## SUPPLEMENTARY MATERIAL

## Toward Radiation-Resistant Ionic Liquids. Radiation Stability of Sulfonyl Imide Anions.

Ilya A. Shkrob* ${ }^{1}$, Timothy W. Marin, ${ }^{1,2}$ Sergey D. Chemerisov, ${ }^{1}$ Jasmine Hatcher, ${ }^{3}$ and James F. Wishart ${ }^{3}$
${ }^{1}$ Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60439
${ }^{2}$ Chemistry Department, Benedictine University, 5700 College Road, Lisle, IL 60532
${ }^{3}$ Chemistry Department, Brookhaven National Laboratory, Upton, New York 119735000

## Abbreviations.

| ADE | adiabatic electron detachment energy |
| :---: | :---: |
| B3LYP | a DFT functional |
| BDE | bond dissociation energy |
| DFT | density functional theory |
| DMSO | dimethylsulfoxide |
| EA | electron affinity |
| ESI MS | electrospray ionization tandem mass spectrometry |
| EPR | electron paramagnetic resonance |
| hfcc | hyperfine coupling constant |
| IL | ionic liquid |
| NMR | nuclear magnetic resonance |
| $\mathrm{NTf}_{2}{ }^{-}$ | bis(trifluoromethanesulfonyl)imide (or bistriflimide) anion |
| PA | proton affinity |
| $\mathrm{P}_{666,14}{ }^{+}$ | trihexyltetradecylphosphonium cation |
| EtPy ${ }^{+}$ | N -ethylpyridinium cation |
| TMS | tetramethylsilane |

## List of reactions:

## General reactions

$$
\begin{align*}
& \mathrm{A}^{-* *} \rightarrow \mathrm{e}^{-\bullet}+\mathrm{A}^{\bullet}  \tag{1}\\
& \mathrm{C}^{+* *} \rightarrow \mathrm{e}^{-\bullet}+\mathrm{C}^{2+\bullet}  \tag{2}\\
& \mathrm{C}^{+* *} \rightarrow \mathrm{C}(-\mathrm{H})^{\bullet}+\mathrm{H}^{\bullet}  \tag{18}\\
& \mathrm{C}^{2+\bullet}+\mathrm{A}^{-} \rightarrow \mathrm{C}(-\mathrm{H})^{\bullet}+\mathrm{H}^{\delta+} \mathrm{A}^{\delta-}  \tag{3}\\
& \mathrm{C}^{2+\bullet}+\mathrm{A}^{-} \rightarrow \mathrm{C}^{+}+\mathrm{A}^{\bullet}  \tag{4}\\
& \mathrm{C}^{+}+\mathrm{e}^{-\bullet} \rightarrow \mathrm{C}^{\bullet}  \tag{5}\\
& \mathrm{C}^{\bullet}+\mathrm{H}^{\delta+} \mathrm{A}^{\delta-} \rightarrow \mathrm{CH}^{+\bullet}+\mathrm{A}^{-}  \tag{6}\\
& \mathrm{RB}^{-*} \rightarrow \mathrm{e}^{\bullet}+\mathrm{RB}^{\bullet}  \tag{7a}\\
& \mathrm{RB}^{\bullet} \rightarrow \mathrm{R}^{\bullet}+\mathrm{B}  \tag{7b}\\
& \mathrm{RB}^{\bullet}+\mathrm{C}^{\bullet} \rightarrow \mathrm{RB}^{-}+\mathrm{C}^{+} \tag{8}
\end{align*}
$$

Imide reactions.
$\mathrm{NTf}_{2}{ }^{-} * * \rightarrow{ }^{\bullet} \mathrm{CF}_{3}+{ }^{\bullet} \mathrm{SO}_{2} \mathrm{NTf}^{-}$
$\mathrm{NTf}_{2}{ }^{-* *} \rightarrow \mathrm{CF}_{3} \mathrm{SO}_{2}{ }^{\bullet}+\mathrm{TfN}^{-\bullet}$
$\mathrm{NTf}_{2}{ }^{-}+\mathrm{e}^{-\bullet} \rightarrow \mathrm{F}^{-}+{ }^{\bullet} \mathrm{CF}_{2} \mathrm{SO}_{2} \mathrm{NTf}^{-}$
$>\mathrm{N}^{-} \rightarrow>\mathrm{N}^{\bullet}+\mathrm{e}^{-\bullet}$
$>\mathrm{N}^{-}+\mathrm{e}^{-\bullet} \rightarrow>\mathrm{N}^{2-\bullet}$
$>\mathrm{N}^{2-\bullet}+>\mathrm{N}^{\delta} \mathrm{H}^{\delta+} \rightarrow>\mathrm{NH}^{\bullet}+>\mathrm{N}^{-}$
$>\mathrm{N}^{\bullet}+\mathrm{C}^{+} \rightarrow>\mathrm{N}^{\delta \cdot} \mathrm{H}^{\delta+}+\mathrm{C}(-\mathrm{H})^{\bullet}$
$>\mathrm{N}^{-}+>\mathrm{N}^{\bullet} \Longrightarrow\{>\mathrm{N}-\mathrm{N}<\}^{-}$
$>\mathrm{N}^{-*}\left(\mathrm{~S}_{1}\right)+>\mathrm{N}^{\delta} \mathrm{H}^{\delta+} \rightarrow>\mathrm{N}^{\bullet}+>\mathrm{NH}^{\bullet}$
$>\mathrm{N}^{\delta} \mathrm{H}^{\delta+}+\mathrm{e}^{-\bullet} \rightarrow>\mathrm{N}^{-}+\mathrm{H}^{\bullet}$
$>\mathrm{N}^{-}+\mathrm{H}^{\bullet} \rightarrow 2,2^{\prime}$ or $3,3^{\prime} \mathrm{H}$ adducts of $>\mathrm{N}^{-}$
$>\mathrm{NH}^{-\bullet}+\mathrm{C}(-\mathrm{H})^{\bullet} \rightarrow>\mathrm{N}^{-}+\mathrm{C}^{+}$

## Section 1S: Synthetic methods.

Trihexyltetradecylphosphonium saccharinate. $2.12 \mathrm{~g} \mathrm{P}_{666,14} \mathrm{Cl}$ in $10 \mathrm{~mL} \mathrm{CH} \mathrm{Cl}_{2}$ is vigorously stirred with 5 g of a $1.6 \mathrm{~mol} / \mathrm{kg}$ aqueous solution of potassium saccharinate hydrate for 15 min . The phases are separated, the aqueous solution is replaced, and the procedure is repeated. The organic layer is washed with distilled water ( $1: 1 \mathrm{v} / \mathrm{v}$ ) two times. A silver nitrate test showed no presence of chloride in the aqueous phase after the second wash. The layers are separated by centrifugation at 3000 rpm , and the organic solution is reduced to an oil at $80^{\circ} \mathrm{C}$ in vacuo and then dried in a vacuum oven at $95^{\circ} \mathrm{C}$ for 12 h . An ${ }^{1} \mathrm{H}$ NMR spectrum of the dried IL (Figure 4 S ) indicates $100 \%$ substitution of chloride and the mass spectrum is consistent with the nominal compound (Table 1S). The chemical shifts are reported vs. tetramethylsilane (TMS).

Trihexyltetradecylphosphonium acesulfamate. $2.31 \mathrm{~g} \mathrm{P} \mathrm{P}_{666,14} \mathrm{Cl}$ in $10 \mathrm{~mL} \mathrm{CH} \mathrm{Cl}_{2}$ is vigorously stirred with 8 g of $0.93-\mathrm{m}$ aqueous solution of potassium acesulfamate for 15 min , and the aqueous solution is replaced 3 X and restirred with each replacement. The rest of the synthetic procedure was the same as for the saccharinate. See Figure 5S for the final ${ }^{1} \mathrm{H}$ NMR spectrum and Table 1S for the mass peaks.

