Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Structural characterization of protonated benzeneseleninic acid, the dihydroxyselenonium ion

Henning Osholm Sørensen,[a] Nicolai Stuhr-Hansen,[b] Lars Henriksen[b] and Sine Larsen[a]*

[a]Centre for Crystallographic Studies, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and [b]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Correspondence e-mail: sine@ccs.ki.ku.dk

Received 4 May 2000
Accepted 31 July 2000

The structure of the dihydroxyphenylselenonium ion ($C_6H_7O_2Se^+$) has been determined in its benzenesulfonate ($C_6H_5O_3Se^-$) and *p*-toluenesulfonate ($C_7H_7O_3S^-$) salts. Whereas the former salt is disordered, the latter less dense salt is well defined. This difference in crystallization behaviour is attributed to a C—H···O hydrogen bond involving the methyl group of the *p*-toluenesulfonate ion. The two salts display very similar hydrogen-bond arrangements and differ only with respect to the stacking of the phenyl groups. The dihydroxyselenonium ion is a strong acid with a pK value of −0.9 determined from the variation of the ^{77}Se chemical shift. A comparison with the two deprotonated species reveals a systematic increase in the Se—O bond lengths and the pyramidal configuration around Se with the number of protons attached.

1. Introduction

Although the organic chemistry of selenium is assumed to be quite similar to the equivalent chemistry of sulfur, there are some systematic differences. The decrease in acidity of the inorganic selenium oxy acids relative to the equivalent sulfur compounds is also observed for their organic oxy acids. Benzeneseleninic acid (1) with a pK value of 4.79 (McCullough & Gould, 1949) is a much weaker acid than benzenesulfinic acid with pK = 2.16 (Burkhard *et al.*, 1959). This explains why only benzenesulfinic acid is known as the free acid and as its deprotonated form, whereas benzeneseleninic acid is amphoteric and can be deprotonated to the seleninate ion (2) and protonated to the dihydroxyphenylselenonium ion (3).

$$\underset{(3)}{\mathrm{PhSe(OH)_2^+}} \xrightleftharpoons{\mathrm{H^+}} \underset{(1)}{\mathrm{PhSeO_2H}} \xrightleftharpoons{\mathrm{OH^-}} \underset{(2)}{\mathrm{PhSeO_2^-}}$$

The existence of a dihydroxy selenonio group in a series of protonated alkaneseleninic acids was previously inferred from a study of their vibrational spectra (Paetzold *et al.*, 1960) and a report of the *p*-toluenesulfonate salt of (3) was given as one of the products from a redox reaction between (1) and *p*-toluenesulfinic acid (Gancarz & Kice, 1980).

We have recently shown that it is possible to obtain crystals of the *p*-toluenesulfonate and the benzenesulfonate salt of the dihydroxyphenylselenonium ion from an equimolar mixture of (1) and the appropriate arenesulfonic acid in glacial acetic acid (Henriksen & Stuhr-Hansen, 1996; Stuhr-Hansen & Henriksen, 1997). This enabled us to perform a structural characterization of the dihydroxyphenylselenonium ion in two similar crystalline environments and make a comparison of the

© 2000 International Union of Crystallography
Printed in Great Britain – all rights reserved

Table 1
Experimental details.

