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Influence of aromatic sulfonation on the geometry of [2.2]paracyclophane: crystal structures of one sulfonate, one disulfonic anhydride and five disulfonimides

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The crystal structures of potassium [2.2]paracyclophane-4-sulfonate (1), [2.2]paracyclophane-4,15-disulfonic anhydride (2), [2.2]paracyclophane-4,15-disulfonimide (3), *N*-*n*-propyl-[2.2]paracyclophane-4,15-disulfonimide (4), *N*-isopropyl-[2.2]paracyclophane-4,15-disulfonimide (5), *N*-cyclopropyl-[2.2]paracyclophane-4,15-disulfonimide (6) and *N*-phenyl-[2.2]paracyclophane-4,15-disulfonimide (7) were established by single-crystal X-ray diffraction. The structural changes caused by sulfonation are discussed with respect to the parent [2.2]paracyclophane (tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene). The main features are a change in the non-bonding distances between the *para*-phenylene rings and a rotation of these rings with respect to the molecular symmetry plane. The rings are rotated away from each other in the case of monosulfonation (1), but are rotated in the opposite way in the case of the disulfonic anhydride (2) or the disulfonimide compounds (3)–(7). The results are also discussed in terms of the parameters proposed by Keehn [(1983), *Organic Chemistry, A Series of Monographs 45*, edited by P. H. Keehn & S. M. Rosenfeld, Vol. 1, pp. 69–238. New York: Academic Press] showing that (bonded and non-bonded) angles involving the *para*-phenylene rings are mainly affected.

1. Introduction

Cyclophanes are cyclic systems, consisting of at least one aromatic moiety, bridged by one or more aliphatic chains. Since their discovery, X-ray crystallography has afforded the most direct description of the structural features responsible for the unique phenomena associated with these compounds. Keehn (1983) collated the X-ray crystal structure determinations of cyclophanes known up to early 1982.

In the family of [2.2]paracyclophanes two phenylene rings (C_6H_4) are connected to each other in their *para* position by an ethylene bridge ($-C_2H_4-$). From the crystal structure determination of [2.2]paracyclophane ([2.2]PCP: Brown & Farthing, 1949; Brown, 1953) the non-planarity of the phenylene rings and the further displacement of the bridging benzylic C atoms from the aromatic plane were shown to be the most important identifying features. Additional structural characteristics typical of these strained systems are bond stretching and angle strain in the bridge and at the phenylene ring atom bound to the bridge. The overall geometry, which is quite distorted in the lower [*m.n*]*meta*- and [*m.n*]paracyclophanes (*m* is equal to or different from *n*), is a compromise between maintaining the ideal hybridization geometry in the individual moieties of the cyclophane while reducing the *trans*-

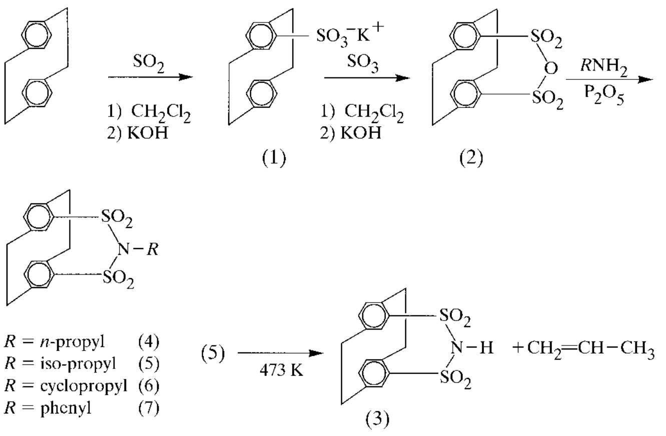
annular π–π and other non-bonded interactions within the molecule.

[2.2]PCP is the lowest member of the [*m.n*]paracyclophanes. It has a strain energy of 130 kJ mol^{-1} (Keehn & Rosenfeld, 1983). The bridgehead C atoms of each *para*-phenylene moiety are bent out of the plane through the other four ring C atoms by 12.6° (Hope *et al.*, 1972). The distance between the two opposite bridgehead C atoms of the two *para*-phenylene rings is only 2.78 Å (Hope *et al.*, 1972), considerably less than the van der Waals distance of 3.4 Å between two parallel 'free' benzene rings (Pauling, 1960). Thus, the strain energy of [2.2]PCP seems to be mainly determined by π–π repulsions and out-of-plane deformations of the *para*-phenylene moieties (Greenberg & Liebman, 1978; Wiberg, 1986*a*,*b*). An additional feature of [2.2]PCP is the dynamic disorder that occurs by twisting the two *para*-phenylene moieties in opposite directions about their common normal by ~3°, leading to relief of eclipsing within the two ethylene bridges (Hope *et al.*, 1972).

In order to study the influence of aromatic sulfonation on the geometry of [2.2]PCP, in particular the effects of the expected steric overcrowding, the structures of a series of sulfonated [2.2]PCP derivatives have been established by single-crystal X-ray diffraction and are reported here.

2. Experimental

The general synthetic route for these compounds is shown below.



Full details for (1) and (2) are reported by van Lindert *et al.* (1992) and for the disulfonimides (3)–(7) by van Lindert *et al.* (1996). Crystals suitable for X-ray analysis were located in samples supplied by the Laboratory of Organic Chemistry (Institute of Molecular Chemistry) at the University of Amsterdam.

Intensity data for all crystal structures were collected with an Enraf–Nonius CAD-4 automatic diffractometer employing graphite-monochromated Cu $K\alpha$ [for (1), (2), (4), (5) and (7); λ = 1.5418 Å] or Mo $K\alpha$ [for (3) and (6); λ = 0.71069 Å] and θ–2θ scans. Compounds (1) and (2) were measured at reduced temperature, (3)–(7) at room temperature. All structures were determined by the direct methods program *SIMPEL* (Schenk & Hall, 1992). The H-atom positions were introduced at their calculated positions and restrained so that the distances C—H and N—H were restrained at 1.00 Å. Full-matrix least-squares refinement on *F*, anisotropic for the non-H atoms and isotropic for the H-atoms was used with a weighting scheme $w^{-1} = a + b\sigma^2(F_{\rm obs}) + c/\sigma(F_{\rm obs})$. Extinction corrections were made according to Zachariasen (1967). Complete experimental details are given in Table 1.

3. Results and discussion

Final coordinates and equivalent atomic displacement parameters of the non-H atoms have been deposited.[1] Selected bond distances and angles are given in Table 2. Relevant torsion angles are collected in Table 3. *ORTEP* (Davenport *et al.*, 1992) drawings of the molecules, showing the geometry and the numbering system, are given in Figs. 1–7. To compare the different molecules on one hand and to take account of crystallographic mirror symmetry on the other, the numbering system used is different from the IUPAC nomenclature.

The main geometric features of the parent [2.2]PCP are indicated in §1. In the following sections bonded and non-bonded parameters involving the [2.2]PCP moiety will be discussed systematically in order to express the additional strain induced by the sulfur substituent(s).

3.1. Bond distances

C—C distances in the ethylene bridges are in the range 1.56 (2)–1.613 (5) Å, longer than the standard value for —CH$_2$–CH$_2$— of 1.524 (14) Å (Allen *et al.*, 1987), but comparable to the range observed in 21 [2.2]PCP derivatives in the Cambridge Structural Database (Allen & Kennard, 1993): 1.557–1.630 Å. [The C8—C8 distance of 1.50 (2) Å in (4) is considered to be an outlier.] The C—C distance is somewhat longer in the ethylene bridge *ortho* to the sulfur substituent than in the ethylene bridge *meta* to S.