Trihexyltetradecylphosphonium o-benzenedisulfonimide. $\quad 1 \quad \mathrm{~g} ~ o$-benzenedisulfonyl chloride (Alfa Aesar, No. H50375) is dissolved in 20 mL of benzene, and 50 mL of 2-M ammonia in absolute ethanol is added in three equal portions over 1 h at room temperature; this reaction mixture is stirred for another 15 min . The reaction is
$o-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{SO}_{2} \mathrm{Cl}\right)_{2}+4 \mathrm{NH}_{3} \rightarrow o-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{SO}_{2}\right)_{2} \mathrm{~N} \mathrm{NH}_{4}+2 \mathrm{NH}_{4} \mathrm{Cl}$
The white precipitate is filtered out and the mixture is reduced to dryness at $80^{\circ} \mathrm{C}$ and 25 mm Hg (the yield is 0.91 g ). 45 mL of water is added to the solid residue and then the aqueous solution is vigorously stirred with $1.84 \mathrm{~g} \mathrm{P}_{666,14} \mathrm{Cl}$ in $25 \mathrm{~mL} \mathrm{CH}_{2} \mathrm{Cl}_{2}$ for 30 min . The phases are separated and the dichloromethane fraction is filtered to remove the residual white precipitate (of polymeric material) formed during the first stage of the synthesis. The chloride and ammonium ions present in the reaction mixture do not interfere with interphase transfer of the imide anion. The filtered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution is reduced at $80^{\circ} \mathrm{C}$ in vacuo and the residual oil is dried in a vacuum oven at $90^{\circ} \mathrm{C}$ for 12 h . The ${ }^{1} \mathrm{H}$ NMR spectrum of the resulting ionic liquid (Figure 6 S ) indicates $96 \%$ exchange of the chloride with the imide anion. The ${ }^{13} \mathrm{C}$ chemical shifts for this anion (Figure 7S) are $142.5,131.1$, and 120.5 ppm (vs. TMS; the reported ${ }^{13} \mathrm{C}$ chemical shift for anions a and $\mathbf{b}$ are given in the plot). The observed mass peaks (Table 1S) are consistent with the nominal compound.

Ammonium o-benzenedisulfonimide/chloride. The synthesis proceeded as the first step of the previous synthesis. The precipitate was filtered out and the reaction mixture was reduced to dryness. The residue was dissolved in 50 mL of water and the slightly opalescent aqueous solution was filtered once more and reduced to dryness; the resulting residue was dried in a vacuum oven at $80^{\circ} \mathrm{C}$ for 8 h . Part of the resulting solid was dissolved in $\mathrm{D}_{2} \mathrm{O}$ and an aliquot of methanol was added. ${ }^{1} \mathrm{H}$ NMR analysis of this
solution indicated that the solid contains $3.68 \mathrm{~mol} / \mathrm{kg}$ of the ammonium salt of $o$ -benzenedisulfonimide-imide. Assuming that the formula of this solid is $o-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{SO}_{2}\right)_{2} \mathrm{~N}$ $\mathrm{NH}_{4} \cdot x \mathrm{NH}_{4} \mathrm{Cl}$, the mole fraction $x$ of ammonium chloride is $\sim 0.67$. The ${ }^{14} \mathrm{~N}$ NMR spectrum shown below revealed a narrow peak from tetrahedral nitrogen from ammonium at -363 ppm (vs. aqueous nitrate) and a trigonal nitrogen from the imide at -225 ppm ; the ratio of the peak areas corresponds to $\mathrm{x} \sim 0.74$, which is consistent with an estimate obtained using ${ }^{1} \mathrm{H}$ NMR. ESI MS ${ }_{1}{ }^{-}$mode, water: $m / z-218.3$. The reaction yield was $80 \%$. The resulting polycrystalline solid was ground under nitrogen and used in the experiments described in the text.

${ }^{14} \mathrm{~N}$ NMR spectrum of the ammonium salt in $\mathrm{D}_{2} \mathrm{O}$.
Potassium o-benzenedisulfonimide. 1 g of ammonium $o$-benzenedisulfonimide/chloride (see above) was diluted in 3 mL of water and 2 g of $27 \mathrm{wt} \%$ hydrochloric acid was added at room temperature. The reaction mixture was reduced to dryness in vacuum and then 10 mL water was added and the resulting solution was again reduced to dryness in vacuum to remove the excess of $\mathrm{HCl} . \mathrm{Ca} .5 \mathrm{~mL}$ of 1 M potassium hydroxide was added to this evaporate so that the aqueous solution had weak basic reaction. The salt began to crystallize immediately as the base was added. The mixture was heated to $75{ }^{\circ} \mathrm{C}$ to dissolve the precipitate, and potassium $o$-benzenedisulfonimide monohydrate crystallized out at room temperature as transparent needles. Two more crystallizations were used to obtain ultrapure material used in EPR studies. Crystallographic parameters are given in Section 2S. ESI MS ${ }_{1}{ }^{ \pm}$spectra of the methanol solution of this salt revealed $\mathrm{K}^{+}(\mathrm{KA})_{\mathrm{m}}$ and $\mathrm{A}^{-}(\mathrm{KA})_{\mathrm{m}}$ series of ions ( $m=1-7$ ), where $\mathrm{A}^{-}$is the $o$-benzenedisulfonimide (Figure $8 \mathrm{~S}(\mathrm{a})$ ).

The ${ }^{1} \mathrm{H}$ NMR spectrum of the potassium salt in $\mathrm{D}_{2} \mathrm{O}$ was the same as for the ammonium salt. To remove water, the monohydrate was lyophilized and then heated for 4 hr in vacuum at $75{ }^{\circ} \mathrm{C}$. The resulting solid material is a highly dispersed, hygroscopic white powder.

Ethylpyridinium- $\boldsymbol{d}_{10}$ bromide. $10 \mathrm{~g}(0.088 \mathrm{~mol})$ of bromoethane- $d_{5}$ (Aldrich) was dissolved in 20 mL of acetonitrile. 7.34 g ( 1 eq. ) of pyridine- $d_{5}$ (Aldrich or Cambridge Isotope Laboratories) in 15 mL of acetonitrile was added drop-wise to the solution. The solution was placed in an ice bath for 3 h . It was then set to reflux for 72 h . The solution was reduced in vacuum to remove acetonitrile. 30 mL of cold ethyl acetate was added to the solution to encourage crystallization. The white crystals formed were isolated using vacuum filtration under dry nitrogen and washed ( 5 X 15 ml ) with cold ethyl acetate. The crystals were dried in a vacuum oven for 12 h at ambient temperature. Yield 80-96\%. No ${ }^{1} \mathrm{H}$ NMR lines were observed. $\delta^{13} \mathrm{C}$ (vs. TMS): [15.13, 15.33, 15.53] $\mathrm{NCD}_{2} \mathrm{CD}_{3}, 55.36$ $\mathrm{NCD}_{2} \mathrm{CD}_{3}$, [127.25, 127.52, 127.78] CDCDCDN, [143.80, 144.10, 144.39] CDCDCDN, and [144.63, 144.90, 145.16] CDCDCDN.

Ethylpyridinium- $\boldsymbol{d}_{10}$ bistriflimide. $16.7 \mathrm{~g}(0.084 \mathrm{~mol})$ of ethylpyridnium- $d_{10}$ bromide was dissolved in as little water as possible. 1.02X molar excess ( 24.04 g ) of lithium bistriflimide (Iolitec) was also dissolved in as little water as possible and added to the mixture. The solution was left to stir at ambient temperature for 24 h . The resulting oil was washed with deionized water until no presence of halide was detected (the wash solutions were tested with a drop of $50-\mathrm{mM}$ aqueous silver nitrate). The sample was then dried in a vacuum oven for 48 h at $65^{\circ} \mathrm{C}$. The sample crystallized upon cooling. Yield $88 \% . \delta^{13} \mathrm{C}$ (vs. TMS) $[14.30,14.49,14.69,14.88,15.08] \mathrm{NCD}_{2} \mathrm{CD}_{3},[55.22,55.44,55.66$, 55.87, 56.10] $\mathrm{NCD}_{2} \mathrm{CD}_{3},[127.14,127.40,127.67]$ CDCDCDN, [143.50, 143.79, 144.07] CDCDCDN, [144.39, 144.65, 145.91] CDCDCDN, and [114.59, 117.78, 120.98, 124.67] $\mathrm{N}\left(\mathrm{SO}_{2} \mathrm{CF}_{3}\right)_{2}$

## Section 2S. Crystal structure of potassium o-benzenedisulfonimide monohydrate.

The crystal lattice corresponds to $\mathrm{P}_{1} / \mathrm{c}$ space group (monoclinic prismatic) with the unit cell parameters $a=11.4 \AA, b=12.95 \AA, c=6.94 \AA$, and $\beta=106.6^{\circ}$ ( $983.3 \AA^{3}$ unit cell). Each nitrogen and oxygen in the imide anion are coordinated with two $\mathrm{K}^{+}$cations (Figure $8 \mathrm{~S}(\mathrm{~b})$ ).

The anion is non-planar, with a CCSN dihedral angle equal to $15.1^{\circ}$. We have obtained another crystalline compound of this imide anion, N -butyl- N -methylpyrrolidinium $o$ benzenedisulfonimide, in which this anion is planar, with a CCSN dihedral angle of $0.9^{\circ}$. The S-N and S-O bonds in the potassium salt are also longer than in this organic salt $(1.591 \AA$ vs. $1.574 \AA$ and $1.45 \AA$ vs. $1.438-1.44 \AA$ ), respectively. These differences indicate considerable strain and significant deviation from the $C_{2 \mathrm{v}}$ symmetry in the potassium salt.