	TOL	BEN
Crystal data		
Chemical formula	$C_6H_7O_2Se^{+}\cdot C_7H_7O_3S^{-}$	$C_6H_7O_2Se^{+}\cdot C_6H_5O_3S^{-}$
Chemical formula weight	361.26	347.24
Cell setting	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Fdd2$
a (Å)	5.8838 (11)	40.641 (5)
b (Å)	16.0925 (19)	22.268 (3)
c (Å)	14.929 (2)	5.7881 (13)
β (°)	95.547 (15)	90
V (Å^3)	1407.0 (4)	5238.4 (15)
Z	4	16
D_x (Mg m^{-3})	1.705	1.761
Radiation type	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.54184	1.54184
No. of reflections for cell parameters	23	20
θ range (°)	39.49–42.30	39.13–40.64
μ (mm^{-1})	5.165	5.521
Temperature (K)	122.0 (5)	122.0 (5)
Crystal form	Needle	Needle
Crystal size (mm)	0.36 × 0.08 × 0.07	0.36 × 0.08 × 0.07
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	ω–θ scans	ω–θ scans
Absorption correction	Numerical	Numerical
$T_{\min}$	0.370	0.361
$T_{\max}$	0.726	0.737
No. of measured reflections	5288	5592
No. of independent reflections	2906	2669
No. of observed reflections	2820	2552
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.0325	0.0383
$\theta_{\max}$ (°)	74.87	74.93
Range of h, k, l	$-7 \rightarrow h \rightarrow 4$ $0 \rightarrow k \rightarrow 20$ $-18 \rightarrow l \rightarrow 18$	$-50 \rightarrow h \rightarrow 50$ $-27 \rightarrow k \rightarrow 0$ $-7 \rightarrow l \rightarrow 6$
No. of standard reflections	5	4
Frequency of standard reflections	Every 166 min	Every 166 min
Intensity decay (%)	9.9	0
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0269	0.0737
$wR(F^2)$	0.0752	0.1425
S	2.386	5.839
No. of reflections used in refinement	2906	2669
No. of parameters used	237	166
H-atom treatment	All H-atom parameters refined	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^{\,2})]$	$w = 1/[\sigma^2(F_o^{\,2})]$
$(\Delta/\sigma)_{\max}$	0.029	0.036
$\Delta\rho_{\max}$ (e Å^{-3})	0.44	1.19
$\Delta\rho_{\min}$ (e Å^{-3})	−0.86	−1.13
Extinction method	None	None
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)
Computer programs		
Data collection	*CAD*-4 *Express* (Enraf–Nonius, 1995)	*CAD*-4 *Express* (Enraf–Nonius, 1995)
Cell refinement	*CAD*-4 *Express* (Enraf–Nonius, 1995)	*CAD*-4 *Express* (Enraf–Nonius, 1995)
Data reduction	*DREADD* (Blessing, 1987)	*DREADD* (Blessing, 1987)
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

geometry of its two deprotonated species (1) and (2). In order to fully characterize the acid–base properties of the benzeneseleninic acid we have also measured the acidity constant of the dihydroxyphenylselenonium ion.

2. Experimental

Dihydroxyphenylselenonium *p*-toluenesulfonate (TOL) and dihydroxyphenylselenonium benzenesulfonate (BEN) were prepared as described previously (Henriksen & Stuhr-Hansen, 1996; Stuhr-Hansen & Henriksen, 1997). Crystals suitable for the X-ray diffraction experiments were obtained by slow crystallization of the salts from glacial acetic acid.

pH measurements were carried out using a Radiometer PHM61 instrument equipped with a combination electrode and calibrated with standard pH 4.00 and 7.00 buffers. The observed pH values in 0.100 *M* aqueous solutions of hydrochloric acid, *p*-toluenesulfonic acid and TOL were 1.11, 1.13 and 1.12 ± 0.02, respectively.

^{77}Se NMR spectra were measured on a Varian Mercury 300 MHz instrument. Chemical shifts are referred to Me_2Se as the external reference. Solutions (0.2 *M*) of analytically pure benzeneseleninic acid prepared according to Henriksen & Stuhr-Hansen (1996) at known H_0 levels (Hammet, 1970) were prepared as appropriate mixtures of stock solutions (0.2 *M*) in water and 80% *w*/*w* sulfuric acid, respectively.

2.1. X-ray crystallography

Data collections were performed with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation. The crystals were cooled to 122.0 (5) K. An initial data set collected for BEN conformed with a *C*-centered orthorhombic cell with dimensions 40.66 (1), 22.115 (6) and 5.802 (2) Å. Since severe problems were encountered to solve the structure from these data, Weissenberg photographs were recorded at room temperature for the crystal used for the data collection. They showed the same cell and the possible space group to be either *Fdd*2 or *Fddd*. It could not be excluded that this change in space group was due to the difference in temperature. Therefore, two additional data sets were collected for BEN, one at room temperature and another at 122.0 (5) K. Analysis of these data sets established the space group to be *Fdd*2 at both temperatures. This leads us to conclude that the crystal of BEN investigated had undergone a phase transition from a *C*-centred to an *F*-centered cell. We assume that the *C*-centred cell represents a metastable form of BEN obtained by rapid precipitation. This form subsequently transforms to the thermodynamically stable *F*-centred cell during the initial data collection, explaining the difficulties in determining the structure from this data set. Table 1 contains information for TOL and the last [122.0 (5) K] data set for BEN.

