution of a vinyl sulphide **5** or **10/11** (20 mmol) in acetic acid (150 ml) was kept at (65 ± 2)°C. Sodium perborate tetrahydrate (18.5 g, 120 mmol) was added in portions within 1 h, and the solution was stirred at this temp. for 3.5 h. The white suspension was cooled to 20−25°C and diluted with water (200 ml). The precipitate was filtered off, washed carefully with water and dried under vacuum over powdered potassium hydroxide to yield a colourless powder.

2,6-Bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**6a**): 8.13 g (98%).

Table 6. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, 1,5-dimethyl-3,7-bis(phenylsulphonyl)semibullvalene (**8b**)

	x	y	z	U(eq)
S(1)	7209(1)	7232(1)	1479(1)	59(1)
S(2)	6923(1)	3522(1)	-2067(1)	65(1)
O(11)	6837(1)	6888(2)	2568(2)	80(1)
O(12)	6623(1)	7924(1)	694(2)	75(1)
O(21)	6022(2)	3812(1)	-2801(2)	92(1)
O(22)	7830(2)	3511(1)	-2603(2)	89(1)
C(1)	7708(2)	5159(2)	1043(2)	53(1)
C(2)	7434(2)	6191(2)	583(2)	60(1)
C(3)	7658(2)	6329(2)	-598(2)	54(1)
C(4)	8035(2)	5463(2)	-1000(3)	83(1)
C(5)	8059(2)	4644(2)	-102(2)	53(1)
C(6)	7081(2)	4295(2)	-774(2)	62(1)
C(7)	6296(2)	4564(2)	-213(2)	60(1)
C(8)	6628(2)	5118(3)	855(2)	90(1)
C(10)	8291(2)	4978(2)	2269(2)	83(1)
C(11)	8392(2)	7771(2)	1884(2)	55(1)
C(12)	8752(2)	8418(2)	1086(3)	73(1)
C(13)	9673(2)	8846(2)	1422(3)	93(1)
C(14)	10215(2)	8605(3)	2509(3)	90(1)
C(15)	9864(2)	7945(2)	3282(3)	83(1)
C(16)	8934(2)	7526(2)	2981(2)	67(1)
C(21)	6740(2)	2320(2)	-1474(2)	55(1)
C(22)	5792(2)	1950(2)	-1474(2)	68(1)
C(23)	5675(2)	1001(2)	-1028(3)	77(1)
C(24)	6479(2)	433(2)	-598(2)	75(1)
C(25)	7415(2)	810(2)	-592(3)	75(1)
C(26)	7555(2)	1758(2)	-1026(2)	65(1)
C(50)	8949(2)	3953(2)	98(3)	80(1)

Table 7. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, for 3,7-bis(phenylsulphonyl)semibullvalene (**15a**)

	x	y	z	U(eq)
S(3)	1915(1)	5349(1)	956(1)	52(1)
S(7)	81(1)	1856(1)	2769(1)	57(1)
C(1)	706(2)	1736(5)	-590(3)	62(2)
C(2)	839(2)	3472(5)	-260(3)	53(1)
C(3)	1516(2)	3520(4)	448(3)	43(1)
C(4)	1769(2)	2037(5)	686(3)	53(1)
C(5)	1255(2)	752(5)	224(4)	61(2)
C(6)	981(2)	515(5)	1419(3)	57(1)
C(7)	459(2)	1520(4)	1453(3)	48(1)
C(8)	283(2)	2412(5)	285(3)	55(1)
O(31)	2392(1)	4991(4)	2013(2)	74(1)
O(32)	1410(2)	6572(3)	1023(3)	71(1)
C(31)	2369(2)	5886(5)	-261(3)	51(1)
C(32)	2046(3)	6717(5)	-1257(4)	73(2)
C(33)	2411(4)	7122(7)	-2192(5)	105(3)
C(34)	3074(3)	6716(8)	-2110(6)	110(3)
C(35)	3382(3)	5867(7)	-1116(5)	99(3)
C(36)	3029(2)	5451(6)	-187(4)	73(2)
O(71)	333(2)	664(3)	3672(3)	79(1)
O(72)	-624(1)	1943(5)	2405(3)	99(2)
C(71)	367(2)	3790(5)	3289(3)	50(1)
C(72)	1027(3)	4003(6)	3708(4)	74(2)
C(73)	1237(3)	5537(8)	4173(5)	104(3)
C(74)	774(4)	6769(8)	4174(6)	115(3)
C(75)	124(4)	6530(7)	3760(5)	106(3)
C(76)	-86(3)	5049(6)	3301(3)	76(2)

