Benzene-1,2-disulfonate Dianion: Another Compound with Meshed Cogwheel Substituents?

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Abstract

Crystal structures of the dipotassium and potassium tetramethylammonium salts of benzene-1,2-disulfonic acid have been determined at 200 K and a *PM*3 enthalpy hypersurface for the substituent rotations of the free benzene-1,2-disulfonate dianion was calculated. The cogging of the two sulfonate groups as well as the possible pathways of conformational isomerization are discussed and compared with already investigated molecules containing adjacent threefold substituents.

1. Introduction

Molecular subunits with a conformational degree of freedom towards their molecular frame are termed chemical rotors. Two or more chemical rotors in close proximity, which due to sterical crowding enforce their correlated rotation, are often designated as geared or meshed cogwheels (*e.g.* Kwart & Alekman, 1968; Bürgi, Hounshell, Nachbar & Mislow, 1983). Static overlap as well as dynamics in numerous molecules with cogwheeled substituents have already been investigated. In most the coupling of the chemical rotors originates in nonbonded sterical interactions (*e.g.* Mislow, 1976) and sometimes is rationalized by orbital symmetry control (Edidin, Norton & Mislow, 1982; Schilling & Hoffmann, 1979).

In this report the steric crowding and possible dynamics of the benzene-1,2-disulfonate dianion are compared with *stereochemically correspondent* (Gust, Finocchiaro & Mislow, 1973; Mislow, Gust, Finocchiaro & Boettcher, 1974) compounds, which contain at least two adjacent substituents such as methyl, *tert*-butyl or 9-triptycyl groups. Geminal methyl groups, *e.g.* in propane, favor the gear-clashed conformation (II, Table 1). They cannot be labeled as chemical rotors, because their torsion is uncorrelated (Bürgi, Hounshell, Nachbar & Mislow, 1983). In contrast, systems with geminal or vicinal *tert*-butyl groups in close proximity favor conformational arrangements of approximate C_2 symmetry (Table 1, IV). Their preferred pathways of conformational isomerization involve correlated rotation of the rotors (Nachbar, Johnson & Mislow, 1982). Molecules containing

Table 1. *Possible arrangements of two threefold substituents in proximity with nontrivial symmetry*

Conformation arrangement	I	II	III	IV	V
Symmetry*	C_{2v}	C_{2v}	C_s	C_2	C_s

* The symmetry of molecular fragments is given in Schoenfliess notation.

geminal 9-triptycyl groups represent a tightly meshed and almost frictionless bevel gear system, which also adopts a C_2 symmetry conformation (Table 1, IV) in the energy minimum. The transition state during conformational isomerization (Table 1, III) is predicted at only slightly higher energy. The geminal 9-triptycyl groups undergo almost unhindered, but strongly coupled disrotation (Bürgi, Hounshell, Nachbar & Mislow, 1983; Guenzi, Johnson, Cozzi & Mislow, 1983).

Substitution of the *tert*-butyl groups by trimethylsilyl groups reduces the steric overlap between the threefold substituents, because the carbon–carbon single bond length of only ~1.53 Å is stretched to a Si—C bond length of ~1.86 Å (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). Nevertheless, the crystal structures of 1,2,4,5-tetrakis(trimethylsilyl)benzene and its radical anion (Bock, Ansari, Nagel & Havlas, 1995), as well as its dianion (Sekiguchi, Ebata, Kabuto & Sakurai, 1991), indicate that the preferred spatial arrangement for trimethylsilyl groups in neutral molecules and their anions is of approximately C_2 symmetry (Table 1, IV). To date, however, more extensive investigations are still needed.