Below we report crystallographic parameters in a CIF (Crystallographic Information File) format:

```
data_p21c
_audit_creation_method
SHELXL-97
_chemical_name_systematic
;
;
_chemical_name_common ?
_chemical_melting_point ?
_chemical_formula_moiety ?
_chemical_formula_sum
    'C5 H6 K N O5 S2'
_chemical_formula_weight 263.33
loop_
    _atom_type_symbol
    _atom_type_description
    _atom_type_scat_dispersion_real
    _atom_type_scat_dispersion_imag
    _atom_type_scat_source
    'C' 'C' 0.0033 0.0016
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
    'H' 'H' 0.0000 0.0000
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
    'N' 'N' 0.0061 0.0033
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
    'O' 'O' 0.0106 0.0060
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
    'S' 'S' 0.1246 0.1234
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
    'K' 'K' 0.2009 0.2494
    'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
_symmetry_cell_setting ?
_symmetry_space_group_name_H-M ?
loop_
```

```
    _symmetry_equiv_pos_as_xyz
    'x, y, z'
    '-x, y+1/2, -z+1/2'
    '-x, -y, -z'
    'x, -y-1/2, z-1/2'
_cell_length_a 11.4149(2)
_cell_length_b 12.9530(2)
_cell_length_c 6.93860(10)
_cell_angle_alpha 90.00
_cell_angle_beta
_cell_angle_gamma
_cell_volume
__cell_formula_units_Z
_cell_measurement_temperature
__cell_measurement_reflns_used
_cell_measurement_theta_min ?
_cell_measurement_theta_max ?
_exptl_crystal_description ?
_exptl_crystal_colour ?
_exptl_crystal_size_max 0.50
_exptl_crystal_size_mid 0.25
__exptl_crystal_size_min 0.25
_exptl_crystal_density_meas ?
_exptl_crystal__density_diffrn 1.779
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000
5 3 6
__exptl_absorpt_coefficient_mu 0.959
_exptl_absorpt_correction_type ?
__exptl_absorpt_correction_T_min 0.6456
_exptl_absorpt_correction_T_max 0.7955
_exptl_absorpt_process_details ?
_exptl_special_details
;
    ?
;
_diffrn_ambient_temperature
_diffrn_ambient_temperature
_diffrn_radiation_type
__diffrn_radiation_source
__diffrn_radiation_monochromator
100(2)
0.71073
MoK\a
    fine-focus sealed tube'
_diffrn_measurement_device_type
    graphite
?
_diffrn_measurement_method ?
_diffrn_detector_area_resol_mean ?
_diffrn_standards_number _
__diffrn_standards_interval_count ?
_diffrn_standards_interval_time ?
_diffrn_standards_decay_%% ?
_diffrn_reflns_number 13161
_diffrn_reflns_av_R_equivalents 0.0148
__diffrn_reflns_av_sigmaI/netI 0.0122
_diffrn_reflns_limit_h_min -16
__diffrn_reflns_limit_h_max 16
_diffrn_reflns_limit_k_min -18
__diffrn_reflns_limit_k_max 18
_diffrn_reflns_limit_l_min -10
_diffrn_reflns_limit_l_max 10
__diffrn_reflns_theta_min 1.86
_diffrn_reflns_theta_max 31.55
_reflns_number_total 3273
_reflns_number_gt 3166
_reflns_threshold_expression >2sigma(I)
```

```
_computing_data_collection ?
_computing_cell_refinement ?
_computing_data_reduction ?
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics ?
_computing_publication_material
?
_refine_special_details
;
    Refinement of F^^2^ against ALL reflections. The weighted R-factor wR
and
    goodness of fit S are based on F^^2^, conventional R-factors R are based
    on F, with F set to zero for negative F^^^^. The threshold expression of
    F^2^^
is
    not relevant to the choice of reflections for refinement. R-factors
based
    on F^^2^ are statistically about twice as large as those based on F, and
R-
    factors based on ALL data will be even larger.
;
_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
    'calc w=1/[\s^^2^(Fo^2^) +(0.0529P)^2^+1.2183P] where P=(Fo^2^^2Fc^2^)/3'
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refiñe_ls_hyydrogen_treatment mixed
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_number_reflns 3273
_refine_ls_number_parameters 142
_refine_ls_number_restraints 3
_refine_ls_R_factor_all 0.0368
_refine_ls_R_factor_gt 0.0357
_refine_ls_wR_factor_ref 0.1085
_refine_ls_wR_factor_gt 0.1075
_refine_ls_goodness_of_fit_ref 1.173
__refine_ls_restrained_S_all}1.18
_refine_ls_shift/su_max 0.000
_refine_ls_shift/su_mean 0.000
loop_
    _atom_site_label
    _atom_site_type_symbol
    _atom_site_fract_x
    __atom_site_fract_y
    _atom_site_fract_z
    _atom_site_U_iso_or_equiv
    _atom_site_adp_type
    _atom_site_occupancy
    _atom_site_symmetry_multiplicity
    _atom_site_calc_flag
    _atom_site_refinement_flags
    _atom_site_disorder_assembly
    _atom_site_disorder_group
K1 K 0.50488(4) 0.63501(3) 0.19470(6) 0.01992(11) Uani 1 1 d . . .
N1 N 0.35559(14) 0.99480(12) -0.0925(2) 0.0160(3) Uani 1 1 d . . .
C1 C 0.13270(15) 1.05490(13) -0.2198(2) 0.0132(3) Uani 1 1 d. . .
C2 C 0.00611(16) 1.05967(14) -0.2645(3) 0.0167(3) Uani 1 1 d . . .
```

```
H2 H -0.0367 1.0212 -0.1896 0.020 Uiso 1 1 calc R . .
C3 C -0.05557(18) 1.12297(15) -0.4231(3) 0.0205(3) Uani 1 1 d . . .
H3 H -0.1421 1.1276 -0.4575 0.025 Uiso 1 1 calc R . .
C4 C 0.00752(19) 1.17980(15) -0.5326(3) 0.0232(4) Uani 1 1 d . . .
H4 H -0.0367 1.2229 -0.6395 0.028 Uiso 1 1 calc R . .
C5 C 0.13437(19) 1.17433(15) -0.4877(3) 0.0204(3) Uani 1 1 d . . .
H5 H 0.1775 1.2127 -0.5623 0.024 Uiso 1 1 calc R . .
C6 C 0.19531(16) 1.11066(13) -0.3299(3) 0.0142(3) Uani 1 1 d . . .
S1 S 0.23528(4) 0.98676(3) -0.02092(6) 0.01318(10) Uani 1 1 d . . .
O1 O 0.19931(12) 0.87935(11) -0.0199(2) 0.0182(3) Uani 1 1 d . . .
O2 O 0.24426(13) 1.04173(12) 0.1640(2) 0.0204(3) Uani 1 1 d . . .
S2 S 0.35515(4) 1.09383(3) -0.22852(6) 0.01420(10) Uani 1 1 d . . .
O3 O 0.40095(13) 1.18588(11) -0.1126(2) 0.0202(3) Uani 1 1 d . . .
O4 O 0.41401(13) 1.06828(12) -0.3810(2) 0.0209(3) Uani 1 1 d . . .
O5 O 0.34262(17) 0.73041(15) -0.1598(3) 0.0350(4) Uani 1 1 d D . .
H5A H 0.283(2) 0.772(2) -0.135(5) 0.042 Uiso 1 1 d D . .
H5B H 0.294(3) 0.694(2) -0.265(4) 0.042 Uiso 1 1 d D . .
loop_
    _atom_site_aniso_label
    _atom_site_aniso_U_11
    _atom_site_aniso_U_22
    _atom_site_aniso_U_33
    __atom_site_aniso_U_23
    _atom_site_aniso_U_13
_atom_site_aniso_U_12
K1 0.02081(19) 0.02083(19) 0.02125(19) 0.00266(13) 0.01104(15) -
0.00263(13)
N1 0.0123(6) 0.0170(6) 0.0201(7) 0.0021(5) 0.0068(5) 0.0008(5)
C1 0.0135(7) 0.0138(7) 0.0130(6) -0.0001(5) 0.0046(5) 0.0006(5)
C2 0.0148(7) 0.0197(8) 0.0170(7) -0.0015(6) 0.0066(6) 0.0016(6)
C3 0.0170(8) 0.0214(8) 0.0204(8) -0.0029(6) 0.0012(6) 0.0060(6)
C4 0.0277(9) 0.0185(8) 0.0195(8) 0.0030(6) 0.0002(7) 0.0048(7)
C5 0.0276(9) 0.0155(8) 0.0176(8) 0.0026(6) 0.0059(7) -0.0013(6)
C6 0.0157(7) 0.0138(7) 0.0139(7) -0.0006(5) 0.0054(6) -0.0006(5)
S1 0.01179(18) 0.01603(19) 0.01210(18) 0.00109(13) 0.00401(13) -
0.00087(13)
O1 0.0179(6) 0.0170(6) 0.0195(6) 0.0053(5) 0.0048(5) -0.0017(5)
O2 0.0201(6) 0.0280(7) 0.0135(6) -0.0034(5) 0.0056(5) -0.0018(5)
S2 0.01437(19) 0.01562(19) 0.01480(19) -0.00225(13) 0.00767(14) -
0.00328(13)
03 0.0228(6) 0.0185(6) 0.0205(6) -0.0045(5) 0.0082(5) -0.0075(5)
04 0.0209(6) 0.0272(7) 0.0194(6) -0.0030(5) 0.0133(5) -0.0025(5)
05 0.0308(8) 0.0348(9) 0.0367(9) -0.0115(7) 0.0054(7) -0.0004(7)
_geom_special_details
;
    All esds (except the esd in the dihedral angle between two l.s. planes)
    are estimated using the full covariance matrix. The cell esds are
taken
    into account individually in the estimation of esds in distances,
angles
    and torsion angles; correlations between esds in cell parameters are
only
    used when they are defined by crystal symmetry. An approximate
(isotropic)
    treatment of cell esds is used for estimating esds involving l.s.
planes.
;
loop_
    _geom_bond_atom_site_label_1
    _geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_2
```

```
_geom_bond_publ_flag
K1 03 2.6854(14) 3_675 ?
K1 O4 2.7370(14) 2_644 ?
K1 O4 2.8240(16) 4_576 ?
K1 O3 2.8672(15) 2_645 ?
K1 O5 2.900(2) . ?
K1 O5 2.925(2) 4_576 ?
K1 O2 3.0033(15) 2_645 ?
K1 N1 3.0573(16) 4_576 ?
K1 N1 3.3084(17) 2_645 ?
K1 S2 3.5370(6) 4_576 ?
K1 S2 3.6308(6) 2_645 ?
K1 S1 3.7121(6) 2_645 ?
N1 S1 1.5913(15) . ?
N1 S2 1.5918(16) . ?
N1 K1 3.0573(16) 4_575 ?
N1 K1 3.3084(17) 2_655 ?
C1 C6 1.388(2) . ?
C1 C2 1.390(2) . ?
C1 S1 1.7699(17) . ?
C2 C3 1.392(3) . ?
C2 H2 0.9500 . ?
C3 C4 1.396(3) . ?
C3 H3 0.9500 . ?
C4 C5 1.393(3) . ?
C4 H4 0.9500. ?
C5 C6 1.389(2) . ?
C5 H5 0.9500 . ?
C6 S2 1.7718(18) . ?
S1 O2 1.4451(14) . ?
S1 O1 1.4512(14) . ?
S1 K1 3.7122(6) 2_655 ?
O2 K1 3.0034(15) 2_655 ?
S2 O4 1.4441(14) . ?
S2 O3 1.4498(14) . ?
S2 K1 3.5370(6) 4_575 ?
S2 K1 3.6308(6) 2_655 ?
O3 K1 2.6855(14) 3_675 ?
O3 K1 2.8673(15) 2_655 ?
O4 K1 2.7370(14) 2_654 ?
O4 K1 2.8240(16) 4_575 ?
O5 K1 2.925(2) 4_575 ?
O5 H5A 0.917(17) . ?
O5 H5B 0.910(18) . ?
loop_
    _geom_angle_atom_site_label_1
    _geom_angle_atom_site_label_2
_geom_angle_atom_site_label_3
_geom_angle
_geom_angle_site_symmetry_1
_geom_angle_site_symmetry_3
    _geom_angle_publ_flag
03 K1 O4 81.81(4) 3_675 2_644 ?
O3 K1 O4 156.09(4) 3_675 4_576 ?
O4 K1 O4 75.36(5) 2_644 4_576 ?
O3 K1 O3 87.63(4) 3_675 2_645 ?
O4 K1 O3 139.69(4) 2_644 2__645 ?
O4 K1 O3 114.47(4) 4_576 2_645 ?
O3 K1 O5 69.48(5) 3_675 . ?
O4 K1 O5 74.88(5) 2_644 . ?
O4 K1 O5 97.34(5) 4_576 . ?
O3 K1 O5 136.43(5) 2_645 . ?
O3 K1 O5 83.65(5) 3_675 4_576 ?
O4 K1 O5 148.63(5) 2_644 4_576 ?
```