Table 8. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, for for 1,5-dimethyl-2,6-bis(phenylsulphonyl)semibullvalene (**15b**)

	x	y	z	U(eq)
S(3)	2815(1)	4551(2)	6119(1)	56(1)
S(7)	1156(1)	1220(2)	3245(1)	53(1)
C(1)	1073(2)	5285(7)	5472(4)	50(2)
C(2)	1636(2)	5557(7)	5145(4)	53(2)
C(3)	2074(2)	4600(7)	6070(4)	49(2)
C(4)	1832(2)	3657(7)	6808(4)	55(2)
C(5)	1177(2)	3732(7)	6392(4)	53(2)
C(6)	1111(2)	2193(7)	5559(5)	55(2)
C(7)	1102(2)	2662(6)	4411(4)	49(2)
C(8)	1118(2)	4533(7)	4269(4)	53(2)
C(10)	676(2)	6729(7)	5598(5)	69(2)
O(31)	3104(2)	3934(6)	7315(3)	78(2)
O(32)	2975(2)	6182(5)	5713(4)	73(2)
C(31)	2894(2)	3015(6)	5029(4)	46(2)
C(32)	2986(2)	3541(7)	3923(4)	52(2)
C(33)	3066(2)	2330(8)	3080(5)	60(2)
C(34)	3057(2)	649(8)	3337(6)	66(2)
C(35)	2963(3)	109(8)	4453(6)	74(3)
C(36)	2876(2)	1316(7)	5303(5)	64(2)
C(50)	842(2)	3716(8)	7391(5)	73(2)
O(71)	1639(1)	1722(5)	2764(3)	63(1)
O(72)	1125(2)	-480(5)	3704(4)	76(2)
C(71)	530(2)	1582(7)	2087(5)	54(2)
C(72)	564(3)	2455(9)	1058(5)	80(3)
C(73)	69(3)	2689(11)	133(6)	103(4)
C(74)	-446(3)	2083(11)	276(7)	102(4)
C(75)	-479(3)	1227(11)	1301(7)	101(4)
C(76)	6(3)	959(9)	2210(6)	78(3)

Table 9. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, for 1,5-trimethylene-3,7-bis(phenylsulphonyl)semibullvalene (**15c**)

	x	y	z	U(eq)
S(3)	1105(1)	9261(1)	3356(1)	51(1)
S(7)	2822(1)	5958(1)	6070(1)	48(1)
O(31)	1601(1)	8874(3)	2876(2)	66(1)
O(32)	1028(1)	10962(3)	3788(2)	73(1)
O(71)	2983(1)	4302(3)	5673(2)	65(1)
O(72)	3112(1)	6601(3)	7242(2)	70(1)
C(1)	1125(1)	5166(4)	5650(2)	45(1)
C(2)	1128(1)	5912(4)	4418(2)	46(1)
C(3)	1088(1)	7794(4)	4544(2)	47(1)
C(4)	1120(1)	8292(4)	5708(2)	53(1)
C(5)	1237(1)	6733(4)	6542(2)	46(1)
C(6)	1874(1)	6853(4)	6861(2)	47(1)
C(7)	2096(1)	5914(3)	6087(2)	40(1)
C(8)	1664(1)	4903(3)	5234(2)	44(1)
C(9)	724(1)	3934(4)	6090(3)	60(1)
C(10)	452(2)	5075(6)	6907(3)	93(2)
C(11)	885(1)	6358(5)	7513(3)	62(1)
C(31)	507(1)	8740(4)	2203(2)	48(1)
C(32)	578(1)	7747(5)	1221(3)	63(1)
C(33)	110(2)	7370(5)	304(3)	81(2)
C(34)	-417(2)	7992(6)	389(3)	85(2)
C(35)	-484(2)	8966(5)	1363(4)	84(2)
C(36)	-19(1)	9356(4)	2289(3)	64(1)
C(71)	2892(1)	7503(3)	4944(2)	42(1)
C(72)	2839(1)	9227(4)	5176(3)	56(1)
C(73)	2923(1)	10420(4)	4313(3)	66(1)
C(74)	3055(1)	9868(4)	3232(3)	63(1)
C(75)	3102(1)	8144(4)	3003(3)	60(1)
C(76)	3020(1)	6940(4)	3864(2)	49(1)

1,5-Dimethyl-2,6-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**6b**): 7.02 g (91%).