Data reductions were performed with the program package *DREADD* (Blessing, 1987). They included corrections for background, Lorentz, polarization and absorption effects. A correction for the 9.9% decrease in the intensity of the standard reflections was also employed for TOL. The structures were solved by Patterson and Fourier methods using *SHELXS*86 (Sheldrick, 1985). *SHELXL*97 (Sheldrick, 1997) was used for the refinement of the two structures which included anisotropic displacement parameters for all the non-H atoms and positional and isotropic displacement parameters for the H atoms in TOL. The anion in BEN displayed a disorder that could be modelled by two almost equally populated conformations of the sulfonate group, $A = 0.518$ (8) and $B = 0.482$ (8). The isotropic displacement parameters of the O atoms and S—O distances were restrained to be identical in the refinement. Anisotropic displacement parameters were employed for the other non-H atoms. Only the positions of the H atoms of the phenyl groups in BEN could be localized in the difference electron density map; they were restrained to positions corresponding to idealized geometry and to have an isotropic displacement parameter 1.2 times the displacement parameter of the atom to which it is bonded. The refined Flack parameter −0.007 (54) established the absolute structure of BEN. The results from the refinements are listed in Table 1[1].

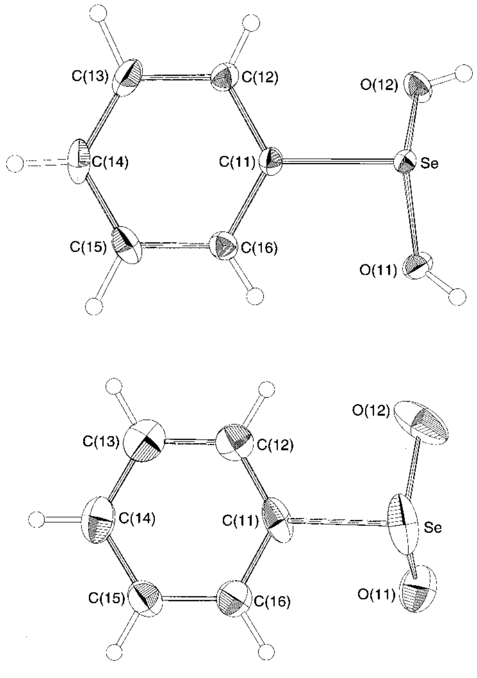

Figure 1
*ORTEP*II (Johnson, 1976) drawing showing the atomic labelling of the dihydroxyphenylselenonium ion in (*a*) TOL and (*b*) BEN.

3. Results and discussion

3.1. Disorder of the benzenesulfonate salt

The crystal structure determinations revealed a pronounced disorder of the phenylsulfonate anion in BEN, which could be modelled into two almost equally populated conformations of the sulfonate group. The displacement parameters of the cation are also significantly larger in BEN than in TOL. A Rigid Body Motion (TLS) analysis (Spek, 1990) of these parameters revealed librational and translational tensors for the cation that have much larger eigenvalues in BEN than in TOL. These results could be interpreted as a disorder of the cation that matches the larger disorder of the anion. Further support for this interpretation is given by the fact that BEN is the more closely packed salt (Table 1) and should not be expected to exhibit the largest thermal displacements.