The substituent conformation in these compounds is dominated by the steric interactions between the two threefold groups. Intermolecular interactions within the crystal lattice, *i.e.* packing effects, influencing the molecular conformational arrangement, are considered to be negligible and, therefore, the principle of *structure correlation* (Bürgi & Dunitz, 1994*a*; Dunitz, 1979*a*; Bürgi, 1973, 1975*a,b*) can be applied. In our case, however, additional factors can influence the conformational arrangement: Intramolecular stereoelectronic effects at the oxygen might play a role (Kirby, 1983) and, in addition, coulombic interactions with the counter-cations should influence the conformational arrangement, especially if contact ion pairs are formed

Table 2. *Experimental details*

Crystal data

Chemical formula	$C_6H_4S_2O_6{}^{2-}.2K^+.CH_3OH$	$C_6H_4O_6S_2{}^{2-}.K^+[N(CH_3)_4]^+.0.5H_2O$
Chemical formula weight	346.45	358.47
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/m$
a (Å)	10.674 (1)	10.891 (2)
b (Å)	10.790 (1)	6.657 (2)
c (Å)	10.543 (1)	21.212 (3)
β (°)	99.97 (1)	101.64 (2)
V (Å^3)	1195.9 (2)	1506.3 (6)
Z	4	4
D_x (Mg m^{-3})	1.924	1.581
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	84	84
θ range (°)	9.5–19	9.5–19.0
μ (mm^{-1})	1.163	0.656
Temperature (K)	200 (2)	200 (2)
Crystal form	Prism	Needle
Crystal size (mm)	0.6 × 0.4 × 0.35	0.7 × 0.4 × 0.4
Crystal color	Colorless	Colorless

Data collection

Diffractometer	Siemens P4	Siemens P4
Data collection method	ω	ω
Absorption correction	None	None
No. of measured reflections	4831	3996
No. of independent reflections	4244	3735
No. of observed reflections	3565	2975
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0270	0.0302
θ_{max} (°)	32.50	27.53
Range of h, k, l	$-16 \rightarrow h \rightarrow 15$	$-14 \rightarrow h \rightarrow 13$
	$-16 \rightarrow k \rightarrow 0$	$-4 \rightarrow k \rightarrow 8$
	$-1 \rightarrow l \rightarrow 14$	$0 \rightarrow l \rightarrow 27$
No. of standard reflections	4	4
Frequency of standard reflections (min)	120	120
Intensity decay (%)	Negligible	Negligible

Refinement

Refinement on	F^2	F^2
R^*	0.0389	0.0329
$wR\dagger$	0.0970	0.0931
S	1.083	1.109
No. of reflections used in refinement	4243	3731
No. of parameters used	173	250
H-atom treatment	All parameters refined for H centers bonded to solvent O centers; other H centers placed in calculated positions and only U's refined	All parameters refined for H centers bonded to solvent O centers; other H centers placed in calculated positions and only U's refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.1541P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 0.4005P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.001	-0.002
$\Delta\rho_{max}$ (e Å^{-3})	0.931	0.492
$\Delta\rho_{min}$ (e Å^{-3})	-0.737	-0.517
Extinction method	None	SHELXL93 (Sheldrick, 1993)
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.   † $wR = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]$.

on crystallization. Interactions between the benzene-1,2-disulfonate dianion and cations have been observed even in solution (Yokoyama, Koyama & Masuda, 1988). The investigation of the conformation and dynamics of the dianion in solution has to be based on the accurate measurement and difficult interpretation of nonstandard ^{33}S NMR spectra (Kosugi & Okazaki, 1990; Crumrine & Gillece-Castro, 1985). Therefore, we present two crystal structures and semiempirical enthalpy hypersurface calculations for the rotation of the sulfonate groups in the *ortho* position of the benzene ring.

2. Experimental

2.1. *Materials and crystallization*

Dipotassium benzene-1,2-disulfonate–methanol: Commercially available dipotassium benzene-1,2-disul-