Table 10. Atomic parameters (× 10^4) and equivalent isotropic displacement parameters U_{equiv} (× 10^{-1}) [pm^2], as defined in Table 4, for 1,5-tetramethylene-3,7-bis(phenylsulphonyl)semibullvalene (**15d**)

	x	y	z	U(eq)
S(3)	7502(2)	1091	3457(2)	51(1)
S(7)	10723(2)	4392(4)	1624(2)	57(1)
O(31)	8454(4)	1469(9)	4200(5)	62(2)
O(32)	7381(5)	-611(9)	2992(5)	70(2)
O(71)	11025(5)	5985(10)	2131(6)	76(2)
O(72)	11302(5)	3750(11)	624(5)	84(3)
C(1)	7391(7)	5116(12)	1171(7)	49(3)
C(2)	7492(6)	4363(13)	2387(6)	53(3)
C(3)	7462(7)	2547(12)	2270(7)	51(3)
C(4)	7460(7)	1994(12)	1131(7)	58(3)
C(5)	7615(7)	3533(12)	351(6)	52(3)
C(6)	8871(6)	3455(12)	377(6)	53(3)
C(7)	9334(6)	4401(12)	1221(6)	48(2)
C(8)	8471(6)	5390(11)	1827(6)	49(3)
C(9)	6581(7)	6426(14)	772(8)	70(3)
C(10)	5981(12)	6019(26)	-322(12)	170(9)
C(11)	6183(16)	4662(27)	-966(13)	218(12)
C(12)	6941(7)	3475(16)	-823(7)	68(4)
C(31)	6293(6)	1580(11)	4194(7)	51(3)
C(32)	6398(8)	1674(20)	5427(8)	97(5)
C(33)	5416(11)	2055(20)	5996(10)	112(6)
C(34)	4445(10)	2147(17)	5396(14)	99(6)
C(35)	4365(9)	1998(20)	4226(13)	105(6)
C(36)	5299(7)	1672(16)	3649(9)	82(4)
C(71)	10853(6)	2815(12)	2723(6)	46(3)
C(72)	10762(8)	1149(14)	2415(8)	69(3)
C(73)	10917(8)	-73(14)	3299(9)	81(4)
C(74)	11120(7)	480(14)	4464(9)	70(4)
C(75)	11163(8)	2133(14)	4752(8)	66(4)
C(76)	11034(6)	3350(13)	3900(7)	54(3)

Table 11. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton spectra recorded from [D]trichloromethane solutions

Cpd.	1–H	3–H	4–H	4–H'	$^2J_{4,4'}$	$^3J_{3,4}$	$^3J_{3,4'}$	Me	Ph
2,6-Substituted Bicyclo[3.3.0]octa-2,6-diene Derivatives									
5a[a]	3.36	5.55	2.41 – 2.65		17.3	2.3	2.3		7.1–7.7
5b		5.45	2.14	2.65	17.1	2.0	3.1	1.16	7.1–7.5
6a[b]	3.01	6.18	2.11	2.65	19.2	2.5	2.5		6.8–7.1 7.6–7.7
6b		6.43	2.23	2.95	18.8	2.2	3.1	1.14	7.4–7.9
7a[c]	3.86	6.71	5.48			2.5			7.5–7.8 7.9–8.0
7b		6.63	5.72			2.9		1.27	7.5–8.0
2,6-Bis(phenylsulphonyl)semibullvalenes									
8a[d]	3.52	5.85	4.99			4.2			7.5–7.9
8b		5.78	4.95			4.3		1.16	7.4–8.0

[a] $^3J_{1,8} = 3$, $^4J_{1,4} = 3$, $^3J_{1,8'} = 8$, $^4J_{1,4'} = 3$ Hz. – [b] Solvent [D_6]benzene, the coupling constants were determined from decoupled 400-MHz spectra. $^3J_{1,8} = 3.5$, $^4J_{1,4} = 3.5$, $^3J_{1,8'} = 7$, $^4J_{1,4'} = 4$ Hz. – [c] The coupling constants were determined from decoupled 200-MHz spectra. $^3J_{1,8} = 2$, $^4J_{1,4'} = 2$, $^3J_{1,3} = 0.5$, $^4J_{3,5} = 1$ Hz. – [d] The coupling constants were determined from decoupled 200-MHz spectra. $^3J_{1,8} = 3$, $^4J_{1,4} = 2$ Hz.