|  | K1 05 | 112.63(5) 4_576 4_576 |
| :---: | :---: | :---: |
| 03 | K1 05 | 66.77(5) 2_645 4_576 ? |
| 05 | K1 05 | $74.02(4) \cdot 4 \_576$ ? |
| 03 | K1 O2 | 90.85(4) 3_675 2_645 |
| 04 | K1 O2 | 68.00(4) 2_644 2_645 |
| 04 | K1 O2 | 87.20(4) 4_576 2_645 |
| 03 | K1 O2 | 73.42(4) 2_645 2_645 |
| 05 | K1 O2 | 140.11(5) . 2_645 |
| 05 | K1 O2 | 139.97(5) 4_576 2_645 |
| 03 | K1 N1 | 152.81(4) 3_675 4_576 |
| 04 | K1 N1 | 124.89(5) 2_644 4_576 ? |
| 04 | K1 N1 | 49.55(4) 4_576 4_576 |
| 03 | K1 N1 | 74.79(4) 2_645 4_576 |
| 05 | K1 N1 | 109.57(5) . 4_576 ? |
| 05 | K1 N1 | 70.49(5) 4_576 4_576 |
| 02 | K1 N1 | 103.41(4) 2_645 4_576 |
| 03 | K1 N1 | 121.64(4) 3_675 2_645 |
| 04 | K1 N1 | 107.37(4) 2_644 2_645 |
| 04 | K1 N1 | 72.98(4) 4_576 2_645 ? |
| 03 | K1 N1 | 47.93(4) 2_645 2_645 |
| 05 | K1 N1 | 168.70(5) . 2_645 ? |
| 05 | K1 N1 | 103.94(5) 4_576 2_645 |
| 02 | K1 N1 | 47.11(4) 2_645 2_645 ? |
| N1 | K1 N1 | 59.81(5) 4_576 2_645 ? |
| 03 | K1 S2 | 174.74(4) 3_675 4_576 |
| 04 | K1 S2 | 98.21(3) 2_644 4_576 ? |
| 04 | K1 S2 | 22.92(3) 4_576 4_576 |
| 03 | K1 S2 | 95.63(3) 2_645 4_576 |
| 05 | K1 S2 | 105.41(4) . 4_576 |
| 05 | K1 S2 | 93.83(4) 4_576 4_576 ? |
| 02 | K1 S2 | 94.04(3) 2_645 4_576 |
| N1 | K1 S2 | 26.69(3) 4_576 4_576 |
| N1 | K1 S2 | 63.43(3) 2_645 4_576 ? |
| 03 | K1 S2 | 104.89(3) 3_675 2_645 ? |
| 04 | K1 S2 | 127.93(3) 2_644 2_645 |
| 04 | K1 S2 | 94.83(3) 4_576 2_645 ? |
| 03 | K1 S2 | 22.02(3) 2_645 2_645 |
| 05 | 1 S2 | 156.46(4) . 2_645 ? |
| 05 | K1 S2 | 82.72(4) 4_576 2_645 |
| 02 | K1 S2 | 60.43(3) 2_645 2_645 |
| N1 | S2 | 64.54(3) 4_576 2_645 |
| N1 | K1 S2 | 25.99(3) 2_645 2_645 ? |
| S2 | K1 S2 | $79.294(13)$ 4_576 2_645 |
| 03 | K1 S1 | 106.12(4) 3_675 2_645 ? |
| 04 | K1 S1 | 85.93(3) 2_644 2_645 ? |
| 04 | K1 S1 | 79.53(3) 4_576 2_645 ? |
| 03 | K1 S1 | 59.88(3) 2_645 2_645 ? |
| 05 | K1 S1 | 160.68(4) . 2_645 ? |
| 05 | K1 S1 | 124.91(4) 4_576 2_645 |
| 02 | K1 S1 | 21.74(3) 2_645 2_645 ? |
| N1 | K1 S1 | 83.08(3) 4_576 2_645 |
| N1 | K1 S1 | 25.37(3) 2_645 2_645 ? |
| S2 | K1 S1 | 79.110(12) 4_576 2_645 |
| S2 | K1 S1 | 42.203(10) 2_645 2_645 |
| S1 | N1 S2 | 112.37(9) . . ? |
| S1 | N1 K1 | 139.84(8) . 4_575 |
| S2 | N1 K1 | 93.71(7) . 4_575 ? |
| S1 | N1 K1 | 91.65(7) . 2_655 |
| S2 | N1 K1 | 88.39(7) . 2_655 ? |
| K1 | N1 K1 | 120.19(5) 4_575 2_655 |
| C6 | C1 C2 | 121.30(16) . . ? |
| C6 | C1 S1 | 111.00(12) . . ? |
| C2 | C1 S1 | 127.64(13) . . ? |
| C1 | C2 C3 | 117.51(17) |
|  | C2 H2 | 121.2 . . ? |

```
C3 C2 H2 121.2 . . ?
C2 C3 C4 121.18(18) . . ?
C2 C3 H3 119.4 . . ?
C4 C3 H3 119.4 . . ?
C5 C4 C3 121.04(18) . . ?
C5 C4 H4 119.5 . . ?
C3 C4 H4 119.5 . . ?
C6 C5 C4 117.49(17) . . ?
C6 C5 H5 121.3 . . ?
C4 C5 H5 121.3 . . ?
C1 C6 C5 121.47(16) . . ?
C1 C6 S2 110.54(13) . . ?
C5 C6 S2 127.85(14) . . ?
O2 S1 O1 114.63(9) . . ?
O2 S1 N1 113.30(9) . . ?
O1 S1 N1 109.56(8) . . ?
O2 S1 C1 108.07(8) . . ?
O1 S1 C1 110.89(8) . . ?
N1 S1 C1 99.34(8) . . ?
O2 S1 K1 50.34(6) . 2_655 ?
O1 S1 K1 132.14(6) . 2_655 ?
N1 S1 K1 62.98(6) . 2_655 ?
C1 S1 K1 116.96(6) . 2_655 ?
S1 O2 K1 107.92(7) . 2_655 ?
O4 S2 O3 115.17(8) . . ?
O4 S2 N1 109.05(9) . . ?
O3 S2 N1 113.20(9) . . ?
O4 S2 C6 112.27(8) . . ?
O3 S2 C6 106.66(9) . . ?
N1 S2 C6 99.40(8) . . ?
O4 S2 K1 49.60(6) . 4_575 ?
O3 S2 K1 131.25(6) . 4_575 ?
N1 S2 K1 59.61(6) . 4_575 ?
C6 S2 K1 122.04(6) . 4_575 ?
O4 S2 K1 128.29(6) . 2_655 ?
O3 S2 K1 47.86(6) . 2_655 ?
N1 S2 K1 65.62(6) . 2_655 ?
C6 S2 K1 119.39(6) . 2_655 ?
K1 S2 K1 100.706(13) 4_575 2_655 ?
S2 O3 K1 134.08(8) . 3_675 ?
S2 O3 K1 110.12(8) . 2_655 ?
K1 O3 K1 110.84(5) 3_675 2_655 ?
S2 O4 K1 147.54(9) . 2_654 ?
S2 O4 K1 107.48(8) . 4_575 ?
K1 O4 K1 104.64(5) 2_654 4_575 ?
K1 O5 K1 103.45(6) . 4_575 ?
K1 O5 H5A 114(2) . . ?