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Dipotassium salt				
K1	1.11423 (4)	1.01563 (4)	0.14974 (4)	0.01935 (9)
K2	0.98973 (4)	0.66653 (3)	0.04050 (4)	0.01815 (9)
S1	0.79674 (4)	1.20578 (3)	0.12996 (4)	0.01420 (9)
S2	0.84053 (4)	0.89396 (3)	0.22527 (4)	0.01253 (9)
O1	0.73172 (14)	1.29801 (12)	0.04090 (14)	0.0230 (3)
O2	0.89081 (13)	1.13799 (12)	0.07299 (14)	0.0214 (3)
O3	0.84663 (14)	1.25798 (13)	0.25536 (13)	0.0227 (3)
O4	0.87664 (13)	0.87342 (12)	0.09962 (12)	0.0182 (2)
O5	0.93003 (12)	0.97411 (11)	0.30798 (12)	0.0169 (2)
O6	0.81677 (13)	0.77955 (12)	0.29001 (13)	0.0207 (3)
C1	0.6744 (2)	1.09837 (15)	0.1530 (2)	0.0141 (3)
C2	0.6911 (2)	0.97402 (14)	0.1928 (2)	0.0134 (3)
C3	0.5847 (2)	0.9029 (2)	0.2038 (2)	0.0193 (3)
C4	0.4626 (2)	0.9522 (2)	0.1772 (2)	0.0253 (4)
C5	0.4466 (2)	1.0755 (2)	0.1400 (2)	0.0264 (4)
C6	0.5514 (2)	1.1470 (2)	0.1279 (2)	0.0211 (3)
O7	0.7720 (2)	1.54093 (14)	0.0969 (2)	0.0299 (3)
C7	0.6594 (2)	1.6055 (2)	0.0437 (2)	0.0282 (4)
Potassium tetramethylammonium salt				
K1	−0.06928 (4)	3/4	0.99861 (2)	0.02235 (13)
K2	0.43469 (4)	1/4	0.50162 (2)	0.02437 (14)
S1	0.24804 (5)	3/4	1.08459 (2)	0.01979 (14)
S2	0.17082 (5)	3/4	0.91448 (2)	0.01778 (14)
S3	0.24285 (5)	3/4	0.42676 (2)	0.01911 (14)
S4	0.33652 (5)	3/4	0.59591 (2)	0.02124 (14)
O10	0.3235 (2)	3/4	1.14900 (8)	0.0355 (4)
O11	0.17327 (14)	0.5702 (2)	1.07077 (7)	0.0515 (4)
O12	0.10971 (11)	0.5688 (2)	0.93028 (6)	0.0348 (3)
O13	0.1878 (2)	3/4	0.84841 (7)	0.0288 (4)
O20	0.1610 (2)	3/4	0.36397 (8)	0.0334 (4)
O21	0.31810 (13)	0.5699 (2)	0.43883 (6)	0.0448 (4)
O22	0.39608 (13)	0.5704 (2)	0.57848 (7)	0.0496 (4)
O23	0.3265 (2)	3/4	0.66286 (8)	0.0416 (5)
O30	0.3749 (4)	1/4	0.6785 (2)	0.0788 (14)
C10	0.3568 (2)	3/4	1.03116 (10)	0.0177 (4)
C11	0.3262 (2)	3/4	0.96301 (10)	0.0185 (4)
C12	0.4226 (2)	3/4	0.92885 (11)	0.0245 (5)
C13	0.5477 (2)	3/4	0.96029 (12)	0.0295 (5)
C14	0.5778 (2)	3/4	1.02625 (13)	0.0283 (5)
C15	0.4830 (2)	3/4	1.06130 (12)	0.0253 (5)
C20	0.1404 (2)	3/4	0.48357 (10)	0.0180 (4)
C21	0.1779 (2)	3/4	0.55142 (10)	0.0179 (4)
C22	0.0864 (2)	3/4	0.58845 (11)	0.0234 (4)
C23	−0.0408 (2)	3/4	0.56120 (13)	0.0280 (5)
C24	−0.0778 (2)	3/4	0.49468 (12)	0.0277 (5)
C25	0.0122 (2)	3/4	0.45711 (11)	0.0232 (4)
N1	0.6816 (2)	3/4	0.75381 (9)	0.0278 (4)
N2	−0.1176 (2)	3/4	0.23425 (9)	0.0269 (4)
C30	0.8043 (3)	3/4	0.80098 (13)	0.0420 (6)
C31	0.5775 (3)	3/4	0.78968 (15)	0.0472 (7)
C32	0.6725 (2)	0.5665 (3)	0.71289 (11)	0.0546 (6)
C40	−0.2435 (2)	3/4	0.18961 (12)	0.0350 (6)
C41	−0.0159 (3)	3/4	0.19698 (13)	0.0383 (6)
C42	−0.1072 (2)	0.5663 (2)	0.27604 (8)	0.0343 (4)