Table 12. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton spectra recorded from [D]trichloromethane solutions

Cpd.	CH_2		1-H	=CH				$(CH_2)_n$	Ph
	H_A	H_B	H_M	H_X	$^2J_{AB}$	$^4J_{AX}$	$^4J_{BX}$		
3,7-Substituted Bicyclo[3.3.0]octa-2,6-diene Derivatives[a]									
10a	2.25	2.4–2.7	3.41	5.39	16.1	[b]	[b]		7.1–7.5
10c	2.44	2.47		5.66	16.8	1.9	2.1	1.6–1.7	7.2–7.4
10f	2.31	2.44		5.47	16.1	1.8	1.7	1.2–1.8	7.2–7.6
10h	2.25	2.38		5.32	15.9	1.7	1.5	1.2–1.6	6.9–7.4
12a[c]	2.42	2.7–2.9	3.67	6.58	16.4	1.8	1.4		7.5–7.9
12c	2.51	2.63		6.60	16.6	1.8	1.9	1.4–1.9	7.5–7.9
12f	2.25	2.53		6.49	16.5	1.8	1.6	1.1–1.7	7.4–7.9
12h	2.13	2.47		6.50	16.2	1.8	1.5	1.2–1.7	7.4–7.9
3,7-Substituted Bicyclo[3.3.0]octa-2,7-diene Derivatives[d]									
11a	2.11	2.4–2.7	3.04[e] 3.73	5.49	16.3	[b]	[b]		7.1–7.5
11c	2.34	2.52		5.60	16.7	1.8	2.1	1.6–1.7	7.2–7.4
11f	2.24	2.64		5.36	16.3	0.8	2.1	1.2–1.8	7.2–7.6
11h	2.27	2.46		5.32	16.2	0.4	2.1	1.2–1.6	6.9–7.4
13a[f]	2.25	2.7–2.9	3.25 4.05	6.41	16.6	2.0	1.7		7.5–7.9
13c	2.49	2.55		6.51	17.0	2.2	1.7	1.4–1.9	7.5–7.9
13f	2.39	2.79		6.23	17.1	0.3	1.7	1.1–1.8	7.4–7.9
13h	2.40	2.63		6.30	16.8	0.4	1.6	1.2–1.7	7.4–7.9
3,7-Bis(phenylsulphonyl)semibullvalenes									
	CH								
15a[g]	4.74		3.38[h]						7.5–7.8
15b	4.65							1.11 (Me)	7.5–7.8
15c[g]	4.76							1.47, 1.74[i]	7.5–7.8
15d[g]	4.64							1.31, 1.58	7.5–7.8
15f[g]	4.69							0.8–1.7	7.5–7.8
15h	4.67							1.2–1.7	7.4–7.8

[a] The solution used for recording the proton spectrum contained also the isomeric bicyclo[3.3.0]octane-2,7-diene derivative. – [b] The coupling constants were not determined. – [c] The coupling constants were determined from decoupled 200-MHz spectra. $^3J_{AM} = 2.5$, $^4J_{A,M'} = 2.5$, $^3J_{B,M} = 7$, $^4J_{B,M'} = 4.5$ Hz. – [d] The solution used for recording the proton spectrum contained also the isomeric bicyclo[3.3.0]octane-2,6-diene derivative. – [e] $^3J_{M,N} = 8$ Hz. – [f] The coupling constants were determined from decoupled 200-MHz spectra. $^3J_{A,M} = 4$, $^3J_{B,M} = 8$, $^3J_{M,N} = 8$, $^3J_{N,X} = 2.5$ Hz. – [g] Solvent [D_2]dichloromethane/[D_6]acetone (4:1), 400-MHz. – [h] $^3J_{M,X} = 3$, $^4J_{M',X} = 2$ Hz. – [i] $^3J = 7$ Hz.

3,7-Bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**12a**) and *3,7-Bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,7-diene* (**13a**) (1:1): 6.97 g (84%). The 1:1 mixture was recrystallized four times from

Table 13. ^{13}C chemical shifts from [D]trichloromethane solutions

Cpd.	C-1	C-2	C-3	C-4	Me	*ipso*-C	*o, m*-C	*p*-C
2,6-Substituted Bicyclo[3.3.0]octa-2,6-diene Derivatives								
5a	50.2	138.1	129.7	36.7		133.9	129.0 131.6	127.1
5b	60.1	143.5	130.2	41.5	21.0	135.9	128.8 130.9	126.7
6a	48.5	144.7	142.3	37.0		139.3	127.7 129.2	133.6
6b	60.7	148.6	142.9	40.3	20.1	140.9	127.6 129.1	133.4
7a	49.1	144.3	140.8	58.9		137.7	128.4 129.7	134.4
7b	63.3	148.8	141.6	55.2	20.2	139.7	128.1 129.6	134.2
2,6-Bis(phenylsulphonyl)semibullvalenes								
8a	54.6	111.3	125.6	93.0		139.4	128.1 129.4	134.0
8b	66.2	112.7	125.2	95.7	12.1	140.5	127.9 129.2	133.6

EA to afford pure **12a** (HPLC, NMR) as colourless prisms (m.p. 218°C).