3.2. The dihydroxyselenonium anions

The cations found in the *p*-toluenesulfonate and the benzenesulfonate salts are shown in Fig. 1. The molecular geometry of the cation is very similar in the two structures. The disorder of the anion in BEN influences the overall accuracy of this structure, leading to significantly larger standard uncertainties. The cations differ slightly with respect to the orientation of the dihydroxyselenonio group: in TOL the dihedral angle O(11)—Se—C(11)—C(12) is −151.8 (2)°, whereas it is *ca* 25° smaller in BEN [−126.6 (6)°]. This does not influence the bond lengths and angles of the cations in the two salts, which are identical within experimental error. The Se atom is displaced 0.1 Å out of the plane of the phenyl group and its pyramidal configuration brings the two O atoms to the same side of the phenyl group. The protonization of the seleninic acid leads to a dihydroxyselenonio group with two completely identical Se—O distances adopting a value [1.731 (7) Å] which is between an Se═O double and Se—O single bond.

3.3. The two sulfonate anions

The geometry of the benzenesulfonate and the *p*-toluenesulfonate ions is apparent from Fig. 2. Their bond lengths,

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0057). Services for accessing these data are described at the back of the journal.

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the cations of TOL, BEN and the deprotonated forms in seleninic acid and the selenate anion. The pK values are also tabulated.

	TOL	BEN	Seleninic acid[(a)]	Seleninate[(b)]
pK	−0.9		4.79	
Se−O(11)	1.7350 (14)	1.727 (7)	1.707 (15)	1.689 (5)
Se−O(12)	1.7331 (16)	1.730 (6)	1.765 (15)	1.672 (6)
Se−C(11)	1.9173 (19)	1.922 (7)	1.903 (21)	1.966 (7)
O(11)−Se−O(12)	98.46 (8)	99.3 (3)	103.5 (7)	103.9 (3)
O(11)−Se−C(11)	94.81 (8)	94.8 (3)	99.0 (9)	98.8 (3)
O(12)−Se−C(11)	93.76 (8)	96.2 (3)	98.5 (9)	101.3 (3)
C(12)−C(11)−Se	118.74 (15)	120.5 (6)	–	–
C(16)−C(11)−Se	118.82 (15)	117.6 (6)	–	–
O(11)−Se−C(11)−C(12)	−151.80 (16)	−126.6 (6)	–	–
O(12)−Se−C(11)−C(12)	−52.97 (17)	−26.7 (6)	–	–
Se−C(11)−C(12)−C(13)	−176.58 (16)	−175.8 (6)	–	–
Se deviation (Å) from COO plane	0.944	0.934	0.897	0.861

References: (*a*) Bryden & McCullough (1954); (*b*) Antolini *et al.* (1991).

bond and torsion angles are listed in Table 3. The two anions have very similar bond lengths and angles, apart from the disordered sulfonate group in BEN. A search in the Cambridge Structural Database, version 5.14 (Allen & Kennard, 1993) for benzenesulfonate salts resulted in 21 structures. Their sulfonate groups have O−S−O angles in the range 109–116°. The equivalent angles in TOL, between 110 and 115°, fit well into this picture, whereas the O−S−O angles in BEN deviate more from the normal behaviour with angles in the range 97–120° for population *A* and in the range 107–121° for population *B*.

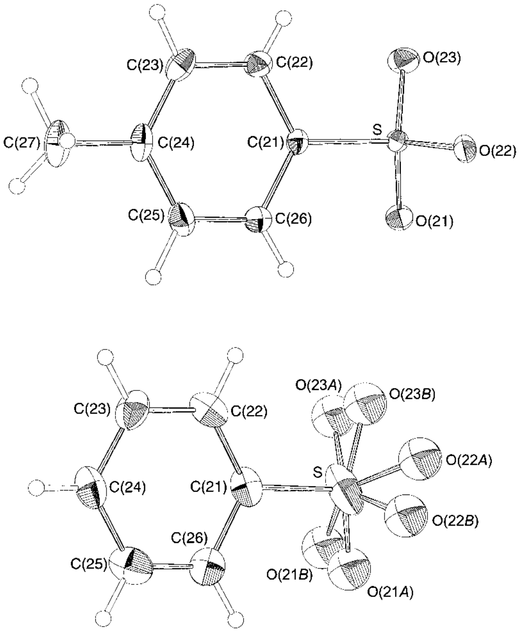

Figure 2
*ORTEP*II (Johnson, 1976) drawing showing the atomic labelling of (*a*) the *p*-toluenesulfonate anion in TOL and (*b*) the benzenesulfonate anion in BEN.