fonate (Aldrich) with an unspecified amount of crystal water was dissolved in dimethylsulfoxide. Isothermal distillation of methanol into this solution yielded colorless prisms of dipotassium benzene-1,2-disulfonate with 1 equiv. of methanol. Elemental analysis: exp. C 24.39, H 2.29; calc. C 24.27, H 2.33%.

Potassium tetramethylammonium benzene-1,2-disulfonate hemihydrate: Dipotassium benzene-1,2-disulfonate (Aldrich) was dissolved in water and excess tetramethylammonium chloride was added. On slow cooling colorless needles of potassium tetramethylammonium benzene-1,2-disulfonate hemihydrate crystallized. Elemental analysis: exp. C 33.47, H 5.03, N 4.18; calc. C 33.51, H 4.78, N 3.91%.

On heating the transparent crystals of both compounds become opaque, which possibly indicates a loss of solvent molecules, but up to 623 K they neither melt nor seem to decompose further.

2.2. X-ray crystal structure determination

The data sets were collected with a Siemens P4 four-circle diffractometer in the ω scan mode (Siemens, 1992). Intensities have been collected to $2\theta \leq 65°$ $-16 \leq h \leq 15$, $-16 \leq k \leq 0$, $-1 \leq l \leq 14$) for the dipotassium salt and to $2\theta \leq 55°$ $(-14 \leq h \leq 13$, $-4 \leq k \leq 8, 0 \leq l \leq 27)$ for the potassium tetramethylammonium salt. Unit-cell parameters for both salts resulted from least-squares treatment of 84 reflections with $19 \leq 2\theta \leq 38°$, respectively (Siemens, 1992). No significant variation of the intensities of the standard reflections was observed during data collection. Correction for Lorentz and polarization effect but not for absorption were applied (Siemens, 1992). The structures were solved by direct methods using *SHEXLS*86 (Sheldrick, 1990) and refined by full-matrix least-squares (based on F^2) using *SHELXL*93 (Sheldrick, 1993). The final difference electron-density maps show that the maximum peak of $0.93 \mathrm{e\,Å^{-3}}$ in the structure of the dipotassium salt is close to one potassium cation and that the maximum peak of $0.49 \mathrm{e\,Å^{-3}}$ in the structure of the potassium tetramethylammonium salt is located on a carbon–sulfur bond. In the last least-squares cycles of both refinements all hydrogens except those bound to the oxygens of the solvent molecules were positioned according to standard geometrical criteria. The isotropic displacement parameters of all hydrogens and the positions of the hydrogens bound to oxygen have been refined. For the potassium tetramethylammonium salt the extinction correction $F^* = F_c/(k[1.0 + (0.001xF_c^2)\lambda^3/\sin 2\theta]^{0.25})$ was applied and the extinction variable refined to $x = 0.018(1)$. Table 2 gives the crystal data for both salts and atomic coordinates of all non-H atoms, together with their equivalent isotropic displacement parameters which are presented in Table 3.*

2.3. Semiempirical calculations

Based on crystal structure data with hydrogen–carbon bond distances normalized to 1.09 Å, a semiempirical enthalpy of formation hypersurface for the torsional dynamics in the benzene-1,2-disulfonate dianion has

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* Lists of structure factors and complete geometry have been deposited with the IUCr (reference: SE0184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

been calculated using the program *MOPAC* (T. Clark, University Erlangen). Both *AM*1 and *PM*3 methods have been tested. The *PM*3 method reproduced the molecular geometry found in the crystal structures more accurately and was chosen. The conformations of the SO_3 rotors have been varied in steps of 10° and the geometry optimized for each of the conformational arrangements using the Fletcher/Powell subroutine.