3,7-Bis(phenylsulphonyl)tricyclo[3.3.3.0^{1,5}]undeca-2,6-diene (**12c**) and *3,7-Bis(phenylsulphonyl)tricyclo[3.3.3.0^{1,5}]undeca-2,7-diene* (**13c**) (1:1): 8.12 g (96%).

10,13-Bis(phenylsulphonyl)tricyclo[6.3.3.0^{1,8}]tetradeca-9,12-diene (**12f**) and *10,13-Bis(phenylsulphonyl)tricyclo[6.3.3.0^{1,8}]tetradeca-9,13-diene* (**13f**) (1:1): 8.24 g (88%).

14,17-Bis(phenylsulphonyl)tricyclo[10.3.3.0^{1,12}]octadeca-13,16-diene (**12h**) and *14,17-Bis(phenylsulphonyl)tricyclo[10.3.3.0^{1,12}]octadeca-13,17-diene* (**13h**) (1:1): 9.43 g (90%).

Bromination of the Vinyl Sulphones **6** *and* **12**/**13** *with N-Bromosuccinimide. General Procedure:* To a solution of a vinyl sulphone **6** or **12**/**13** (5 mmol) in dichloromethane (300 ml) was added *N*-bromosuccinimide (1.98 g, 12 mmol). The mixture was placed just above a 250-W daylight lamp (Philips ML, held in a vertical position) and irradiated at reflux temperature. The reaction ran to completion within 2 (**12f**/**13f**) to 5 h (**12a**/**13a**), as monitored by HPLC. The cold reaction mixture was diluted with dichloromethane (200 ml), extracted with 0.5 M aqueous sodium hydroxide (100 ml) and a saturated aqueous solution of sodium chloride (2 × 100 ml) and dried with sodium sulphate. The solvent was distilled under vacuum and the residue purified by flash chromatography on silica gel with PE/EA 60:40 (**7a,b**), 65:35 (**14a–d**), or 70:30 (**14f,h**) yielding pale brown to colourless crystals.

Table 14. ^{13}C chemical shifts from [D]trichloromethane solutions

Cpd.	C		CH	$\overset{\text{S}}{\text{C}}$	CH	(CH$_2$)$_n$					*ipso*-C	*o, m*-C		*p*-C
3,7-Substituted Bicyclo[3.3.0]octa-2,6-diene Derivatives[a]														
10a	48.6		40.6	135.72	134.05						134.44	127.01	131.36	128.93
10c	67.9		48.4	133.89	137.7	26.3	40.7				133.61	128.92	131.28	127.00
10f	60.2		49.6	134.10	141.6	24.97	25.31	32.4			133.87	128.91	131.29	126.91
10h	61.0		45.4	132.14	140.5	23.32	24.00	26.30	27.33	33.48	134.17	128.20	130.84	126.70
12a	48.9		34.9	143.42	143.56						139.40	127.89	129.30	133.73
12c	68.4		42.1	141.97	142.50	25.95	39.84				138.93	127.81	129.28	133.68
12f	61.1		40.0	149.52	140.22	24.61	24.71	31.28			138.97	127.84	129.23	133.63
12h	62.1		39.8	148.82	141.36	22.87	23.61	26.05	26.93	32.31	138.97	127.67	129.22	133.62
3,7-Substituted Bicyclo[3.3.0]octa-2,7-diene Derivatives[b]														
11a	39.9	58.4	43.3	133.69	134.05						133.50	127.15	131.36	128.93
11c	59.4	76.2	50.7	133.08	135.8	25.7	37.8	41.8			133.84	128.92	131.28	127.05
11f	54.2	67.4	45.8	132.97	139.29	23.37 24.97	25.21	26.15	26.53	34.0	136.01	128.91	131.84	127.19
11h	55.3	68.0	47.4	133.14	135.31	21.26 21.68	22.95 23.53	24.97 26.68	27.05 27.42	31.52 33.33	137.59	128.05	131.48	126.71
13a	40.6	58.2	38.3	139.43	139.29						138.85	127.93	129.30	133.73
13c	60.7	76.1	45.0	143.52	145.24	25.20	36.30	41.49			138.93	127.77	129.28	133.68
13f	56.4	67.3	43.7	142.82	144.41	23.04 25.32	25.86	26.14	30.37	32.20	138.97	127.71	129.23	133.63