The C—S distances observed in (3)–(7) are somewhat larger than the average distance of 1.751 Å (Bombicz *et al.*, 1996; hereinafter BCKK96) for 13 C—S(=O)$_2$—N*Q*—S(=O)$_2$—C fragments (with *Q* = H, C, Si). The S=O distances in (3)–(7) are comparable to BCKK96. The C—S distances in (2)–(7) are shorter than the corresponding distances in (1); in (1) and (2) this difference is substantial [1.786 (6) Å for (1) *versus* 1.750 (5) Å for (2)] and can be ascribed to the additional ring formation.

BCKK96 calculated an average S—N distance of 1.641 Å for *Q* = H, which is smaller than 1.664 (2) Å in (3). Analogously, the average S—N distance calculated by BCKK96 of 1.675 Å for *Q* = C, Si is comparable to (4) and smaller than (5)–(7). In general, the S—N distances in (3)–(7) are larger, probably because in (3)–(7) the disulfonimide bridge is bonded to two parallel *para*-phenylene rings; in the BCKK96

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0584). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_{16}H_{15}SO_3^-K^+$-·$2H_2O$	$C_{16}H_{14}S_2O_5$-·$1/2CH_2Cl_2$	$C_{16}H_{15}NS_2O_4$-·$2CH_3CN$	$C_{19}H_{21}NS_2O_4$	$C_{19}H_{21}NS_2O_4$
Chemical formula weight	362.5	392.9	431.54	391.5	391.5
Cell setting, space group	Monoclinic, $P2_1/a$	Monoclinic, $C2/c$	Monoclinic, $P2_1/m$	Orthorhombic, *Pmcn*	Orthorhombic, *Pbca*
a, *b*, *c* (Å)	11.493 (3), 7.685 (1), 18.150 (3)	15.927 (2), 7.7031 (4), 26.257 (2)	8.725 (7), 10.259 (7), 10.950 (6)	10.587 (2), 10.779 (3), 15.644 (5)	12.845 (2), 15.0121 (7), 18.6430 (8)
β (°)	91.49 (2)	98.17 (1)	92.87 (4)	90	90
V (Å^3)	1602.5 (5)	3188.7 (5)	979 (1)	1785.3 (8)	3594.8 (5)
Z	4	8	2	4	8
D_x (Mg m^{-3})	1.50	1.641	1.46	1.457	1.447
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
No. of reflections for cell parameters	23	23	23	23	23
θ range (°)	39.9–42.8	40.0–44.9	19.0–20.9	25.0–38.5	39.9–41.8
μ (mm^{-1})	4.340	4.803	0.306	2.924	2.904
Temperature (K)	213	211	293	293	293
Crystal form, colour	Rod, colourless	Plate, colourless	Rod, colourless	Block, colourless	Block, colourless
Crystal size (mm)	1.25 × 0.70 × 0.20	0.88 × 0.25 × 0.06	1.0 × 0.35 × 0.25	0.30 × 0.25 × 0.10	0.50 × 0.40 × 0.40
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
No. of measured, independent and observed parameters	2709, 2709, 2633	2357, 2357, 2125	2982, 2982, 2011	1939, 1939, 804	3679, 3679, 3190
Criterion for observed reflections	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
$\theta_{\max}$ (°)	64.86	59.86	29.93	74.71	74.71
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 9$ $-21 \rightarrow l \rightarrow 21$	$-17 \rightarrow h \rightarrow 17$ $0 \rightarrow k \rightarrow 8$ $0 \rightarrow l \rightarrow 29$	$-12 \rightarrow h \rightarrow 12$ $-14 \rightarrow k \rightarrow 0$ $0 \rightarrow l \rightarrow 15$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 13$ $-19 \rightarrow l \rightarrow 0$	$0 \rightarrow h \rightarrow 16$ $0 \rightarrow k \rightarrow 18$ $0 \rightarrow l \rightarrow 23$
No. and frequency of standard reflections	2 every 60 min	2 every 60 min	2 every 60 min	2 every 60 min	2 every 60 min
Intensity decay (%)	0	0	10	0	0
Refinement					
Refinement on	*F*	*F*	*F*	*F*	*F*
R, *wR*, *S*	0.086, 0.087, 1.362	0.061, 0.067, 1.026	0.056, 0.064, 0.764	0.089, 0.095, 0.872	0.064, 0.069, 0.984
No. of reflections and parameters used in refinement	2633, 269	2125, 283	2011, 175	804, 125	3190, 320
No. of restraints	19	15	12	11	21
H-atom treatment	Riding	Riding	Riding	Riding	Riding
Weighting scheme	$1/[5.9 + 0.0038\sigma(F_o)^2 + 0.00002/\sigma(F_o)]$	$1/[7.6 + 0.0038\sigma(F_o)^2 + 0.00002/\sigma(F_o)]$	$1/[8.3 + 0.0072\sigma(F_o)^2 + 0.00006/\sigma(F_o)]$	$1/[3.7 + 0.027\sigma(F_o)^2 + 0.00009/\sigma(F_o)]$	$1/[6.9 + 0.0056\sigma(F_o)^2 + 0.00004/\sigma(F_o)]$
$(\Delta/\sigma)_{\max}$	0.09	0.337	0.307	0.021	0.258
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.059, −0.656	0.877, −0.554	0.545, −0.576	0.594, −0.485	0.726, −0.893
Extinction method	Zachariasen	Zachariasen	None	Zachariasen	Zachariasen
Extinction coefficient	26 (8) × 10^1	144 (9) × 10^1	–	40 (10) × 10^1	500 (30) × 10^1

	(6)	(7)
Crystal data		
Chemical formula	$C_{19}H_{19}NS_2O_4$	$C_{22}H_{19}NS_2O_4$
Chemical formula weight	389.5	425.5
Cell setting, space group	Orthorhombic, *Pbca*	Orthorhombic, *Pmcn*
a, *b*, *c* (Å)	9.826 (2), 14.632 (2), 23.770 (4)	9.915 (2), 12.426 (1), 15.418 (2)
β (°)	90	90
V (Å^3)	3418 (1)	1899.6 (5)
Z	8	4
D_x (Mg m^{-3})	1.51	1.488
Radiation type	Mo $K\alpha$	Cu $K\alpha$

Table 1 (continued)

	(6)	(7)
No. of reflections for cell parameters	23	23
θ range (°)	20.0–20.9	40.1–45.2
μ (mm^{-1})	0.338	2.805
Temperature (K)	293	293
Crystal form, colour	Block, colourless	Block, colourless
Crystal size (mm)	0.50 × 0.45 × 0.40	0.60 × 0.60 × 0.25
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans
No. of measured, independent and observed parameters	4940, 4940, 3089	2069, 2069, 1793
Criterion for observed reflections	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
$\theta_{\max}$ (°)	29.9	74.72
Range of h, k, l	$0 \rightarrow h \rightarrow 13$	$-12 \rightarrow h \rightarrow 0$
	$0 \rightarrow k \rightarrow 20$	$-15 \rightarrow k \rightarrow 0$
	$0 \rightarrow l \rightarrow 33$	$0 \rightarrow l \rightarrow 19$
No. and frequency of standard reflections	2 every 60 min	2 every 60 min
Refinement		
Refinement on	F	F
R, wR, S	0.046, 0.052, 0.772	0.049, 0.054, 0.859
No. of reflections and parameters used in refinement	3089, 312	1793, 185
No. of restraints	19	12
H-atom treatment	Riding	Riding
Weighting scheme	$1/[6.2 + 0.0085\sigma(F_o)^2 + 0.00009/\sigma(F_o)]$	$1/[5.2 + 0.0051\sigma(F_o)^2 + 0.00003/\sigma(F_o)]$
$(\Delta/\sigma)_{\max}$	0.205	0.077
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.289, −0.394	0.394, −0.515
Extinction method	Zachariasen	Zachariasen
Extinction coefficient	1780 (50) × 10^1	740 (20) × 10^1