3. Results and discussion

3.1. Crystal structures

Both salts are monoclinic and contain four formula units in the unit cell. The dipotassium salt crystallizes in space group $P2_1/c$ with one benzene-1,2-disulfonate dianion, two potassium cations and one methanol molecule within the asymmetric unit (Fig. 1*b*).

The asymmetric unit of the potassium tetramethyl-ammonium salt contains two half benzene-1,2-disulfo-nate dianions, two half tetramethylammonium cations, two potassium cations and half a water molecule, all located on a crystallographic mirror plane (Fig. 2*b*). The salt crystallizes in space group $P2_1/m$.

Both crystal structures show polar regions of oxygen-coordinated potassium cations alternating with apolar regions of stacked benzene fragments (Figs. 1*a* and 2*a*). The stacking mode represents an energetically favorable arrangement of benzene fragments (Hobza, Selzle & Schlag, 1994; Hunter, 1994; Hunter & Sanders, 1990) and is similar for both salts. The planes of the benzene rings within a stack are parallel with an interplanar distance of ~3.35 Å and the offsets between the centers of adjacent benzene fragments range from 1.00 to 1.30 Å. The potassium cations in both crystal structures are coordinated by eight oxygens of sulfonate fragments with contact distances ranging from 2.66 (2) to 3.26 (2) Å. The methanol oxygen O7 coordinates K1 and K2 with contact distances of 2.75 (2) and
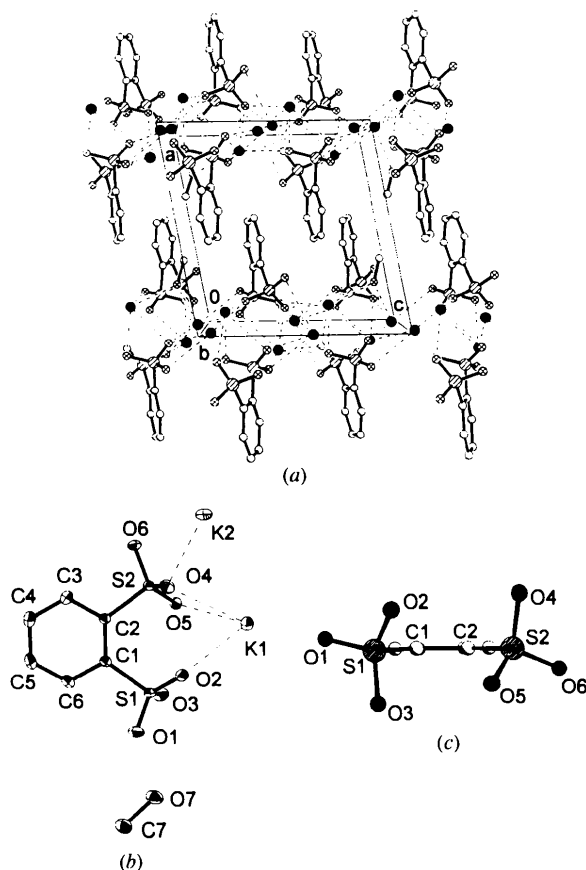