K1 O5 H5A 107(2) 4_575 . ?
K1 O5 H5B 124(2) . . ?
K1 O5 H5B 109(2) 4_575 . ?
H5A O5 H5B 98(2) . . ?
loop_
    _geom_torsion_atom_site_label_1
    _geom_torsion_atom_site_label_2
    _geom_torsion_atom_site_label_3
    _geom_torsion_atom_site_label_4
    _geom_torsion
    _geom_torsion_site_symmetry_1
    _geom_torsion_site_symmetry_2
    _geom_torsion_site_symmetry_3
    _geom_torsion_site_symmetry_4
    _geom_torsion_publ_flag
C6 C1 C2 C3 -0.4(3) . . . . ?
S1 C1 C2 C3 176.68(14) . . . . ?
```

```
C1 C2 C3 C4 -0.2(3) . . . . ?
C2 C3 C4 C5 0.6(3) . . . . ?
C3 C4 C5 C6 -0.2(3) . . . . ?
C2 C1 C6 C5 0.7(3) . . . . ?
S1 C1 C6 C5 -176.80(14) . . . . ?
C2 C1 C6 S2 176.92(14) . . . . ?
S1 C1 C6 S2 -0.59(16) . . . . ?
C4 C5 C6 C1 -0.4(3) . . . . ?
C4 C5 C6 S2 -175.89(15) . . . . ?
S2 N1 S1 O2 -87.73(12) . . . . ?
K1 N1 S1 O2 145.68(12) 4_575 . . . ?
K1 N1 S1 O2 1.20(9) 2_655 . . . ?
S2 N1 S1 O1 142.89(10) . . . . ?
K1 N1 S1 O1 16.30(15) 4_575 . . . ?
K1 N1 S1 O1 -128.18(7) 2_655 . . . ?
S2 N1 S1 C1 26.66(11) . . . . ?
K1 N1 S1 C1 -99.93(13) 4_575 . . . ?
K1 N1 S1 C1 115.59(6) 2_655 . . . ?
S2 N1 S1 K1 -88.93(9) . . . 2_655 ?
K1 N1 S1 K1 144.48(14) 4_575 . . 2_655 ?
C6 C1 S1 O2 103.27(13) . . . . ?
C2 C1 S1 O2 -74.03(18) . . . . ?
C6 C1 S1 O1 -130.31(13) . . . . ?
C2 C1 S1 O1 52.38(18) . . . . ?
C6 C1 S1 N1 -15.11(14) . . . . ?
C2 C1 S1 N1 167.58(16) . . . . ?
C6 C1 S1 K1 49.24(14) . . . 2_655 ?
C2 C1 S1 K1 -128.07(15) . . . 2_655 ?
O1 S1 O2 K1 125.36(8) . . . 2_655 ?
N1 S1 O2 K1 -1.39(10) . . . 2_655 ?
C1 S1 O2 K1 -110.43(8) . . . 2_655 ?
S1 N1 S2 O4 -144.60(10) . . . . ?
K1 N1 S2 O4 4.14(8) 4_575 . . . ?
K1 N1 S2 O4 124.28(7) 2_655 . . . ?
S1 N1 S2 O3 85.79(12) . . . . ?
K1 N1 S2 O3 -125.47(7) 4_575 . . . ?
K1 N1 S2 O3 -5.32(8) 2_655 . . . ?
S1 N1 S2 C6 -26.99(11) . . . . ?
K1 N1 S2 C6 121.75(6) 4_575 . . . ?
K1 N1 S2 C6 -118.10(6) 2_655 . . . ?
S1 N1 S2 K1 -148.74(12) . . . 4_575 ?
K1 N1 S2 K1 120.15(5) 2_655 . . 4_575 ?
S1 N1 S2 K1 91.12(9) . . . 2_655 ?
K1 N1 S2 K1 -120.15(5) 4_575 . . 2_655 ?
C1 C6 S2 O4 131.22(13) . . . . ?
C5 C6 S2 O4 -52.87(19) . . . . ?
C1 C6 S2 O3 -101.75(14) . . . . ?
C5 C6 S2 O3 74.16(18) . . . . ?
C1 C6 S2 N1 16.05(14) . . . . ?
C5 C6 S2 N1 -168.04(17) . . . . ?
C1 C6 S2 K1 75.97(13) . . . 4_575 ?
C5 C6 S2 K1 -108.13(16) . . . 4_575 ?
C1 C6 S2 K1 -51.19(14) . . . 2_655 ?
C5 C6 S2 K1 124.72(15) . . . 2_655 ?
O4 S2 O3 K1 32.02(15) . . . 3_675 ?
N1 S2 O3 K1 158.44(10) . . . 3_675 ?
C6 S2 O3 K1 -93.26(12) . . . 3_675 ?
K1 S2 O3 K1 89.31(12) 4_575 . . 3_675 ?
K1 S2 O3 K1 151.90(15) 2_655 . . 3_675 ?
O4 S2 O3 K1 -119.88(8) . . . 2_655 ?
N1 S2 O3 K1 6.54(10) . . . 2_655 ?
C6 S2 O3 K1 114.84(8) . . . 2_655 ?
K1 S2 O3 K1 -62.59(9) 4_575 . . 2_655 ?
O3 S2 O4 K1 -47.59(19) . . . 2_654 ?
N1 S2 O4 K1 -176.11(14) . . . 2_654 ?
```

```
C6 S2 O4 K1 74.74(17) . . . 2_654 ?
K1 S2 O4 K1 -171.4(2) 4_575 . . 2_654 ?
K1 S2 O4 K1 -102.59(15) 2_655 . . 2_654 ?
O3 S2 O4 K1 123.84(8) . . . 4_575 ?
N1 S2 O4 K1 -4.68(9) . . . 4_575 ?
C6 S2 O4 K1 -113.84(8) . . . 4_575 ?
K1 S2 O4 K1 68.83(8) 2_655 . . 4_575 ?
O3 K1 O5 K1 23.12(5) 3_675 . . 4_575 ?
O4 K1 O5 K1 -63.65(5) 2_644 . . 4_575 ?
O4 K1 O5 K1 -136.27(5) 4_576 . . 4_575 ?
O3 K1 O5 K1 85.89(8) 2_645 . . 4_575 ?
O5 K1 O5 K1 112.22(8) 4_576 . . 4_575 ?
O2 K1 O5 K1 -41.84(10) 2_645 . . 4_575 ?
N1 K1 O5 K1 174.15(5) 4_576 . . 4_575 ?
N1 K1 O5 K1 -166.7(2) 2_645 . . 4_575 ?
S2 K1 O5 K1 -158.17(4) 4_576 . . 4_575 ?
S2 K1 O5 K1 103.19(10) 2_645 . . 4_575 ?
S1 K1 O5 K1 -57.00(14) 2_645 . . 4_575 ?
_diffrn_measured_fraction_theta_max 0.998
_diffrn_reflns_theta_full 3i.55
_diffrn_measured_fraction_theta_full 0.998
_refine_diff_density_max 0.936
_refine_diff_density_min -0.911
_refine_diff_density_rms 0.098
```