3.4. The crystal packing

Both compounds contain cations and anions with identical functional groups, which opens the possibility for similar hydrogen-bond interactions in the two structures. Table 4 displays the important intermolecular interactions in the two salts. Both salts have very short contacts (2.58–3.03 Å) between the Se atom and the O atoms of the sulfonate groups. This suggests that the positive charge of the cation is partly localized on the Se atom. The two OH groups of the dihydroxyphenylselenonium ion in TOL make hydrogen bonds to O(22) from two different *p*-toluensulfonate ions related by translational symmetry along the *a* axis. The two hydrogen bonds have virtually identical donor–acceptor distances [2.630 (3) Å]. Similar hydrogen-bond interactions are found in population *A* of the anion in BEN, where the cation connects O(22*A*) from the two anions related by translational symmetry along the *c* axis. Its translational period of 5.7881 (15) Å is comparable with the *a* axis 5.8838 (11) Å in TOL. The dihydroxyphenylselenonium ion is also able to make hydrogen bonds to population *B* of the benzenesulfonate ion, in this case the hydrogen bonds attach to two different oxygen atoms, O(22*B*) and O(23*B*).

Some of the intermolecular interactions in BEN, listed in Table 4, are significantly shorter than the equivalent interactions in TOL. We attribute this difference to the previously described disorder in BEN, which could lead to apparently shorter hydrogen-bond distances, also for those involving O(11) and O(12). Both crystal structures can be considered as being built from an almost identical motif of cations and anions oriented in a similar way relative to each other. The hydrophilic groups from this ion pair are connected to other ion pairs forming pipelines running through the structure, as illustrated in the schematic diagram of the common hydrogen-

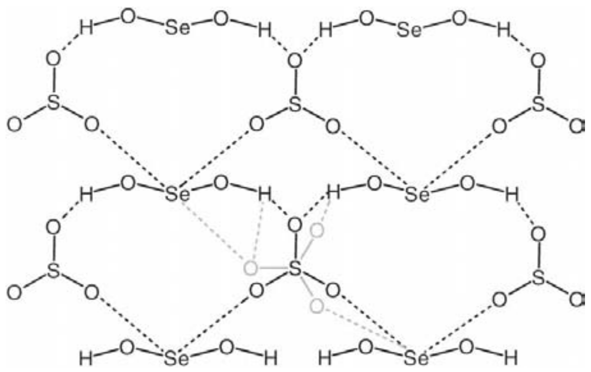

Figure 3
A schematic drawing of the hydrogen bonds and ionic interactions in the two salts. The only difference is in the interactions that involve part *B* (shown in light grey) of the disordered sulfonate group. The dihydroxyselenonio groups in the top of this figure are the same as in the bottom.

Table 3
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the anions.

		BEN	
	TOL	Population *A*	Population *B*
S—O(21)	1.4546 (14)	1.443 (6)	1.447 (6)
S—O(22)	1.4885 (14)	1.424 (6)	1.465 (6)
S—O(23)	1.4477 (15)	1.466 (6)	1.434 (6)
S—C(21)	1.7668 (19)	1.769 (7)	–
O(21)—S—O(22)	109.94 (8)	119.8 (7)	120.7 (8)
O(21)—S—O(23)	114.65 (9)	109.7 (7)	114.9 (8)
O(22)—S—O(23)	112.15 (9)	96.9 (8)	107.0 (7)
O(21)—S—C(21)	107.12 (9)	109.8 (6)	103.4 (6)
O(23)—S—C(21)	107.08 (9)	101.7 (6)	108.4 (7)
O(22)—S—C(21)	105.31 (8)	116.2 (5)	100.8 (6)
C(22)—C(21)—S	119.79 (15)	121.2 (6)	–
C(26)—C(21)—S	119.76 (15)	117.5 (6)	–
O(21)—S—C(21)—C(22)	−149.03 (16)	−153.0 (8)	−128.7 (8)
O(22)—S—C(21)—C(22)	93.96 (17)	67.0 (10)	105.8 (8)
O(23)—S—C(21)—C(22)	−25.57 (19)	−36.8 (8)	−6.4 (9)
S—C(21)—C(22)—C(23)	−178.60 (17)	1.786 (6)	–

Table 4
Intermolecular interactions (Å, °).