Fig. 1. Crystal structure of dipotassium benzene-1,2-disulfonate methanol: (*a*) packing with polar layers of potassium cations and sulfonate groups parallel to the *bc* plane, (*b*) contents of the asymmetric unit with anisotropic displacement ellipsoids at the 50% probability level and the numbering scheme, and (*c*) the benzene-1,2-disulfonate dianion viewed along the benzene plane.
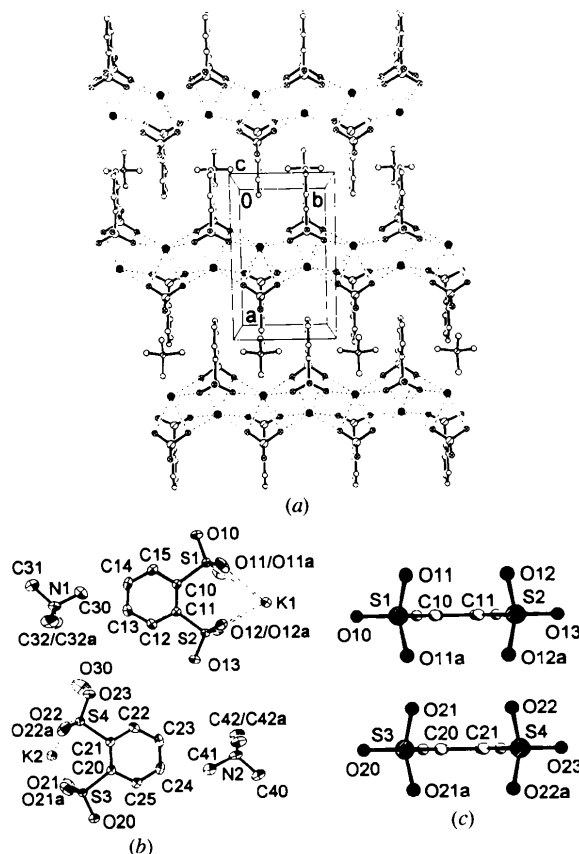
Fig. 2. Crystal structure of potassium tetramethylammonium benzene-1,2-disulfonate hemihydrate: (*a*) crystal packing with chains of oxygen coordinated potassium cations running parallel to the *b* axis, (*b*) center numbering scheme with anisotropic displacement ellipsoids at the 50% probability level and (*c*) both benzene-1,2-disulfonate dianions viewed down the benzene plane.

Table 4. *Selected bond lengths (Å), contact distances (Å), angles (°) and torsional angles (°) of the benzene-1,2-disulfonate dianions in the dipotassium and potassium tetramethylammonium salt*

Dipotassium salt		Potassium tetramethylammonium salt	
C1—C2	1.408 (2)	C10—C11	1.417 (3)
S1—C1	1.794 (2)	C10—C21	1.414 (3)
S2—C2	1.794 (2)	S1—C10	1.797 (2)
S1—O1	1.459 (1)	S2—C11	1.794 (2)
S1—O2	1.454 (1)	S3—C20	1.800 (2)
S1—O3	1.451 (1)	S4—C21	1.794 (2)
O1—K2^i	3.257 (2)	O11—K1	3.020 (2)
O2—K1	2.723 (1)	O11—K1^i	2.706 (2)
O2—K1^i	2.867 (2)	O12—K1	2.915 (2)
O2—K2^i	2.835 (1)	O12—K1^i	2.691 (1)
O3—K1^{ii}	2.960 (1)		
O3—K2^{ii}	2.712 (2)	O21—K2	2.691 (1)
O4—K1	2.933 (1)	O21—K2^v	2.985 (2)
O4—K2	2.663 (1)	O22—K2	2.768 (2)
O4—K1^i	2.906 (1)	O22—K2^v	2.996 (2)
O5—K1	2.826 (1)		
O5—K^{ii}	2.669 (1)		
O5—K2^{iii}	2.860 (1)		
O6—K1^{iv}	2.982 (1)		
O6—K2^{iii}	3.005 (2)		
C2—C1—S1	126.8 (1)	C11—C10—S1	126.4 (2)
C1—C2—S2	125.3 (1)	C10—C11—S2	125.9 (2)
S1—C1—C2—S2	−1.8 (2)	S1—C10—C11—S2	0.0
O1—S1—C1—C2	156.8 (2)	O10—S1—C10—C11	180.0
O2—S1—C1—C2	38.4 (2)	O11—S1—C10—C11	60.0 (1)
O3—S1—C1—C2	−83.9 (2)	O11^{vi}—S1—C10—C11	−60.0 (1)
O4—S2—C2—C1	−72.2 (2)	O12—S2—C11—C10	60.5 (1)
O5—S2—C2—C1	47.9 (2)	O12^{vi}—S2—C11—C10	60.5 (1)
O6—S2—C2—C1	167.5 (1)	O13—S2—C11—C10	180.0

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $z-x, y+\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, x, 1-y, 1-z$; (iv) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $-x, 1-y, 2-z$; (vi) $x, \frac{3}{2}-y, z$.