Table 14 *(Continued)*

Cpd.	C	CH	$\overset{\text{S}}{\overset{\vert}{\text{C}}}$	CH	$(CH_2)_n$					*ipso*-C	*o*, *m*-C		*p*-C
13h	58.1 67.7	42.2	143.88	143.06	21.81 22.21	23.22 23.39	24.90 26.28	26.76 26.94	29.82 33.24	138.97	127.77	129.22	133.62
3,7-Bis(phenylsulphonyl)semibullvalenes													
15a	51.4	87.4	138.69							139.19	127.6	129.4	133.6
15b	62.0	92.3	136.7		14.7 (Me)					139.4	127.7	129.3	133.5
15c	70.8	89.7	138.2		26.4	30.2				139.4	127.6	129.3	133.5
15d	62.4	92.4	137.6		19.6	25.1				139.5	127.7	129.3	133.5
15f	66.7	92.7	136.4		25.3	26.9	27.9			139.5	127.6	129.4	133.5
15h	67.2	92.2	136.4		23.6	24.3	26.3	26.8	28.2	139.6	127.4	129.3	133.3

[a] The solution used for recording the spectrum contained also the isomeric bicyclo[3.3.0]octane-2,7-diene derivative. — [b] The solution used for recording the spectrum contained also the isomeric bicyclo[3.3.0]octane-2,6-diene derivative.

4,8-Dibromo-2,6-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**7a**) formed pale yellow crystals (2.28 g, 86%). — MS: *m/z* (%) = 546, 544, 542 (2, 6, 3) [M$^+$], 465, 463 (6, 5) [M$^+$ − Br], 384 (2) [M$^+$ − 2 Br], 259 (11), 243 (1) [M$^+$ − 2 Br − $C_6H_5SO_2$], 178 (4), 125 (100), 118 (17).

4,8-Dibromo-1,5-dimethyl-2,6-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**7b**) formed pale yellow crystals (2.80 g, 98%). Crystals suitable for X-ray crystallography were obtained from dichloromethane. — MS: *m/z* (%) = 574, 572, 570 (3, 5, 2) [M$^+$], 493, 491 (7, 7) [M$^+$ − Br], 412 (12) [M$^+$ − 2 Br], 271 (21) [M$^+$ − 2 Br − $C_6H_5SO_2$], 146 (33), 145 (28), 130 (72), 129 (57), 128 (44), 125 (100), 115 (36).

4,8-Dibromo-3,7-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**14a**) *and Isomers* formed beige crystals (2.09 g, 77%).

4,8-Dibromo-1,5-dimethyl-3,7-bis(phenylsulphonyl)bicyclo[3.3.0]octa-2,6-diene (**14b**) *and Isomers* formed colourless crystals (2.75 g, 96%).

4,8-Dibromo-3,7-bis(phenylsulphonyl)tricyclo[3.3.3.0^{1,5}]undeca-2,6-diene (**14c**) *and Isomers* formed yellow-brown crystals (2.75 g, 95%).

9,12-Dibromo-8,11-bis(phenylsulphonyl)tricyclo[4.3.3.0^{1,6}]dodeca-7,10-diene (**14d**) *and Isomers* formed beige-yellow crystals (2.23 g, 75%).

11,14-Dibromo-10,13-bis(phenylsulphonyl)tricyclo[6.3.3.0^{1,8}]tetradeca-9,12-diene (**14f**) *and Isomers* formed light brown crystals (1.25 g, 53%).

15,18-Dibromo-14,17-bis(phenylsulphonyl)tricyclo[10.3.3.0^{1,12}]octadeca-13,16-diene (**14h**) *and Isomers* formed beige crystals (1.27 g, 39%).

Bis(phenylsulphonyl)semibullvalenes **8** *and* **15**. *General Procedure:* A brominated disulphone **7** or **14** (3 mmol) was dissolved under Ar in tetrahydrofuran (300 ml). Zinc-copper couple (1.5 g) and copper(I) chloride (347 mg, 3.5 mmol) were added, and the mixture was heated under reflux for 0.5 h under ultrasonic irradation while the conversion was monitored by HPLC. The mixture was cooled to 20−25°C, diluted with ether (200 ml), filtered through a 5-cm layer of kieselguhr, extracted with a saturated aqueous solution of sodium chloride, and dried with sodium sulphate. Vacuum distillation of the solvent afforded a dark yellow to brown residue which was purified by flash chromatography on silica gel with PE/EA 50:50 (**8a**), 60:40 (**8b, 15b−d**), 65:35 (**15a**), or 70:30 (**15f,h**).