## Table 1S.

Mass-to-charge ratios $(\mathrm{m} / \mathrm{z})$ for negative and positive ions detected by ESI MS/MS spectrometry ( $\mathrm{MS}_{1}{ }^{ \pm}$modes) in dilute acetonitrile solutions of synthesized ionic liquids (Section 1S) consisting of trihexyltetradecylphosphonium ( $\mathrm{C}^{+}$) with the listed imide anions ( $\mathrm{A}^{-}$, indicated as in Scheme 1).

| anion | cation, $M S_{1}{ }^{+}$ |  | anion, $M S_{1}{ }^{-}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathrm{C}^{+}$ | $\mathrm{C}_{2} \mathrm{~A}^{+}$ | $\mathrm{CA}_{2}^{-}$ |
| $\mathbf{b}$ | 483.97 | 1148.7 | -847.9 |
|  | $(483.9)^{\mathrm{a}}$ | $(1149.9)$ | $(-848.2)$ |
| $\mathbf{c}$ | 484.0 | 1184.3 | -919.8 |
|  |  | $(1186.0)$ | $(-920.3)$ |
| $\mathbf{d}$ | 483.9 | 1128.3 | -807.8 |
|  |  | $(1129.9)$ | $(-808.1)$ |

a) calculated assuming natural isotope abundance.

## Table 2S.

Isotropic hfcc constants (Gauss) for ${ }^{1} \mathrm{H}$ and ${ }^{14} \mathrm{~N}$ nuclei in radicals derived from the aromatic imides shown in Scheme 1. ${ }^{\text {a }}$

| radical | $\mathrm{H}_{\mathrm{N}}$ | ${ }^{14} \mathrm{~N}$ | $\mathrm{H}_{1}$ | $\mathrm{H}_{2}$ | $\mathrm{H}_{3}$ | $\mathrm{H}_{4}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $>\mathbf{N H}^{-}$(radical $\mathbf{1}$ in Scheme 2) |  |  |  |  |  |  |
| 1a | 0.5 | -1.9 | 0.2 | -2.8 | -2.8 | 0.2 |
| 1b | -0.73 | -0.75 | -1.8 | -1.3 | -6.6 | 1.8 |
| 1c | -0.36 | -0.7 | 1.0 | -5.8 | -5.8 | 1.0 |
| 8 | 5.0 | 6.9 | $\approx 0$ | 0.6 |  |  |
| $>\mathbf{N}^{\bullet}$ (radical $\mathbf{2}$ in Scheme 2) |  |  |  |  |  |  |
| 2a | - | 11.4 | 0.3 | -0.5 | -0.5 | 0.3 |
| 2b | - | 10.9 | 0.4 | -0.4 | -0.1 | -0.1 |
| 2c | - | 11.3 | $\approx 0$ | -0.1 | -0.1 | $\approx 0$ |
| 2d | - | 11.2 | -0.9 | 0.7 | - | - |
| $\mathbf{H}^{\bullet}$ atom adducts (radical $\mathbf{3}$ in Scheme 2) ${ }^{\text {b }}$ |  |  |  |  |  |  |
| 1,1'a | - | 1.3 | (2x)49.4 | -8.6 | 3.2 | -11.9 |
| 2,2'a | - | 1.05 | -7.8 | (2x)42.0 | -10.5 | 3.6 |
| 1,1'b | - | 1.4 | (2x)48.8 | -9.6 | 3.5 | -13.1 |
| 2,2'b | - | 0.1 | -9.8 | (2x)46.2 | -10.0 | 3.6 |
| 3,3'b | - | 1.4 | 3.5 | -9.7 | (2x)44.8 | -9.6 |
| 4,4'b | - | 0.15 | -13.3 | 3.6 | -10.0 | (2x)48.4 |
| 1,1'c | - | 0.2 | (2x)47.6 | -10.5 | 3.7 | -13.9 |
| 2,2'c | - | 0.3 | -10.9 | (2x)47.2 | -9.3 | -10.9 |
| 1,1'd | - | $\approx 0$ | 41.6,8.1 | (3x)17.5 | - | - |
| 2,2'd | - | 1.2 | -20.8 | 37.6 | - | - |
| ketyl (radical 6 in Scheme 2) |  |  |  |  |  |  |
| 6 a | $-1.3{ }^{\text {c) }}$ | -0.7 | -1.1 | -1.1 | -3.7 | 1.0 |
| 6b | - | 2.6 | -3.3 | - | -6.9 | 1.8 |
| $>\mathbf{N}^{\bullet}$ (radical 7 in Scheme 2) |  |  |  |  |  |  |
| 7b | - | 10.1 | 2.8 | -7.6 | 2.4 | -6.0 |
| 7c | - | 9.8 | 2.8 | -7.2 | 1.8 | -5.4 |

a) Notations are as indicated in Scheme 1.
b) The prefix (e.g., 1,1'a) indicates the site of H atom addition (Schemes 1 and 2).
c) hydroxyl proton

## Table 3S.

Reported $g$-factors $\left(\delta \boldsymbol{g}=(\boldsymbol{g}-2 \cdot \mathbf{1}) \times 10^{4}\right)$ and the components of ${ }^{14} \mathrm{~N}$ hyperfine coupling tensors and isotropic hfcc constants for selected aminyl and imidyl radicals and calculated ${ }^{14} \mathrm{~N}$ tensors for imidyl radicals 2a-d.

| radical | $\delta g_{\text {iso }}{ }^{\text {a) }}$ | $\begin{aligned} & {\left[\boldsymbol{A}_{\mathrm{xx},}, \boldsymbol{A}_{\mathrm{yy},} \boldsymbol{A}_{\mathrm{zz}}\right],} \\ & \mathrm{G}\left({ }^{14} \mathrm{~N}\right) \end{aligned}$ | $\begin{gathered} a_{\text {iso }} \\ G \\ \left({ }^{14} \mathrm{~N}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| ${ }^{-} \mathrm{NH}_{2}$ | $46^{\text {b) }}$ | [41.1, 0, 0] | 13.7 |
| $\mathrm{Me}^{\circ} \mathrm{NH}$ | $40^{\text {c) }}$ | [ $40,0,0]$ | 1.3 |
| Et ${ }^{\circ} \mathrm{NH}$ | $40^{\text {c) }}$ | [35, $\sim 0, \sim 0]$ | 12 |
| tert- $\mathrm{Bu}^{\circ} \mathrm{NH}$ | - | [37, $\sim 0, \sim 0]$ | 12 |
| ${ }^{\bullet} \mathrm{NMe}_{2}$ | $40^{\text {c) }}$ | [41, $\sim 0, \sim 0$ ] | 14 |
|  |  |  | 12.5 |
| tert $-\mathrm{Bu}{ }^{\bullet} \mathrm{NSO}_{2} \mathrm{Me}$ | 44 |  | 12.9 |
| tert- $\mathrm{Bu}{ }^{\bullet} \mathrm{NSO}_{2} \mathrm{CHMe}_{2}$ | 42 |  | 13 |
| tert- $\mathrm{Bu}^{\circ} \mathrm{NSO}_{2} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Me}$ | 44 |  | 13 |
| tert- $\mathrm{Bu}^{\bullet} \mathrm{NSO}_{2} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}$ | 46 |  | 12.9 |
| tert- $\mathrm{Bu}^{\bullet} \mathrm{NSO}_{2} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OMe}$ |  |  | 12.8 |
|  | $73^{\text {d) }}$ | [31, ~0, ~0] | 10.2 |
|  | 63 |  | 11.2 |
| $2 \mathrm{a}^{\text {e) }}$ | - | [33.1, -0.8,-0.5] | 11.4 |
| $2 \mathrm{~b}^{\text {e) }}$ | - | [33.2, -0.2,-0.3] | 10.9 |
| $2 \mathrm{c}^{\text {e) }}$ | - | [35.6, -0.8, -0.8] | 11.3 |
| $2{ }^{\text {e) }}$ | - | [33.1, 0.3, 0.2] | 11.2 |