2.84 (2) Å. The hydroxy hydrogen of the methanol and the water hydrogens form O—H···O hydrogen bonds to the sulfonate oxygens. In the dipotassium salt the cations are arranged in layers along the plane through the *b* and *c* axes, whereas in the potassium tetramethylammonium salt the potassium cations form chains running along the *b* axis (Figs. 1*a* and 2*a*). The bond lengths and angles of the benzene-1,2-disulfonate dianion are in the expected range (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994) and are very similar in both crystal structures (Table 4). The intramolecular crowding of the sulfonate groups results in widened angles $(O_3)S$—C—$C(SO_3)$ of ~126°. No significant twist of the S atoms out of the benzene planes is observed. The shortest intramolecular O···O contact distances between the sulfonate groups in both salts are ~290 pm and, therefore, despite the negative charges, shorter than twice the van der Waals radius of neutral oxygen, $152 + 152 = 304$ pm (Bondi, 1964). The conformation of the dianion in the dipotassium salt (Fig. 1*c*) corresponds approximately to an arrangement of C_2 symmetry (Table 1, IV), whereas a C_{2v} arrangement (Table 1, II) is realized by both molecular ions of the potassium tetramethylammonium salt (Fig. 2*c*).

3.2. Potential energy surface

With respect to the center numbering scheme in Fig. 1(*b*), the conformations of the sulfonate groups can be defined by six torsional angles

$$\omega_1(O1—S1—C1—C2), \quad \omega_4(O4—S2—C2—C1),$$

$$\omega_2(O2—S1—C1—C2), \quad \omega_5(O5—S2—C2—C1),$$

$$\omega_3(O3—S1—C1—C2), \quad \omega_6(O6—S2—C2—C1).$$

For a quantitative description of the spatial arrangement of the sulfonate groups, symmetry distortion coordinates (Bürgi & Dunitz, 1994*b*; Nachbar, Johnson & Mislow, 1982; Murray-Rust, Bürgi & Dunitz, 1979; Dunitz, 1979*b*) are used $(0 \leq \omega_i \leq 360°; i = 1, 2, 3, \ldots, 6)$

$$\varphi_1 = (\omega_1 + \omega_2 + \omega_3 - 360)/3 \quad \text{and}$$

$$\varphi_2 = (\omega_4 + \omega_5 + \omega_6 - 360)/3.$$

The semiempirical *PM*3 enthalpy of formation surface for the free benzene-1,2-disulfonate dianion calculated by varying the conformation of both sulfonate groups is periodical with a period of 120° in φ_1 and φ_2. The contour map (Fig. 3) of this energy surface represents a half unit cell of the plane group *c2mm* (No. 9), including four equivalent general positions (Hahn, 1983). The general positions within this map belong to arbitrary conformations of the sulfonate groups and the special positions are images of spatial arrangements with nontrivial symmetry of the dianion (Table 5).
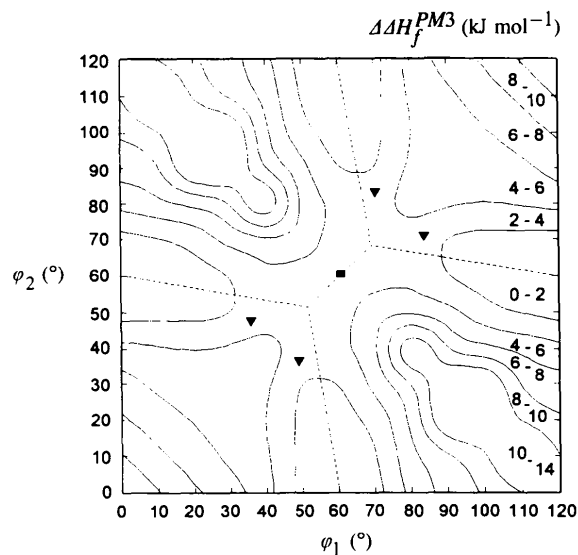

Fig. 3. Contour map of the *PM*3 enthalpy surface of the free benzene-1,2-disulfonate dianion. ▼: the four equivalent positions representing the conformation found in the dipotassium salt; ■: conformation within the potassium tetramethylammonium salt. The dashed lines indicate the minimum energy pathways of conformational rearrangement.