2,6-Bis(phenylsulphonyl)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**8a**) was obtained as a pale yellow powder (1.05 g, 92%). Crystals suitable for X-ray crystallography were obtained from ethyl acetate.

1,5-Dimethyl-2,6-bis(phenylsulphonyl)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**8b**) was obtained as a colourless powder (1.18 g, 96%). Crystals suitable for X-ray crystallography were obtained from dichloromethane.

3,7-Bis(phenylsulphonyl)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**15a**) was obtained as a pale yellow powder (563 mg, 49%). Crystals suitable for X-ray crystallography were obtained from [D]trichloromethane.

1,5-Dimethyl-3,7-bis(phenylsulphonyl)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**15b**) was obtained as colourless prisms (866 mg, 70%). Crystals suitable for X-ray crystallography were obtained from dichloromethane.

3,7-Bis(phenylsulphonyl)tetracyclo[3.3.3.0^{1,5}.0^{2,8}]undeca-3,6-diene (**15c**) was obtained as colourless coarse plates (825 mg, 65%). Crystals suitable for X-ray crystallography were obtained from ethyl acetate.

8,11-Bis(phenylsulphonyl)tetracyclo[4.3.3.0^{1,6}.0^{7,12}]dodeca-8,10-diene (**15d**) was obtained as colourless fine plates (1.05 g, 80%). Crystals suitable for X-ray crystallography were obtained from ethyl acetate.

10,13-Bis(phenylsulphonyl)tetracyclo[6.3.3.0^{1,8}.0^{9,14}]tetradeca-10,12-diene (**15f**) was obtained as colourless fine needles (960 mg, 69%).

14,17-Bis(phenylsulphonyl)tetracyclo[10.3.3.0^{1,12}.0^{13,18}]octadeca-14,16-diene (**15h**) was obtained as a colourless powder which was purified by reversed-phase medium-pressure liquid chromatography yielding a colourless powder (1.02 g, 65%).

Table 15. Relative intensities (%) of the molecular ions and some fragments in low-resolution 70-eV mass spectra

Cpd.	M^+	M^+ −PhS	M^+ −PhSH	M^+ −PhS −PhSH	M^+ −2PhSH	PhS^+	$C_7H_7^+$
Vinyl sulphides							
5a	100	99	15	64	30		8
5b	75	100	15	49	49	34	64
10a/11a	100	99	17	61	39	73	
10c/11c	100	98	4	28	9	44	15
10f/11f	3	9	1	100	28	43	1
10h/11h	44	100	7	21	28	14	22
Vinyl sulphones		M^+ $-PhSO_2$	M^+ $-PhSO_2H$	M^+ $-2PhSO_2$	M^+ $-PhSO_2$ $-PhSO_2H$	$PhSO_2^+$	$PhSO^+$
6a	98	38	6	20	100	4	92
6b	80	23	11	30	100	20	37
12a/13a	24	9	21	19	74	20	100
12c/13c	43	65	16	36	100	24	58
12f/13f	18	100	32	23	84	9	37
12h/13h	1	7	4	22	100	10	20
Bis(phenylsulphonyl)semibullvalenes							
8a	5	3	4	28	3	5	100
8b	26	33	6	100	60	4	60
15a	22	13	10	41	5	65	100
15b	16	74	9	100	63	4	91
15c	35	52	13	67	100	100	71
15d	24	36	10	56	100	16	51
15f	17	26	10	44	100	34	56
15h	18	60	16	54	100	24	14