	D···*A*	H···*A*	*D*—H···*A*
TOL			
O(11)—H(110)···O(22)$^{\rm i}$	2.633 (2)	1.81 (3)	172 (3)
O(12)—H(120)···O(22)$^{\rm ii}$	2.628 (2)	1.99 (3)	157 (4)
C(27)—H(27*B*)···O(11)$^{\rm iii}$	3.337 (3)	2.52 (4)	164 (4)
Se···O(21)$^{\rm iv}$	2.786 (2)		
Se···O(23)$^{\rm v}$	2.714 (2)		
BEN			
O(11)···O(22*A*)$^{\rm vi}$	2.74 (2)		
O(12)···O(22*A*)$^{\rm vii}$	2.50 (2)		
O(12)···O(22*B*)$^{\rm vii}$	2.57 (2)		
O(11)···O(23*B*)$^{\rm vi}$	2.51 (2)		
Se···O(21*A*)	2.584 (7)		
Se···O(21*B*)	2.88 (2)		
Se···O(23*A*)$^{\rm iv}$	2.88(2)		
Se···O(23*B*)$^{\rm vi}$	3.034 (9)		

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

bond pattern in Fig. 3 and the crystal packing shown in Figs. 4 (TOL) and 5 (BEN). These latter figures also illustrate that despite the great similarities in the hydrogen patterns the crystal packing of the two structures are markedly different. These differences can be attributed to the variations in the overall arrangement of the phenyl groups in the two structures. The phenyl groups of the cations and anions in TOL form layers parallel to the *a*–*c* plane with interacting methyl groups between the layers. The lack of a methyl group on the anion in BEN leads to a more complex stacking of the phenyl groups. However, the interplanar angles between the phenyl groups of the cation and anion are virtually identical, *ca* 52° in both arrangements.

The most significant difference between the packing in TOL and BEN is the presence of an additional C—H···O hydrogen bond in TOL. It is likely that it is this interaction that locks the dihydroxyselenonio group into one well defined conformation and therefore excludes the disorder found in BEN. The difficulties encountered in the prediction of crystal packing are well illustrated by the disorder in BEN caused only by the lack of a methyl group. Thus, it is able to form only a weak C—H···O hydrogen bond stabilizing one of the conformers.

3.5. Acidity constants

Acidities of various seleninic acids have been described in the literature. The lower aliphatic members have p*K* values in the range 5.2–5.3 (Backer & van Dam, 1935) and a series of aromatic seleninic acids conform to a Hammet correlation, $pK = 5.8 + 1.0\sigma$ (McCullough & Gould, 1949). In contrast, little information is available on the acidities of the protonated acids, the dihydroxy organyl selenonium ions. The vibrational spectrum of the dihydroxymethylselenonium ion indicates that this species is partially deprotonated in concentrated aqueous solution (Paetzold *et al.*, 1960). A pH value of 1.12 in a 0.100 *M* aqueous solution of TOL was measured. This result shows that (3) is a strong acid with $pK \leq -0.3$. In order to obtain a more precise estimate of the p*K* value we have utilized the observation (Henriksen & Stuhr-Hansen, 1998) that the ^{77}Se NMR chemical shifts of the protonated seleninic acid derivatives differ markedly from those of the parent

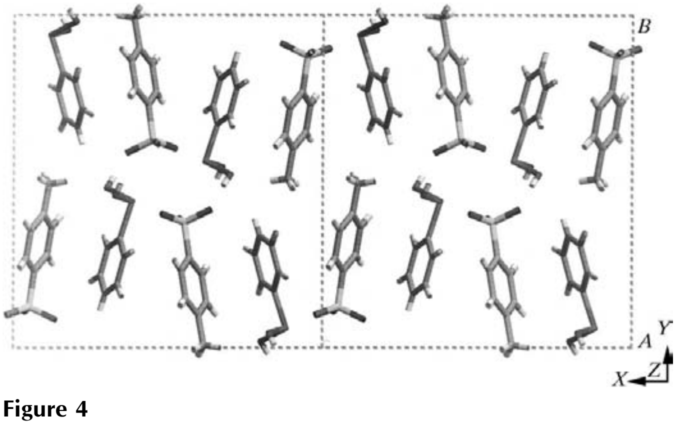

Figure 4
Crystal packing in TOL seen down the *a* axis. The drawing was prepared using *Cerius*^{2} (Molecular Simulations Inc., 1997).