Computer programs used: *CAD*-4 (Enraf–Nonius, 1989), *CELCON* program comparable to *Xtal*_LATCON, *Xtal*_SORTRF (Hall *et al.* 1992), *Xtal*_SIMPEL (Schenk & Hall, 1992), *Xtal*_CRYLSQ (Olthof-Hazekamp, 1992), *Xtal*_BONDLA (Dreissig *et al.*, 1992), *Xtal*_CIFIO (Hall, 1992), *Xtal*_ADDREF (Davenport & Hall, 1992).

compounds the disulfonimide bridge is generally attached to one benzene ring in an *ortho* position. The S—N distance increases from 1.664 (2) Å for the hydrogen-substituted nitrogen in (3) to 1.705 (2) Å for the phenyl-substituted nitrogen in (7): this correlates with the increased size of the N-substituent.

3.2. Exocyclic angles of the *para*-phenylene rings

The steric strain due to non-bonded repulsions between the —SO_3 substituent, the —SO_2—O3—SO_2— or —SO_2—N—SO_2— bridge, and the nearest ethylene bridge in (1)–(7) becomes apparent from the comparison of the exocyclic bond angles made by the ethylene bridges or the sulfur substituent at the *para*-phenylene rings.

In (1) the C2—C3—S1 angle is substantially larger than the C4—C3—S1 angle [121.5 (4) *versus* 117.4 (4)°], as is C1—C2—C3 compared with C1—C2—C7 [124.8 (5) *versus* 118.3 (5)°]. This reflects steric strain between the sulfonate substituent and the adjacent C1H_2 methylene, in particular its H102 [the interatomic distance O3—H102 is 2.69 (6) Å]. This is the more obvious since the C4—C5—C8, C6—C5—C8, C12—C13—C16 and C14—C13—C16 exocyclic bond angles, which will be devoid of any direct steric interaction with the sulfonate substituent, are equal within two e.s.d.'s [120.8 (6)–121.6 (6)°], and close to that expected for an sp^2 carbon. The exocyclic bond angle C1—C2—C3 is substantially larger than the structurally equivalent C9—C10—C11 angle [124.8 (5) *versus* 119.7 (6)°], whereas C1—C2—C7 is smaller than C9—C10—C15 [118.3 (5) *versus* 122.5 (6)°]. This illustrates that C1 is pushed aside in the direction of the plane through C6, C7, C14 and C15, which induces a reduction in the degree of eclipsing within the C1H_2—C9H_2 ethylene bridge.

The tendency for different exocyclic bond angles at C2 (C10) and C3 (C11) is maintained in (2)–(7), in which there is a supplementary bridge between the two *para*-phenylene rings. Indeed, the angle C1—C2—C3 (or its equivalent C9—C10—C11) is substantially larger than the C1—C2—C7 angle (or C9—C10—C15), the ranges being 123.4–124.6 and 118.1–120.8°, respectively. The effect of a non-bonded interaction between the two adjacent bridges is also apparent from the C—C—S bond angles: the C2—C3—S1 angle (C10—C11—S2) is substantially larger than C4—C3—S1 (C12—C11—S2), the respective ranges being 119.9–122.3 and 115.4–117.0°. This indicates that in (2)–(7) the C1H_2—C9H_2 (or C1H_2—C1*H_2) ethylene bridge is again pushed aside in the direction of the plane through C6, C7, C14 and C15. Although the bridgehead C5 (C13) in (2)–(7) is devoid of any direct steric interaction with the disulfonic anhydride (2) or the disulfonimide substi-

Table 2
Selected bond distances (Å) and angles (°).