a) $g_{\text {iso }}=\left(g_{x x}+g_{y y}+g_{z z}\right) / 3$;
b) $\left.\delta g_{\mathrm{xx}} \approx \delta g_{\mathrm{yy}} \approx 40, \delta g_{\mathrm{zz}} \approx 20 ; \boldsymbol{A}_{\mathrm{xx}}{ }^{[14} \mathrm{N}\right] \approx 41 \mathrm{G} ; \boldsymbol{A}_{\mathrm{yy}} \approx \boldsymbol{A}_{\mathrm{zz}} \approx 0$;
c) $\delta g_{\mathrm{xx}} \approx \delta g_{\mathrm{yy}} \approx 50, \delta g_{\mathrm{zz}} \approx 20$;
d) $\delta g_{\mathrm{xx}} \approx 14.3 ; \delta g_{\mathrm{yy}} \approx 57, \delta g_{\mathrm{zz}} \approx 19 ; \boldsymbol{A}_{\mathrm{xx}}\left[{ }^{14} \mathrm{~N}\right] \approx 31 \mathrm{G} ; \boldsymbol{A}_{\mathrm{yy}} \approx \boldsymbol{A}_{\mathrm{zz}} \approx 0$;
e) Scheme 2; calculated using B3LYP/6-31+G(d,p) method for the lowest energy conformation.

Magnetic parameters given in this table were obtained from volumes 9c1 and 17b of Landolt-Bornstein, New Series, "Magnetic Properties of Free Radicals", Ed. Fischer, H. Springer-Verlag: Berlin, 1987.

## Scheme 1S.

Addition of alkyl radicals ( $\mathbf{R}$ ) to radical anion 1, after ref. 23.


1

## Scheme 2S.

Fragmentation pathways for protonated radical dianion of acesulfamate. Gas-phase electronic energies with respect to the " $\mathrm{H}^{\bullet}$ atom" (that is, $\mathrm{e}^{-\bullet}+\mathrm{H}^{+}$) + the acesulfamate are given in the scheme. The most exergonic reactions involve O-S bond scission.


## Scheme 3S.

Photoisomerization of (a) $N$-alkyl (Y) saccharin in benzene ( $\mathrm{R}=\mathrm{Ph}$ ) after ref. 32 and (b) saccharin-like sultam derivatives ( Y is H , alkyl, or aryl and $\mathrm{X}=\mathrm{CMe}_{2}$ ) after in ref. 32.


## Captions to Figures 1S to 27S.

## Figure 1S.

Energetics of gas-phase dissociation of the bistriflimide anion $\left(\mathrm{NTf}_{2}{ }^{-}\right)$and its oxidized form, radical 1a, according to our B3LYP/6-31+G(p,d) calculations. The bar on the left indicates the energy scale. ADE is the adiabatic electron detachment energy.

The lowest dissociation channel for the anion and the corresponding imidyl radical is homolytic C-S scission, followed by N-S bond scission, which involves a much lower barrier for the anion than the radical. The resulting $\mathrm{CF}_{3} \mathrm{SO}_{2}{ }^{\bullet}$ radical can subsequently dissociate to ${ }^{\circ} \mathrm{CF}_{3}$ and $\mathrm{SO}_{2}$.

## Figure 2S.

As Figure 1S, for the phthalimide anion.

## Figure 3S.

Formation of the staggered $C_{2}$ symmetrical, $N-N$ bound $\sigma^{2} \sigma^{* 1}$ dimer radical anion 4 from the imidyl radical 2 and parent imide anion (see Table 1 for the energetics of this bond formation). The shown optimized structures are for (a) phthalimide and (b) saccharinate. In panel (a) the spin density isosurface is indicated in the plot. It is seen that most of this density is in the overlapping $\sigma$-orbitals on the nitrogen atom. See Table 1 for energetics.

## Figure 4S.

${ }^{1} \mathrm{H}$ NMR spectrum ( 500 MHz ) of $\mathrm{P}_{666,14}$ saccharinate (Section 1S) in chloroform- $d$. The chemical shifts are given vs. TMS. The spectral attributions, chemical structures, and the normalized integrals are given in the plot.

## Figure 5S.

As Figure 4S, for $\mathrm{P}_{666,14}$ acesulfamate.
Figure 6S.
As Figure 4S, for $\mathrm{P}_{666,14} o$-benzenedisulfonimide. The doublet of doublets from aromatic protons is shown separately in the inset.

Figure 7S.
${ }^{13} \mathrm{C}$ NMR spectrum of $\mathrm{P}_{666,14} o$-benzenedisulfonimide, with attributions for the anion. Shown in the inset are the chemical shifts for saccharinate and phthalimide, taken from literature and given for comparison.

## Figure 8S.

(a) ESI $\mathrm{MS}_{1}$ spectra of methanol solution of potassium o-benzenedisulfonimide (A) monohydrate. Mass peaks corresponding to $\mathrm{K}^{+}(\mathrm{KA})_{m}$ and $\mathrm{A}^{-}(\mathrm{KA})_{\mathrm{m}}$ cluster ions are indicated in the plot. (b) Crystallographic structure of potassium o-benzenedisulfonimide monohydrate (Section 2S).

## Figure 9S.

Simulated EPR spectra for(a) radicals 1 (solid lines) and 2 (dashed lines) derived from aromatic imides (labeled as in Scheme 1) and (b) Simulated spectra of imidyl radicals 2 and corresponding contracted radicals 7 (see Schemes 1 and 2 and the inset in the plot).

## Figure 10S.

Thermal evolution of the EPR spectra from irradiated (crystalline) K saccharinate (0.02 $\mathrm{mW})$. The temperatures are given in the plot; the trace at the bottom is the difference of the EPR spectra obtained at 50 K and the same sample annealed at 300 K and cooled down to 50 K . The sharp feature in this spectrum is from the $E_{\gamma}{ }^{\prime}$ center (a silicon dangling bond) in the irradiated Suprasil sample tube. In the difference trace, the resonance lines of radical 2 (indicated by open circles) give the largest contribution (see Figure 2 for simulation).

## Figure 11S.

EPR spectra of irradiated potassium o-benzenedisulfonimide (a) at 50 K and three different microwave power levels (illustrating selective saturation of different spin centers) and (a) at 2 mW , at (i) 50 K and (ii) 220 K , when radicals $\mathbf{1 c}$ and $\mathbf{2 c}$ both decay. In panel (a), the features from radical 2 c are indicated with arrows (cf. Figure 1), and open circles indicate the features attributed to the persistent radical (trace (ii) in panel (b)). The latter can be subtracted from trace (i) to give difference trace (iii) that is also shown in Figure 1a. The open square indicates the resonance line of $E_{\gamma}{ }^{\prime}$ defect in the sample tube. The box in panel (b) indicates the resonance lines from radical 1c; see Figure 8.

## Figure 12S.

Wide-sweep EPR spectra for crystalline potassium saccharinate monohydrate irradiated by $3-\mathrm{MeV}$ electrons at 77 K and observed at 150 and $200 \mathrm{~K}(0.02 \mathrm{~mW})$. The central resonance lines (shown separately in Figure 10S) are excluded from the plot. The resonance line indicated with an open square is from a different radical than the doublet of triplets indicated by the vertical lines. The four traces at the bottom are simulated EPR spectra of radicals $\mathbf{3 b}$ (see the reaction above) that are numbered as indicated in the insets (see Table 2 S for magnetic parameters). In the gas-phase, the energies of these adducts increase in the order: $4,4^{\prime}<1,1^{\prime}<3,3^{\prime}<2,2^{\prime}$. Nevertheless, as shown by comparison with the experimental traces, the radicals $\mathbf{3 b}$ observed in this system are 2,2' and 3,3'.