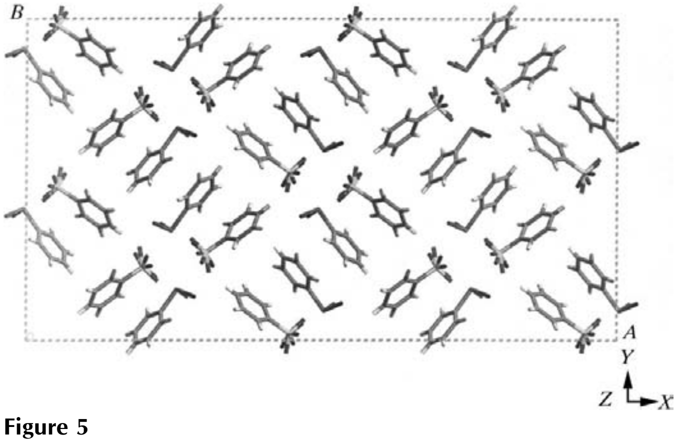

Figure 5
Crystal packing of compound BEN seen down the *c* axis. The drawing was prepared using *Cerius*^{2} (Molecular Simulations Inc., 1997).

substances. The ^{77}Se NMR spectra of (1) were recorded in a series of water–sulfuric acid mixtures and the chemical shifts were correlated with the Hammet acidity values, H_0 (Hammet, 1970). The δ^{77}Se plotted as a function of H_0 is shown in Fig. 6, together with the theoretical (no solvent effects included) S-shaped curves for three different pK levels, −0.7, −0.9 and −1.1. We interpret the shift from 1170.8 p.p.m. in water to the minimum value of 1144.1 p.p.m. at $H_0 = -2.85$ as a result of the conversion of (1) into (3). The gradual increase in δ at lower H_0 is a solvent-induced shift of the signal from (3). This interpretation gives an estimated pK value of -0.9 ± 0.2 for the dihydroxyphenylselenonium ion.

The difference in the pK values for protonated and the nonprotonated form of benzeneseleninic acid is quite large, 5.6. Assuming the same difference in pK values for the sulfur analogue leads to a pK value of −3.4 for the protonated benzenesulfinic acid. This explains why this ion has not been isolated, but only observed by NMR in a solution of FSO_3H–SbF_5–SO_2ClF (Olah *et al.*, 1970).

3.6. Comparisons with related compounds

Structural data are available for both benzeneseleninic acid (Bryden & McCullough, 1954, as the deprotonated dihydroxyphenylselenonium ion) and the seleninate ion in the *N*,*N*′-diphenylguanidinium salt (Antolini *et al.*, 1991). This provides an opportunity to compare the structural features of the closely related compounds, just differing in their degree of protonization. The geometry of the C—Se—O_2 moiety in the two latter compounds is listed in Table 2. Despite the lower accuracy of the structure determination for benzeneseleninic acid some obvious trends emerge from the comparison. The C—Se distance does not vary systematically with the protonization, whereas the two Se—O distances in the seleninate ion have decreased from an average of 1.734 Å in TOL to 1.68 Å in the doubly deprotonated anion. The two Se—O distances in the seleninic acid are significantly different (0.06 Å), but it is noteworthy how well their average value compares with the Se—O distances in TOL. Similar systematic variations are seen in the angles around the Se atom. All three compounds have a pyramidal Se atom, but the angles around Se decrease systematically giving rise to a more and more pyramidal Se atom with a degree of protonization. We have calculated the distance from the Se atom to the plane defined by its three substituents. This distance changes from 0.86 Å in the seleninate to 0.944 Å in TOL. Only the structure of the benzenesulfinic acid is known (Minkwitz *et al.*, 1996) of the equivalent sulfur compounds. The O—S—OH group is asymmetric and the two S—O distances show the same difference as the Se—O distances in benzeneseleninic acid. An inspection of the angles reveals that the sulfur analogue is considerably more planar than the selenium analogue. The NMR study of protonated benzenesulfinic acid revealed equivalent S—O distances (Olah *et al.*, 1970) in analogy to the selenium compounds TOL and BEN. Although the variations in pK values are likely to be related to variations in the geometrical differences between the compounds, no obvious relation could be deduced from the present study.