Heading Keehn represents 'structural characteristics of Keehn'; see text.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	[2.2]PCP	Keehn
C1—C2	1.517 (8)	1.523 (9)	1.513 (5)	1.51 (2)	1.505 (7)	1.491 (5)	1.511 (5)	1.511	*a*
C1—C9/C1—C1*	1.57 (1)	1.610 (9)	1.613 (5)	1.56 (2)	1.604 (7)	1.592 (6)	1.608 (4)	1.593	*b*
C2—C3	1.392 (8)	1.377 (7)	1.409 (5)	1.44 (2)	1.411 (6)	1.412 (4)	1.401 (4)	1.386	*e*
C2—C7	1.390 (9)	1.394 (8)	1.396 (5)	1.40 (2)	1.388 (7)	1.401 (5)	1.393 (5)	1.386	*e*
C3—C4	1.393 (8)	1.418 (8)	1.395 (5)	1.39 (2)	1.384 (6)	1.395 (5)	1.396 (4)	1.387	*f*
C3—S1	1.786 (6)	1.750 (5)	1.767 (4)	1.76 (1)	1.765 (4)	1.753 (3)	1.759 (3)		
C4—C5	1.399 (8)	1.396 (8)	1.396 (5)	1.40 (2)	1.381 (7)	1.397 (5)	1.389 (5)	1.386	*g*
C5—C6	1.394 (9)	1.372 (8)	1.393 (6)	1.40 (2)	1.410 (7)	1.383 (5)	1.388 (5)	1.386	*g*
C5—C8	1.514 (9)	1.528 (9)	1.519 (6)	1.53 (2)	1.495 (7)	1.512 (5)	1.508 (5)	1.511	*a*
C6—C7	1.382 (9)	1.398 (9)	1.387 (6)	1.39 (2)	1.360 (8)	1.387 (6)	1.385 (5)	1.387	*f*
C8—C16/C8—C8*	1.57 (1)	1.594 (9)	1.610 (7)	1.50 (2)	1.597 (9)	1.582 (6)	1.583 (6)	1.593	*b*
C9—C10	1.51 (1)	1.526 (9)	–	–	1.512 (7)	1.501 (5)	–	1.511	*a*
C10—C11	1.400 (9)	1.383 (7)	–	–	1.416 (6)	1.421 (5)	–	1.386	*e*
C10—C15	1.40 (1)	1.386 (8)	–	–	1.374 (7)	1.405 (5)	–	1.386	*e*
C11—C12	1.387 (9)	1.403 (8)	–	–	1.376 (6)	1.382 (5)	–	1.387	*f*
C11—S2	–	1.761 (5)	–	–	1.764 (4)	1.774 (3)	–		
C12—C13	1.394 (9)	1.392 (8)	–	–	1.386 (6)	1.390 (5)	–	1.386	*g*
C13—C14	1.390 (9)	1.368 (8)	–	–	1.400 (7)	1.389 (6)	–	1.386	*g*
C13—C16	1.51 (1)	1.523 (9)	–	–	1.496 (7)	1.515 (6)	–	1.511	*a*
C14—C15	1.381 (9)	1.403 (9)	–	–	1.371 (7)	1.384 (6)	–	1.387	*f*
S1—O1	1.449 (4)	1.436 (5)	1.426 (3)	1.434 (8)	1.426 (3)	1.426 (3)	1.426 (2)		
S1—O2	1.455 (5)	1.402 (4)	1.435 (3)	1.441 (9)	1.426 (3)	1.433 (3)	1.435 (3)		
S1—O3	1.437 (5)	1.657 (4)	–	–	–	–	–		
S1—N	–	–	1.664 (2)	1.676 (7)	1.693 (3)	1.693 (3)	1.705 (2)		
S2—O3	–	1.640 (4)	–	–	–	–	–		
S2—O4	–	1.403 (4)	–	–	1.438 (4)	1.428 (3)	–		
S2—O5	–	1.431 (5)	–	–	1.435 (4)	1.438 (3)	–		
S2—N/S1*—N	–	–	1.664 (2)	1.676 (7)	1.697 (3)	1.686 (3)	1.705 (2)		
C2—C1—C9/C2—C1—C1*	112.7 (5)	112.2 (5)	112.4 (3)	113.5 (9)	112.2 (4)	112.5 (3)	112.1 (3)		
C1—C2—C3	124.8 (5)	124.6 (5)	124.3 (3)	123.5 (9)	124.2 (4)	123.9 (3)	124.2 (3)	113.7	γ
C1—C2—C7	118.3 (5)	118.1 (5)	119.0 (3)	120.6 (9)	120.5 (4)	120.7 (3)	119.3 (3)		
C3—C2—C7	115.8 (5)	116.3 (5)	115.6 (3)	114 (1)	114.3 (4)	114.2 (3)	115.3 (3)		
C2—C3—C4	121.0 (5)	121.8 (5)	121.6 (3)	122.9 (9)	121.7 (4)	122.2 (3)	121.9 (3)		λ
C2—C3—S1	121.5 (4)	122.0 (4)	121.3 (2)	119.9 (8)	121.6 (3)	121.1 (2)	121.6 (2)		
C4—C3—S1	117.4 (4)	115.5 (4)	116.7 (3)	117.0 (7)	116.6 (3)	116.6 (2)	116.4 (2)		
C4—C5—C6	116.7 (5)	118.2 (5)	117.4 (3)	118 (1)	116.0 (5)	116.8 (3)	117.0 (3)		
C4—C5—C8	121.6 (6)	119.6 (5)	119.9 (4)	119 (1)	121.5 (4)	120.0 (3)	120.5 (3)		λ
C6—C5—C8	120.8 (6)	121.1 (5)	121.7 (3)	121 (1)	121.0 (5)	122.1 (3)	121.5 (3)		
C5—C8—C16/C5—C8—C8*	113.4 (6)	112.4 (5)	112.1 (3)	114.2 (9)	112.2 (4)	112.2 (3)	112.6 (3)		
C1—C9—C10	114.1 (6)	112.6 (5)	–	–	111.7 (4)	112.4 (3)	–	113.7	γ
C9—C10—C11	119.7 (6)	123.5 (5)	–	–	123.4 (4)	124.2 (3)	–	113.7	γ
C9—C10—C15	122.5 (6)	119.2 (5)	–	–	120.1 (4)	119.9 (3)	–		
C11—C10—C15	116.6 (6)	116.0 (5)	–	–	115.0 (4)	114.0 (3)	–		
C10—C11—C12	120.5 (6)	122.1 (5)	–	–	121.5 (4)	122.8 (3)	–		λ
C10—C11—S2	–	122.3 (4)	–	–	121.4 (3)	121.2 (2)	–		
C12—C11—S2	–	115.4 (4)	–	–	117.0 (3)	116.0 (2)	–		
C12—C13—C14	116.8 (6)	118.0 (5)	–	–	116.6 (4)	117.6 (4)	–		
C12—C13—C16	120.8 (6)	119.4 (5)	–	–	120.8 (5)	119.4 (3)	–		λ
C14—C13—C16	120.9 (6)	121.6 (5)	–	–	121.6 (4)	121.5 (4)	–		
C8—C16—C13	112.5 (6)	112.1 (5)	–	–	112.6 (4)	112.2 (3)	–		
C3—S1—O3	108.7 (3)	101.8 (2)	–	–	–	–	–		
C3—S1—N	–	–	105.8 (2)	104.7 (6)	105.5 (2)	105.0 (1)	104.4 (2)		
C11—S2—O3	–	103.5 (2)	–	–	–	–	–		
C11—S2—N	–	–	–	–	105.4 (2)	106.6 (1)	–		
S1—O3—S2	–	126.2 (3)	–	–	–	–	–		
S1—N—S2/S1—N—S1*	–	–	126.4 (3)	123.1 (8)	119.2 (2)	124.4 (2)	122.8 (2)		

tuent (3)–(7), analogous to the sulfonate group in (1), the exocyclic bond angle C6—C5—C8 (C14—C13—C16) is somewhat larger than the angle C4—C5—C8 (C12—C13—C16); the range is 120.0–122.1° for the former and 119.4–121.5° for the latter. It may be noted that the difference in exocyclic angles at the bridgehead C5 (C13) within a molecule can be substantial and as large as 2.2°. This difference may be due to a relayed structural deformation.

3.3. Configuration of the *para*-phenylene rings

The bridgehead atoms C2, C5, C10 and C13 are displaced out of their *para*-phenylene ring plane towards the *para*-phenylene ring connected by the ethylene bridges, thus giving the *para*-phenylene rings a boat-like conformation. The endocyclic torsion angles of the *para*-phenylene rings can be divided into two groups (Table 3): with the exception of the

Table 3
Relevant torsion angles (°).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C2—C3—C4—C5	3.5 (9)	−1.3 (9)	−0.8 (5)	0 (2)	−1.1 (6)	−0.6 (5)	0.8 (4)
C3—C4—C5—C6	13.7 (9)	−14.0 (9)	−13.8 (5)	12 (2)	−12.9 (7)	15.1 (5)	−14.9 (4)
C4—C5—C6—C7	−16.1 (9)	14.5 (9)	13.8 (6)	−10 (2)	13.0 (7)	−14.5 (5)	14.2 (5)
C5—C6—C7—C2	1 (1)	0.4 (9)	0.9 (6)	−3 (2)	1.2 (8)	−0.9 (6)	0.9 (5)
C6—C7—C2—C3	15.9 (9)	−15.3 (9)	−15.2 (5)	14 (2)	−14.8 (7)	14.9 (5)	−14.6 (4)
C7—C2—C3—C4	−18.1 (8)	15.7 (8)	15.1 (5)	−12 (2)	14.8 (6)	−14.1 (4)	13.8 (4)
C10—C11—C12—C13	0 (1)	−0.0 (9)	–	–	−1.6 (6)	0.8 (5)	–
C11—C12—C13—C14	−15 (1)	14.7 (8)	–	–	14.8 (6)	−13.2 (5)	–
C12—C13—C14—C15	15 (1)	−14.8 (9)	–	–	−14.2 (7)	13.3 (6)	–
C13—C14—C15—C10	0 (1)	0.2 (9)	–	–	0.0 (8)	−0.8 (6)	–
C14—C15—C10—C11	−14 (1)	14.1 (9)	–	–	13.0 (7)	−11.1 (5)	–
C15—C10—C11—C12	14.3 (9)	−14.1 (8)	–	–	−12.2 (6)	11.1 (5)	–
S1—C3—C11—S2	–	2.3 (3)	0	0	0.6 (2)	−4.2 (2)	0