## Figure 13S.

The EPR spectra from irradiated potassium (black lines) and $\mathrm{P}_{666,14}$ saccharinates (red lines) obtained at different microwave powers (indicated in the plot). Black arrows indicate the lines of the formyl radical, blue arrows indicate the lines of radical $\mathbf{1 b}$ (see Figure 3), open circles indicate the lines of radical $\mathbf{2 b}$.

## Figure 14S.

Temperature evolution of the EPR spectra from $\mathrm{P}_{666,14} o$-benzenedisulfonimide. Open circles indicate the resonance lines of $\mathrm{C}(-\mathrm{H})^{\bullet}$ radical, the arrows indicate the cationderived radical (see also Figure 7). In panel (a) the vertical lines indicate the resonance lines of radical $\mathbf{1 c}$, and in panel (b) they indicate the resonance lines of radical $\mathbf{3 c}$ ( 2,2 ' isomer).

## Figure 15S.

Thermal evolution of the EPR spectrum of polycrystalline potassium acesulfamate irradiated at $77 \mathrm{~K}(0.2 \mathrm{~mW})$. The position of the $E^{\prime}{ }_{\gamma}$ defect from the sample tube is indicated with an arrow. These EPR spectra are analyzed in Figures 10, 16S, and 17S.

## Figure 16S.

Simulating the difference trace from Figures 10 and 15 S assuming that the resonance lines indicated by filled circles in Figure 10 are from radical 9 (shown in the inset). We assumed that all proton hfcc tensors are isotropic and neglected small hfcc's on ${ }^{14} \mathrm{~N}$; we also assumed rapid rotation of the methyl group (the hfcc's, in Gauss, are given in the legend). The initial set corresponded to the DFT calculation for the $C_{2}$ symmetrical and/or asymmetrical radical anion (the latter lower-energy species has a puckered ring resulting in nonequivalent $\mathrm{H}_{\mathrm{a}}$ and $\mathrm{H}_{\mathrm{b}}$ protons). An asymmetric $\boldsymbol{g}$-tensor was assumed for this radical. Three refinements of the initial DFT sets are shown in the plot. The degree of nonplanarity for radical 9 in the solid matrix can be different from the gas phase, and the appearance of the EPR spectrum is very sensitive to this distortion, as the axial and equatorial protons have different hfcc's. One of the parameter sets is given in Table 2.

## Figure 17S.

Simulating the 200 K trace from Figure 10 assuming that the progenitor of the resonance lines indicated with open circles in Figure 10 experiences CO loss and results in the imidyl radical 7d shown in the inset. The initial hfcc parameter set is taken from the DFT calculation for the $\mathrm{C}_{\mathrm{s}}$ symmetrical species, with the $\boldsymbol{g}$-tensor coaxial with the $\boldsymbol{A}$ tensor on ${ }^{14} \mathrm{~N}$. Fast rotation in the methyl group is assumed and proton anisotropies are neglected. The principal values for $\boldsymbol{A}\left({ }^{14} \mathrm{~N}\right)$ are given in the curved brackets. Three refinements of this initial set are shown in the plot. Since there are other radicals contributing to this EPR spectrum, the fit cannot be perfect. One of the parameter sets is given in Table 2.

## Figure 18S.

Simulating the 200 K trace from Figure 13, assuming that the latter is from a $C_{s}$ symmetrical radical $\mathbf{1 0}$ shown in the inset. An isotropic $\boldsymbol{g}$-tensor was assumed. Because the hfcc's for the $\mathrm{H}_{\mathrm{a}}, \mathrm{H}_{\mathrm{b}}$, and $\mathrm{H}_{\mathrm{c}}$ protons are nearly degenerate, the simulated EPR spectrum is very sensitive to the differences in the proton hfcc's (isotropic and anisotropic) in the calculation, allowing one to simulate the "split" side lines (indicated with arrows), assuming slight nonequivalence. In this simulation, we assumed $\boldsymbol{A}\left({ }^{1} \mathrm{H}_{\mathrm{a}, \mathrm{b}}\right)\{-$ $22,-7.5,7.0\} \mathrm{G}$ and $\boldsymbol{A}\left({ }^{1} \mathrm{H}_{\mathrm{c}}\right)\{-20.4,-13.2,6\} \mathrm{G}$, with the $z$ axes of these tensors in the direction of the corresponding $\mathrm{C}-\mathrm{H}$ bonds and their $y$ axes perpendicular to the plane of the molecule. The DFT calculation gives the following estimates for the hfcc tensors:
hfcc tensor, Gauss $\quad$ Euler angles (XYZ), ${ }^{\circ}$

| nucleus | $\boldsymbol{a}_{\text {iso }}$ | $\boldsymbol{B}_{\mathrm{xx}}$ | $\boldsymbol{B}_{\mathrm{yy}}$ | $\boldsymbol{B}_{\mathrm{zz}}$ | $\alpha$ | $\boldsymbol{\beta}$ | $\boldsymbol{\gamma}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}_{\mathrm{a}}$ | -14.2 | -7.3 | -0.5 | +7.8 | 0 | 0.9 | 0 |
| $\mathrm{H}_{\mathrm{b}}$ | -15.0 | -8.5 | 0 | +8.5 | 0 | 59. | -180 |
| $\mathrm{H}_{\mathrm{c}}$ | -13.3 | -6.4 | -0.8 | +7.2 | 0 | 0 | 0 |

## Figure 19S.

ESI $\mathrm{MS}_{1}$ spectra for $\mathrm{P}_{666,14}$ saccharinate, before and after 1 hr irradiation to 2.45 MGy (see the inset). Panel (a) is for the anions and panel (b) for the cations.

## Figure 20S.

As Figure 19S, for $\mathrm{P}_{666,14} o$-benzenedisulfonimide.

## Figure 21S.

ESI $\mathrm{MS}_{2}{ }^{-}$spectra obtained for collisionally-activated $\mathrm{m} / \mathrm{z} 218$ (green), 373 (magenta), and 919 (black) mass peaks in Figure 20S(a). The masses of the fragments and their attributions are given in the plot.

## Figure 22S.

${ }^{1} \mathrm{H}$ NMR spectra for the aromatic protons in irradiated (i) $\mathrm{P}_{666,14}$ saccharinate and (ii) $\mathrm{P}_{666,14} o$-benzenedisulfonimide (DMSO- $d_{6}$ solutions).

## Figure 23S.

${ }^{13} \mathrm{C}$ NMR spectra for the aromatic carbons in irradiated $\mathrm{P}_{666,14} o$-benzenedisulfonimide (DMSO- $d_{6}$ solution). Note the logarithmic vertical scale. The resonance lines in the rectangles are attributed to the substituted anion; the lines from the parent anion (open circles) are attributed as shown in the inset. This NMR spectrum was acquired over 50 hr . As the free induction decay was 2 sec , the relaxation of the substituted carbons in the benzene ring was incomplete, which explains the suppression of the resonance lines corresponding to these carbons (i.e., $137-138 \mathrm{ppm}$ and 142 ppm ). The relative amplitude of these lines increased considerably when a paramagnetic relaxant, chromium(III) acetylacetonate, was added to the DMSO- $d_{6}$ solution ( $\sim 30 \mathrm{mM}$ ), supporting our attribution.

## Figure 24S.

${ }^{13} \mathrm{C}$ NMR spectra for the aromatic carbons in irradiated $\mathrm{P}_{666,14}$ saccharinate (DMSO- $d_{6}$ solution). As Figure 23S.

Figure 25S.
As Figure 1S, for saccharinate.
Figure 26S.
As Figure 1S, for $o$-benzenedisulfonimide.
Figure 27S.
As Figure 1S, for acesulfamate.

Figure 1 S.


Shkrob et al.

Figure 2S.


Shkrob et al.

Figure 3 S .



Figure 5S.



Figure 8 S .


K o-benzenedisulfonimide monohydrate
Shkrob et al.

Figure 9S.


Shkrob et al.

Figure 10S.


Shkrob et al.

Figure 11S.



Shkrob et al.

Figure 12S.


Shkrob et al.

Figure 13S.


Shkrob et al.

Figure 14S.


Shkrob et al.

Figure 15S.


Shkrob et al.

Figure 16S.


Shkrob et al.

Figure 17S.


Shkrob et al.

Figure 18S.


Shkrob et al.

Figure 19S.


Figure 20S.


Shkrob et al.

Figure 21S.


Shkrob et al.

Figure 22S.


Shkrob et al.

Figure 23 S .


Shkrob et al.

Figure 24S.


Shkrob et al.

Figure 25S.


Shkrob et al.

Figure 26S.


Figure 27S.


Shkrob et al.