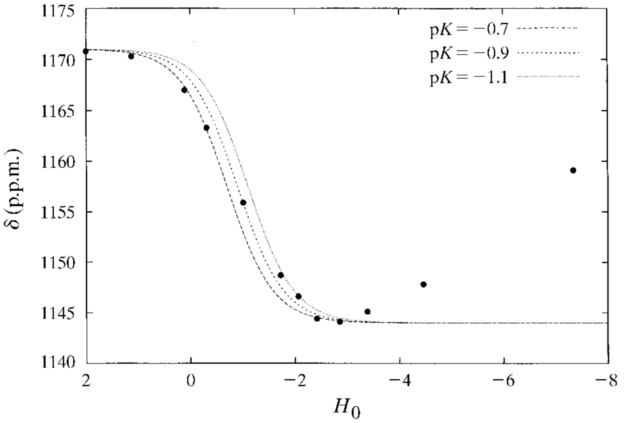

Figure 6
A plot of the ^{77}Se NMR chemical shift *versus* H_0, the black dots are the experimental points. The theoretical S-shaped curves (*in the absence of solvent effects*) are plotted for three pK values.

We thank Mr Flemming Hansen for help with the crystallographic experiments. We are grateful for the comments and suggestions from one of the referees with respect to the treatment of the NMR data. This research was supported by the Danish Natural Science Research Council.

References

Allen, F. H. & Kennard, O. (1993). *J. Chem. Inf. Comput. Sci.* **8**, 31–37.

Antolini, L., Marchetti, A., Preti, C., Tagliazucchi, M., Tassi, L. & Tosi, G. (1991). *Aust. J. Chem.* **44**, 1761.

Backer, H. & van Dam, W. (1935). *Rec. Trav. Chim. Pay-Bas*, **54**, 531.

Blessing, R. (1987). *Cryst. Rev.* **1**, 3–58.

Bryden, J. H. & McCullough, J. D. (1954). *Acta Cryst.* **7**, 833–838.

Burkhard, R., Sellers, D., DeCou, F. & Lambert, J. (1959). *J. Org. Chem.* **24**, 767.

Enraf–Nonius (1995). *CAD*-4 *Express*. Enraf–Nonius, Delft, The Netherlands.

Gancarz, R. & Kice, J. (1980). *Tetrahedron Lett.* **21**, 1697.

Hammet, L. (1970). *Physical Organic Chemistry*, 2nd ed. New York: McGraw-Hill.

Henriksen, L. & Stuhr-Hansen, N. (1996). *Synth. Commun.* **26**, 1897.

Henriksen, L. & Stuhr-Hansen, N. (1998). *Phosphorus Sulfur Silicon*, **136–138**, 175–190.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

McCullough, J. & Gould, E. (1949). *J. Am. Chem. Soc.* **71**, 674–676.

Minkwitz, R., Kornath, A. & Lohmann, U. (1996). *Z. Naturforsch. Teil B*, **51**, 5083.

Molecular Simulations Inc. (1997). *Cerius*^{2} *User Guide*. Molecular Simulations Inc., San Diego, USA.

Olah, G., Ku, A. & Olah, J. (1970). *J. Org. Chem.* **35**, 3908–3912.

Paetzold, R., Schumann, H.-D. & Simon, A. (1960). *Z. Anorg. Allg. Chem.* **305**, 98.

Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stuhr-Hansen, N. & Henriksen, L. (1997). *Synth. Commun.* **27**, 89.