Table 4
Asymmetry parameters (Duax *et al.*, 1976) for the mirror planes of the *para*-phenylene rings (°).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
${}_{2}\Delta C_s{}^{5}$	3.2	0.6	0.1	2.4	0.1	1.0	1.2
${}_{10}\Delta C_s{}^{13}$	0.2	0.1	–	–	1.1	0.1	–
${}_{3\text{–}4}\Delta C_s{}^{7\text{–}6}$	3.1	1.3	1.4	2.8	1.9	0.8	0.8
${}_{11\text{–}12}\Delta C_s{}^{15\text{–}14}$	0.9	0.7	–	–	2.0	2.2	–
${}_{\mathrm{O3/N}}\Delta C_s{}^{\mathrm{C3–C11}}$†	–	3.6	0	0	0.8	6.0	0

† This value is obtained by the preceding calculation of the non-bonded atom torsion angles C3—C11—S2—O3/N and C11—C3—S1—O3/N.

para-phenylene ring carrying the sulfonate substituent in (1) the torsion angles C2—C3—C4—C5 (C10—C11—C12—C13) and C5—C6—C7—C2 (C13—C14—C15—C10) are close to zero; in (1) C2—C3—C4—C5 is 3.5 (9)°. The other torsion angles have an absolute value for (2)–(7) in the range 10–15.7°; in (1) higher values up to 18.1° are observed. There are two mirror planes perpendicular to the *para*-phenylene ring: one goes through both bridgehead atoms involved in the ethylene bridges and the other through the midpoints of the bonds which are not involved in the ethylene bridges. The asymmetry parameters (Duax *et al.*, 1976) for both mirror planes are given in Table 4. The values are small showing that the *para*-phenylene rings have almost ideal C_{2v} symmetry. The highest values of the asymmetry parameters are observed in the *para*-phenylene ring carrying the sulfonate substituent in (1). These structural distortions, *i.e.* the decrease in symmetry of the *para*-phenylene rings from D_{6h} to near C_{2v}, arise because the lengthening of the C—C bond in the ethylene bridges is insufficient to maintain a planar phenylene ring having D_{6h} symmetry.

3.4. Configuration of the S—O3/N—S bridge

In (3), (4) and (7) the molecular symmetry and crystallographic symmetry coincide. This imposes planarity on the two S atoms and the C atoms to which they are bonded. In (2), (5) and (6) these four atoms are also essentially coplanar: the torsion angle S1—C3—C11—S2 (Table 3) has a maximum absolute value of only 4.2 (2)° in (6). The dihedral angle between the plane through these four atoms and the plane through S1—O3—S2 is 63.6 (3)° in the disulfonic anhydride

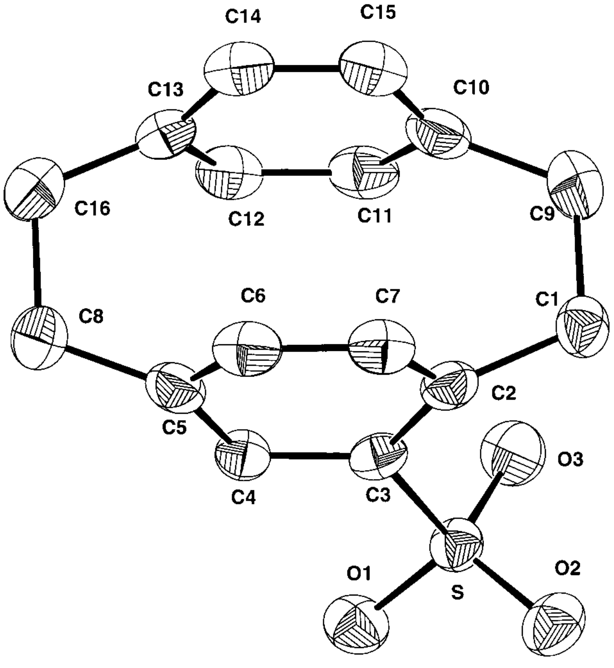

Figure 1
Molecular structure of (1). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

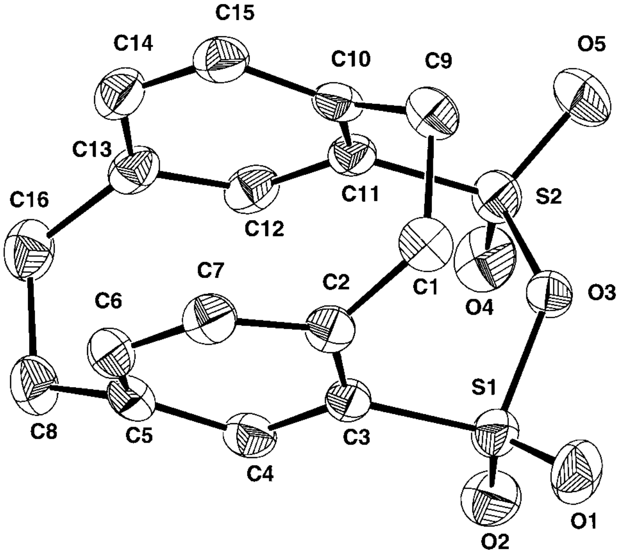

Figure 2
Molecular structure of (2). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

(2). The analogous angle in the disulfonimides (3)–(7) between the former plane and the plane through S1—N—S2 is substantially smaller and varies from 50.9 (2)° in (6) to 58 (1)° in (4); the angle in (3) is 54.6 (3)°. Thus, the five atoms C3—S1—O3/N—S2—C11 form an envelope in which the O3/N tip points towards the C1—C9 ethylene bridge. This dihedral angle in (2)–(7) is significantly larger than in 3,4,5,6-tetramethylbenzene-1,2-disulfonic anhydride (Schagen *et al.*, 1982), where it is only 20.4°. The large difference is related to the nature of the —SO_2—O3/N—SO_2— bridge which is geminal *trans*-annular in (2)–(7), but *ortho* in 3,4,5,6-tetramethylbenzene-1,2-disulfonic anhydride. The substantially larger value of the dihedral angle of the disulfonic anhydride (2) compared with the disulfonimides (3)–(7) suggests different non-bonded interactions with the ethylene bridge, whereas the different values within the series of *N*-alkyl substituents is presumably due to variations in steric hindrance. The fact that C3, S1, O3/N, S2 and C11 are not coplanar is in accordance with the energy calculation of Mezey & Kucsman (1972).

The mirror plane of the C3—S1—O3/N—S2—C11 ring goes through O3 (or N) and the midpoint of the C3···C11 vector. Obviously this mirror plane coincides with the molecular mirror plane through the whole [2.2]PCP unit. Therefore, the molecular symmetry should also be expressed in the symmetry of this envelope. This was checked by calculating the asymmetry parameter ${}_{\rm O3/N}\Delta C_s^{\rm C3-C11}$ for (2)–(7) (Duax *et al.*, 1976). These values are given in Table 4. Where crystallographic symmetry coincides with molecular symmetry [(3), (4) and (7)] this value has to be zero. In the other molecules the asymmetry parameter is small, indicating an almost symmetrical envelope.

3.5. Non-bonded contacts between the *para*-phenylene rings

The steric strain in (1)–(7) is also apparent from a comparison of the interatomic distances between molecular mirror-symmetry-equivalent atoms of the *para*-phenylene rings (*cf.* Table 5) with the parent [2.2]PCP. In the parent the distance between the bridgeheads C2—C10 and C5—C13 is 2.78 Å, whereas the distance between the four other atom pairs is 3.09 Å (Hope *et al.*, 1972). For (1)–(7) the bridgehead distances C2—C10 and C5—C13 are somewhat smaller, in the range 2.731–2.775 Å, but within each compound these distances are approximately equal.