Table 16. Molecular formula and mass, and elemental analyses

Cpd.		Molecular Mass		Elemental Analysis C	H
5a	$C_{20}H_{18}S_2$	322.5	Calcd. Found	74.49 74.11	5.63 5.84
10a/11a			Found	74.51	5.37
5b	$C_{22}H_{22}S_2$	350.5	Calcd. Found	75.38 75.72	6.33 6.79
10c/11c	$C_{23}H_{22}S_2$	362.6	Calcd. Found	76.20 76.02	6.12 5.87
10f/11f	$C_{26}H_{28}S_2$	404.6	Calcd. Found	77.18 77.46	6.97 7.18
10h/11h	$C_{30}H_{36}S_2$	460.7	Calcd. Found	78.21 78.10	7.88 7.97
6a	$C_{20}H_{18}O_4S_2$	386.5	Calcd. Found	62.16 62.08	4.69 4.56
12a/13a			Found	61.98	4.79
6b	$C_{22}H_{22}O_4S_2$	414.5	Calcd. Found	63.74 62.08	5.35 4.91
12c/13c	$C_{23}H_{22}O_4S_2$	426.5	Calcd. Found	64.77 64.65	5.20 5.39
12f/13f	$C_{26}H_{28}O_4S_2$	468.6	Calcd. Found	66.64 66.79	6.02 6.22
12h/13h	$C_{30}H_{36}O_4S_2$	524.7	Calcd. Found	68.67 68.67	6.91 6.95
7a	$C_{20}H_{16}Br_2O_4S_2$	544.3	Calcd. Found	44.14 44.55	2.96 2.76
7b	$C_{22}H_{20}Br_2O_4S_2$	572.3	Calcd. Found	46.17 46.56	3.52 3.40
8a	$C_{20}H_{16}O_4S_2$	384.5	Calcd. Found	62.48 62.41	4.19 4.28
15a			Found	62.10	4.24
8b	$C_{22}H_{20}O_4S_2$	412.5	Calcd. Found	64.06 64.42	4.89 4.86
15b			Found	63.70	4.91
15c	$C_{23}H_{20}O_4S_2$	424.5	Calcd. Found	65.07 65.10	4.75 4.74
15d	$C_{24}H_{22}O_4S_2$	438.6	Calcd. Found	65.73 65.83	5.06 5.10
15f	$C_{26}H_{26}O_4S_2$	466.6	Calcd. Found	66.93 66.43	5.62 5.84
15h	$C_{30}H_{34}O_4S_2$	522.7	Calcd. Found	68.93 68.67	6.56 6.77

X-Ray Diffraction Analyses were performed from colourless transparent crystals. The cell parameters were determined on the basis of 22 reflections. The numbers of reflections reported in Table 2 were obtained with Mo-K_α radiation and $2\Theta_{max} = 55°$ (graphite monochromator, Wyckoff scan). Measurements and computations were carried out by means of the system Nicolet R3m/V (for **7b**, **8a,b**, **15b**) or Siemens R3m/V (for **15a,c,d**) on a computer MicroVax II. The programme SHELXTL-PLUS[41] was employed. The structures were solved by direct methods and refined anisotropically by the least squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of hydrogen atoms were calculated and included in the refinements with isotropic description[42].

CAS Registry Numbers

(±)-**4a**: 139163-42-1 / (±)-**4b**: 139040-23-6 / (±)-**5a**: 139462-70-7 / (±)-**5b**: 139462-71-8 / (±)-**6a**: 139462-79-6 / (±)-**6b**: 139462-80-9 / (±)-7**a**: 139462-88-7 / (±)-**7b**: 139462-89-8 / (±)-**8a**: 139462-63-8 / (±)-**8b**: 139462-64-9 / **9a**: 51716-63-3 / **9c**: 21170-73-0 / **9f**: 58602-56-5 / **9h**: 58602-55-4 / (±)-**10a**: 139462-72-9 / (±)-**10c**: 139462-74-1 / (±)-**10f**: 139493-35-9 / (±)-**10h**: 139462-77-4 / **11a**: 139462-73-0 / **11c**: 139462-75-2 / **11f**: 139462-76-3 / **11h**: 139462-78-5 / (±)-**12a**: 139462-81-0 / (±)-**12b**: 139462-90-1 / (±)-**12c**: 139462-83-2 / (±)-**12d**: 119657-31-7 / (±)-**12f**: 139493-36-0 / (±)-**12h**: 139462-86-5 / **13a**: 139462-82-1 / **13b**: 116564-06-8 / **13c**: 139462-84-3 / **13d**: 119657-32-8 / **13f**: 139462-85-4 / **13h**: 139462-87-6 / **14a**: 139462-92-3 / **14b**: 139462-94-5 / **14c**: 139462-96-7 / **14d**: 139462-98-9 / **14f**: 139463-00-6 / **14h**: 139463-02-8 / **15a**: 139462-65-0 / **15b**: 139462-66-1 / **15c**: 139462-67-2 / **15d**: 139462-68-3 / **15f**: 139493-34-8 / **15h**: 139462-69-4

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