Table 5. *Comparison of molecular symmetry with site symmetry of the hypersurface*

Conformatonal arrangement	I	II	III	IV	V	VI
φ_1, φ_2 (°)	0,0	60, 60	0, 60	x, x	$x, -x$	x, y
Molecular symmetry	C_{2v}	C_{2v}	C_s	C_2	C_s	C_1
Site symmetry of hypersurface*	2mm (a)	2mm (b)	2 (c)	m (d)	m (e)	1 (f)

* Wyckoff letters in parentheses.

The calculated lowest energy conformation (Table 5, III) is found at $\varphi_1, \varphi_2 = (0,60°)$ and at the symmetry-equivalent positions (60,0°), (60,120°) and (120,60°). The energy of the conformational arrangements in the two crystal structures (Fig. 3: ▼ and ■) is less than $4\,\text{kJ}\,\text{mol}^{-1}$ above the energy minimum, although the coulombic interactions with the cations should allow less favorable conformations.

In the least favorable conformation of the benzene-1,2-disulfonate dianion (Table 5, I), two oxygens of adjacent sulfonate groups come in close contact [Fig. 3: (0,0°), as well as the symmetry-equivalent positions (0,120°), (120,0°) and (120,120°)] and its enthalpy of formation is calculated to be $14\,\text{kJ}\,\text{mol}^{-1}$ above the hypersurface energy minimum. The overall shape of the energy surface is similar to that calculated for geminal *tert*-butyl groups (Nachbar, Johnson & Mislow, 1982; Bürgi, Hounshell, Nachbar & Mislow, 1983), although the minimum energy conformations deviate. Our hypersurface is more shallow, a reasonable result for a system of vicinal threefold rotors. Concomitantly, the pathways of conformational rearrangement are rather broad. Nevertheless, the contour map reveals three nonequivalent minimum energy pathways for conformational isomerization, which are indicated by dashed lines. The barrier of rotation along these pathways remains below $4\,\text{kJ}\,\text{mol}^{-1}$. Conformational rearrangements along the first pathway $(0,60°) \longleftrightarrow (60,0°)$ and $(60,120°) \longleftrightarrow (120,60°)$ correspond to correlated disrotation, *i.e.* to the motion of geared cogwheels. The other two pathways pass through the transition state at (60,60°) represented by conformation II (Table 5). The second pathway $(0,60°) \longleftrightarrow (60,120°)$ and $(60,0°) \longleftrightarrow (120,60°)$ starts with the rotation of one sulfonate group until conformation II is adopted and proceeds with the conrotation of the second sulfonate group. The third pathway $(0,60°) \longleftrightarrow (120,60°)$ and $(60,0°) \longleftrightarrow (60,120°)$ represents the rotation of one rotor group, while the other rotor group remains virtually motionless at $\varphi \approx 60°$. These movements can be described as gear slippage (Bürgi, Hounshell, Nachbar & Mislow, 1983) and demonstrate that the gearing of the sulfonate groups is rather weak. Altogether, the ensemble of two *ortho*-sulfonate groups

can be rationalized as intermediate between the systems containing two methyl rotors and those containing *tert*-butyl groups, both with regard to intermeshing and correlated rotation of the substituents.

4. Summary

Structures of the benzene-1,2-disulfonate dianion have been determined by single-crystal X-ray analysis and the potential dynamics elaborated by semiempirical *PM*3 calculations. The crystal structure indicates weak strain between the sulfonate groups. The calculations for a free benzene-1,2-disulfonate dianion suggest almost unhindered conformational rearrangements with rather low activation barriers. These results can be rationalized by assuming that the strain between the sulfonate groups remains almost unchanged during conformational isomerization along the three different minimum energy pathways discovered, which are rather broad due to the overall shallow hypersurface. The sulfonate rotors show only weak intermeshing and their rotation is only slightly correlated.

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