The substantially larger distance between C3 and C11 [3.148 (9) Å] than between C7 and C15 [3.063 (9) Å] in (1) reflects the steric strain due to the presence of the sulfonate group. Although the distance difference between C4—C12 and C6—C14 is rather smaller (0.035 *versus* 0.085 Å), it is still substantial and can be ascribed to steric strain. A comparison of the C3—C11 and C4—C12 distance [3.148 (9) and 3.109 (9) Å] *versus* the C6—C14 and C7—C15 distances [3.074 (9) and 3.063 (9) Å] indicates that, compared with the parent [2.2]PCP, the two *para*-phenylene rings are somewhat rotated around the C2—C5 and the C10—C13 axes, such that

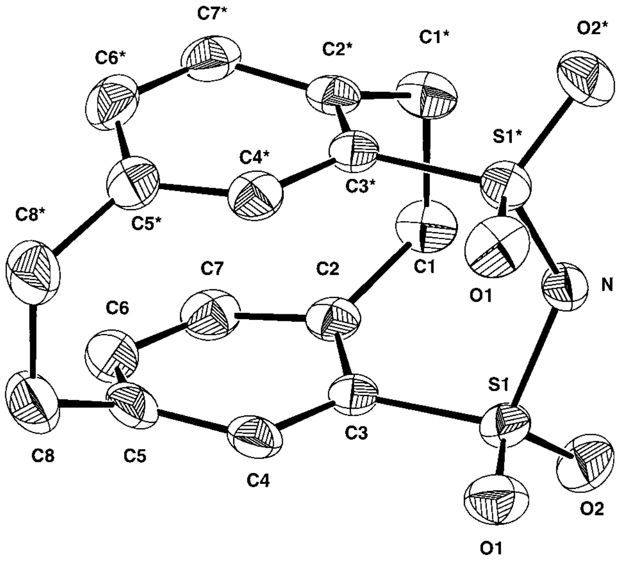

Figure 3
Molecular structure of (3). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

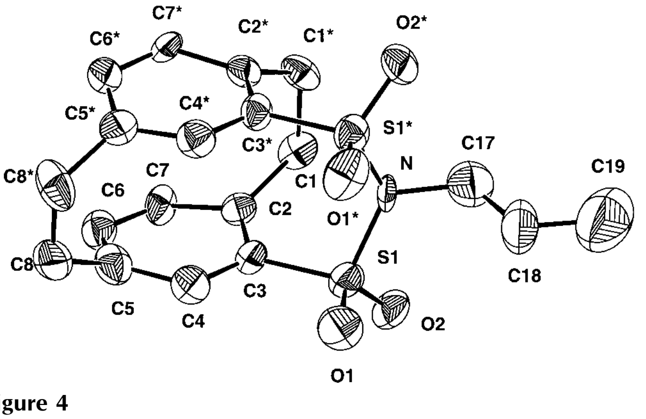

Figure 4
Molecular structure of (4). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

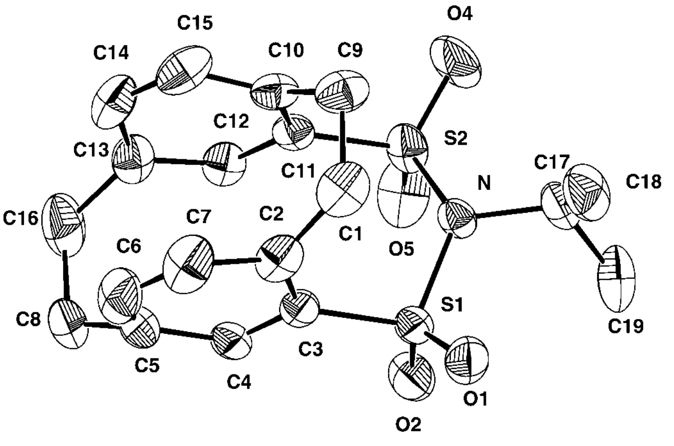

Figure 5
Molecular structure of (5). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

Table 5
Interatomic distances (Å) between the molecular mirror-symmetry-equivalent atoms of the phenylene rings.

Heading Keehn represents 'structural characteristics of Keehn'; see text.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	[2.2]PCP	Keehn
C2—C10/C2*	2.775 (9)	2.772 (8)	2.765 (5)	2.76 (2)	2.731 (6)	2.738 (5)	2.745 (4)	2.78	*p*
C3—C11/C3*	3.148 (9)	3.015 (8)	3.013 (5)	2.93 (2)	2.898 (5)	2.910 (4)	2.940 (4)	3.09	*q*
C4—C12/C4*	3.109 (9)	2.998 (8)	2.992 (6)	2.94 (2)	2.903 (6)	2.928 (5)	2.956 (4)	3.09	*q*
C5—C13/C5*	2.765 (9)	2.756 (8)	2.755 (5)	2.76 (2)	2.735 (7)	2.742 (5)	2.740 (4)	2.78	*p*
C6—C14/C6*	3.074 (9)	3.139 (9)	3.136 (6)	3.10 (2)	3.164 (7)	3.150 (5)	3.153 (5)	3.09	*q*
C7—C15/C7*	3.063 (9)	3.152 (9)	3.159 (6)	3.17 (2)	3.165 (7)	3.149 (5)	3.172 (5)	3.09	*q*

the larger interatomic distances are observed at the side to which the sulfonate group is attached.

The disulfonic anhydride (2) contains an —SO$_2$—O3—SO$_2$— bridge in addition to the two ethylene bridges, rendering it more rigid than the parent [2.2]PCP. The —SO$_2$—O3—SO$_2$— bridge induces more strain, such that the distances C3—C11 and C4—C12 [3.015 (8) and 2.998 (8) Å] are substantially shorter than C6—C14 and C7—C15 [3.139 (9) and 3.152 (9) Å]. The first pair of distances are substantially shorter, whereas the second pair are substantially longer, than for the parent [2.2]PCP. However, C2—C10 and C5—C13 at 2.772 (8) and 2.756 (8) Å, respectively, are very similar to values in the parent [2.2]PCP. Apparently, the additional —SO$_2$—O3—SO$_2$— bridge leads to some rotation of the two *para*-phenylene rings around the C2—C5 and the C10—C13 axes in opposite directions compared with (1). The same trend is observed in the disulfonimides (3)–(7): distances on the side of the —SO$_2$—N—SO$_2$— bridge are substantially smaller [range 2.898–3.013 Å] than on the opposite side [range 3.10–3.172 Å], with a maximum difference of 0.267 Å in (5) [C3—C11 *versus* C7—C15]. However, the C3—C11 distance in the disulfonimides (3)–(7) is, without exception, shorter than in the disulfonic anhydride (2). This is contrary to expectation, since the van der Waals radius for trivalent nitrogen is somewhat larger than for bivalent oxygen (Pauling, 1960). This is probably due to resonance effects of the disulfonimide bridge, which are significantly different from those of the disulfonic anhydride bridge.

3.6. Structural characteristics of Keehn (1983)

3.6.1. Introduction. Keehn (1983) has summarized the distances and angles which characterize the cyclophanes which include among others the [*m.n*]ortho-, [*m.n*]meta- and [*m.n*]paracyclophanes and the same notation (Fig. 8) is followed here. The atomic correspondences of bond distances *a*, *b*, *e*, *f* and *g*, and bond angles γ and λ are given in Table 2. Analogously, the non-bonded distances *p* and *q* are indicated where appropriate in Table 5. Angles α and β describe distortions associated with the phenylene rings, while α^* and β^* (not shown in Fig. 8) are the perpendicular displacements of the appropriate atoms from the adjacent plane: α^* indicates the distance that atom 1 is displaced from the 2,3,5,6 plane and β^* indicates the distance that atom 7 is displaced from the 1,2,6 plane. Values of α, β, α^*, β^* and φ (distortions associated with the phenylene rings), θ and ω (orientation of the phenylene rings with respect to each other) for (1)–(7) are collected in Table 6. Comparative values for the parent [2.2]PCP, calculated by Keehn (1983) from the data of Hope *et al.* (1972), are also included.

3.6.2. Discussion. Keehn (1983) calculated the parameters of Fig. 8 for three different crystal structures of the parent [2.2]PCP, but noted that the study of Hope *et al.* (1972) is the most precise. Thus, compounds in this study are compared with this determination, which was carried out at 98 K. The crystal structures in the present paper were determined at higher temperatures (Table 1) and the assumption is made that the temperature difference has no significant influence on the geometrical parameters.

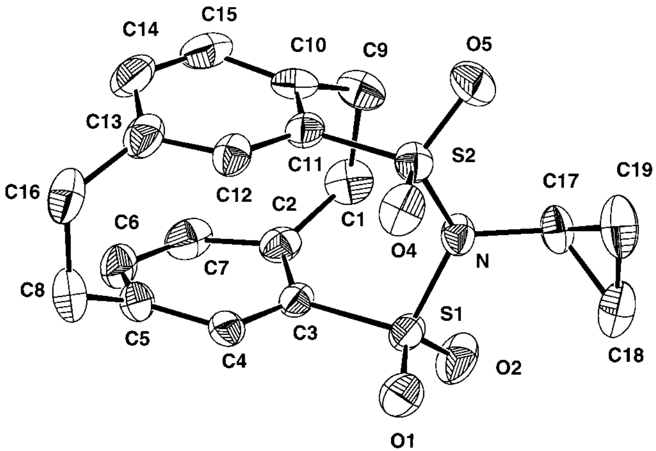

Figure 6
Molecular structure of (6). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

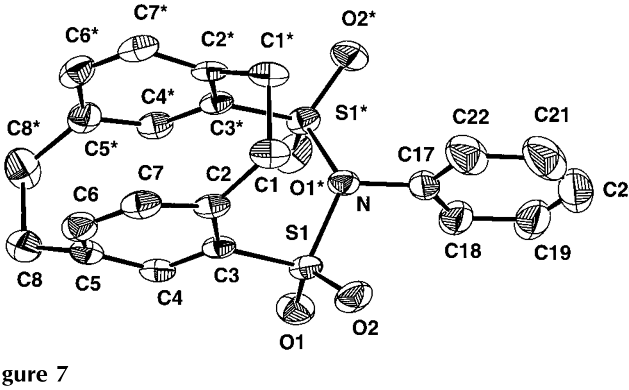

Figure 7
Molecular structure of (7). Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

Table 6
Keehn's (1983) parameters: α, β, ω, φ and θ in °; α^* and β^* in Å.

A hyphen indicates that the value is identical due to crystallographic symmetry (subscript 3 is equal to 1 as 4 is to 2).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	[2.2]PCP
α_1	14.6 (6)	13.2 (6)	12.9 (4)	11 (1)	12.5 (5)	12.2 (4)	12.0 (3)	
α_2	12.7 (6)	12.3 (6)	11.9 (4)	10 (1)	11.0 (5)	12.8 (4)	12.6 (4)	
α_3	12.2 (7)	12.0 (6)	–	–	10.6 (5)	9.3 (4)	–	
α_4	12.5 (7)	12.7 (6)	–	–	12.5 (5)	11.4 (4)	–	
$\langle\alpha\rangle$	13.0 (3)	12.6 (3)	12.4 (3)	10.5 (7)	11.7 (3)	11.4 (2)	12.3 (3)	12.6†
α_1^*	0.188 (9)	0.167 (8)	0.166 (5)	0.15 (2)	0.164 (7)	0.160 (5)	0.154 (5)	
α_2^*	0.160 (9)	0.152 (9)	0.150 (6)	0.12 (2)	0.141 (7)	0.162 (5)	0.158 (5)	
α_3^*	0.155 (10)	0.152 (8)	–	–	0.137 (7)	0.125 (5)	–	
α_4^*	0.158 (10)	0.157 (8)	–	–	0.159 (7)	0.142 (6)	–	
$\langle\alpha^*\rangle$	0.165 (5)	0.157 (4)	0.158 (4)	0.14 (1)	0.150 (4)	0.147 (3)	0.156 (4)	0.158‡
β_1	10.0 (6)	9.5 (6)	10.0 (2)	13 (1)	9.6 (4)	10.3 (3)	10.3 (3)	
β_2	9.6 (6)	10.0 (6)	9.7 (4)	14 (1)	11.6 (5)	10.1 (3)	10.1 (3)	
β_3	10.5 (6)	11.0 (6)	–	–	11.5 (4)	13.3 (3)	–	
β_4	11.7 (6)	9.4 (6)	–	–	9.8 (5)	11.8 (4)	–	
$\langle\beta\rangle$	10.5 (3)	10.0 (3)	9.8 (2)	13.5 (7)	10.6 (2)	11.4 (2)	10.2 (2)	11.2†
β_1^*	0.26 (2)	0.25 (2)	0.27 (1)	0.34 (4)	0.25 (2)	0.27 (1)	0.27 (1)	
β_2^*	0.25 (2)	0.27 (2)	0.26 (1)	0.36 (5)	0.30 (2)	0.27 (1)	0.26 (1)	
β_3^*	0.27 (2)	0.29 (2)	–	–	0.30 (2)	0.34 (1)	–	
β_4^*	0.31 (2)	0.25 (2)	–	–	0.26 (2)	0.31 (1)	–	
$\langle\beta^*\rangle$	0.27 (1)	0.26 (1)	0.265 (7)	0.35 (3)	0.28 (1)	0.298 (5)	0.265 (7)	0.292‡
ω_1	6.7 (1)	0.7 (1)	1.28 (9)	2.7 (3)	2.4 (1)	1.95 (9)	2.12 (8)	
ω_2	8.2 (1)	2.7 (1)	1.27 (9)	2.6 (3)	1.5 (1)	1.76 (9)	2.12 (8)	
ω_3	4.9 (2)	3.7 (1)	–	–	2.7 (1)	2.44 (9)	–	
ω_4	6.3 (1)	5.7 (1)	–	–	3.7 (1)	6.12 (9)	–	
$\langle\omega\rangle$	6.53 (7)	3.20 (5)	1.27 (6)	2.7 (2)	2.58 (5)	3.07 (5)	2.12 (6)	0.32‡
φ_1	16.7 (4)	15.4 (4)	15.1 (3)	13.1 (9)	14.8 (3)	15.5 (2)	15.1 (2)	
φ_2	15.0 (4)	14.9 (4)	–	–	14.2 (3)	12.8 (3)	–	
$\langle\varphi\rangle$	15.8 (3)	15.2 (3)	15.1 (3)	13.1 (9)	14.5 (2)	14.2 (2)	15.1 (2)	2.98‡
θ	1.9 (2)	3.0 (2)	2.5 (1)	5.2 (4)	5.0 (2)	4.4 (1)	4.3 (1)	0.32‡

† Values taken from Keehn (1983). ‡ Values calculated from Hope *et al.* (1972).

Parameters *a* and *b* have already been discussed, and *e* and *g* only need one more remark. Compounds (1)–(7) have two types of C(bridgehead)—C(ring atom *ortho* to bridgehead) distances: those with an S atom *ortho* to the bridgehead atom (*e*) and those without an *ortho*-S atom (*g*). They are almost equal (Table 2), which is unsurprising since the most significant geometric changes will occur first in bond and torsion angles and second in non-aromatic distances. Distances *p* and *q* were also previously discussed.

Angle γ has a general tendency to be smaller than in the parent [2.2]PCP. The endocyclic phenylene ring angle at the bridgehead C atoms (λ) is smaller than 120°, in agreement with the results of Domenicano *et al.* (1975) and Domenicano & Murray-Rust (1979), *i.e.* in aromatic C_6 rings electron-withdrawing substituents increase the endocyclic angle at the substituent site, while electron-donating substituents decrease this angle. Thus, except for (1), the λ value at bridgehead C2 (C10) (114–116.6°) is substantially smaller than at bridgehead C5 (C13) (116.0–118.2°) due to the presence of the $-S(=O)_2-O$ or $-S(=O)_2-N$ substituent *ortho* to C2 (C10) but *meta* to C5 (C13).

The parameter definitions imply a positive correlation between α and α^* and between β and β^*, and a negative correlation between α and β or α^* and β^*, as exemplified in Table 6. This is not unexpected as the atoms of the *para*-phenylene ring and the C atoms of the ethylene bridge directly attached to it have to be coplanar within the limits of accuracy. The indices 1 and 3 of α, α^*, β, β^* and ω correspond to values of angles between planes, or distances from planes, for atoms which are near the additional S—O3/N—S bridge, whereas the indices 2 and 4 correspond to values for atoms which are at somewhat longer distances from this additional bridge. From Table 6 no consistent pattern can be found for indices 1 and 3 on one hand and indices 2 and 4 on the other. Therefore, it cannot be concluded that α, α^*, β, β^* and ω are influenced by the presence of an additional S—O3/N—S bridge in (2)–(7). Presumably the differences have to be ascribed to packing effects. However, there seems to be a significant difference within the α values (and consequently the α^*) of (1): α_1 (and α_1^*) is substantially higher than the other α values and concerns the atoms which are directly involved with the sulfonate substituent. The average value of α and α^* of (1) is also somewhat larger than the values observed in (2)–(7) and should be attributed to the presence of the additional S—O3/N—S bridge in the latter. ω is significantly larger in (1) than in (2)–(7): in the former the molecular symmetry in the [2.2]PCP moiety is broken, whereas in the latter it is 'restored'. This angle is strongly affected by the sulfonation, the calculated value in the parent [2.2]PCP being only 0.32°.

In his work Keehn (1983) presented φ as the angle between two planes (Fig. 8), but his text presents φ as the angle between the plane normals (= 180° − φ). The latter definition is used here. Except for (6) the values of φ_1 and φ_2 for (2)–(7) can be considered to be equal. No reason can be given for the discrepancy in (6). In (1) φ_1 is substantially larger than φ_2, which might again be ascribed to the sulfonate substituent. The average φ value in (1) is larger than in (2)–(7) expressing the greater influence on φ of a sulfonate substituent compared to an additional S—O3/N—S bridge. φ in the parent [2.2]PCP is only 2.98°, which indicates that the φ angles are also strongly affected by sulfonation.

The two *para*-phenylene rings are inclined from each other at the side of the sulfonate group in (1), but are twisted in the opposite direction in (2)–(7). The value of θ in (1) is substantially smaller than in (2)–(7), but θ does not express the relative twisting; the highest θ values are observed in those compounds having an alkyl group attached to the *N*-sulfonimide atom. θ is also strongly influenced by the sulfonation, the calculated value in the parent [2.2]PCP being only 0.32°.

4. Concluding remarks

The structural differences between [2.2]PCP and its 4-sulfonic acid (1) lead to differences in steric hindrance for their sulfonation. In [2.2]PCP the planes through the central C_4H_4 moieties of the two *para*-phenylene rings are strictly parallel, with a distance between them of 3.09 Å (Hope *et al.*, 1972). In the monosulfonate (1) the planes of the two *para*-phenylene moieties are rotated away from each other on the side of the sulfonate substituent. This leads to a reduction in steric hindrance for sulfonation at C11 and C12, but to an enhancement of steric hindrance at C14 and C15, compared with sulfonation at one of the eight equivalent positions of [2.2]PCP. For the 4,15-disulfonic anhydride (2) and for the 4,15-disulfonimide derivatives (3)–(7), the additional $-SO_2-O-SO_2-$ or $-SO_2-N-SO_2-$ bridge leads to a significant complementary strain with the nearest (C1—C9) ethylene bridge, and induces some rotation around C2—C5 and C10—C13 in opposite directions compared with (1). With respect to the parent [2.2]PCP the structural changes caused by sulfonation are mainly expressed in the bonding and torsion angles and the non-bonded distances between the *para*-phenylene moieties and to a lesser degree in the bond distances. Consequently, the largest deviations from [2.2]PCP for Keehn's (1983) parameters are observed for ω, φ and θ.

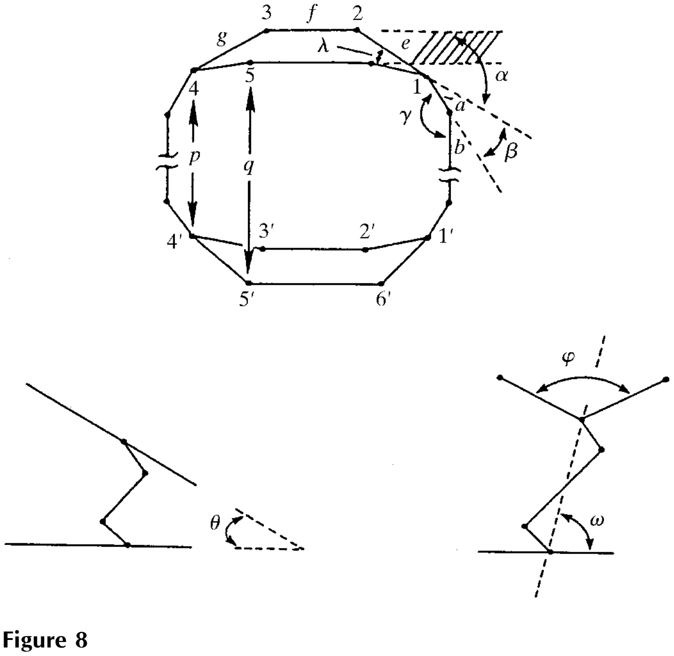

Figure 8
Parameters introduced by Keehn (1983) to describe the crystallographic data of [2.2]paracyclophanes. In (1)–(7) the bond lengths *e* and *g* are unrelated because of molecular dissymmetry and are therefore indicated separately in Table 2. α denotes the interplanar angle between the 2,3,5,6 plane and the 2,1,6 plane, and β the angle between the 2,1,6 plane and the 1–7 bond vector. θ describes the angle of inclination of two least-squares phenylene ring planes. φ describes the angle that the 1,2,3,4 plane and the 4,5,6,1 plane make with one another, and ω defines the angle between the least-squares phenylene plane and the line drawn between the phenylene ring atoms of each ring bound to the same bridge.

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