

power, low modulation amplitude (0.08 G), low temperature (-70°C), and high signal gain. The asymmetry of the satellites implies that they consist of overlapping resonances, although we were unable to resolve them into their components. The magnitude of $\alpha(^{33}\text{S})$ (8.3 G) is similar to that in $\text{CF}_3\text{C}\overline{\text{SS}}\text{CCF}_3^{++}$ (8.6 G) and $\text{MeO}_2\text{C}\overline{\text{C}}\text{SS}\text{CCO}_2\text{Me}^{++}$ (8.0 and 8.9 G)⁶ and is consistent with the uniform distribution of the SOMO over the S_3 moiety (see above).

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Registry No. AsF_6 , 7784-36-3; S, 7704-34-9; CF_3CN , 353-85-5; $\text{CF}_3\text{C}\overline{\text{N}}\text{SS}\text{SAsF}_6$, 140462-71-1.

Supplementary Material Available: IR, Raman, mass, and ESR spectra and an extended mass spectral listing with assignments for (1)- AsF_6 , a tabular summary of other reactions performed with the aim of preparing (1)- AsF_6 , an extended table of crystal data and a listing of anisotropic thermal parameters for (1)- AsF_6 , and tables of bond distances and angles for the AsF_6^- anion and torsional angles for the $\overline{\text{C}}\text{N}\overline{\text{S}}\text{S}\overline{\text{S}}$ ring in (1)- AsF_6 (12 pages); a listing of observed and calculated structure factors for (1)- AsF_6 (10 pages). Ordering information is given on any current masthead page.

Notes

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Deriving Chemical Parameters from Electrostatic Potential Maps of Molecular Anions

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The shapes and sizes of ions are of considerable interest in many diverse areas of chemistry.¹⁻³ There is indeed a long history of the idealized concept of "ionic radius", beginning as early as the 1920s, with the pioneering works⁴ of Landé, Wasastjerna, Yatsimirskii, and Goldschmidt (see Pauling¹ for a lucid discussion on ionic radii). In particular, a clear-cut rigorous treatment of sizes and shapes of polyatomic ions is found to be lacking in the chemical literature. The measure of spatial extent of these ions is normally provided in terms of their "spherical" radii. The latter are calculated by a variety of methods;⁵ for example, the so-called thermochemical radii are obtained via a Born-Haber calculation of the lattice energy of the crystal. That the assumption of sphericity is rather inadequate for the treatment of polyatomic ions is generally recognized in the literature. For example, as Huheey³ has remarked, "In many cases, the fact that the ions (such as CO_3^{2-} , CNS^- , CH_3CO_2^-) are markedly nonspherical, limits the use of these radii". Yet another instance of desirability of a nonspherical anion may be seen from the intuitive picture of CN^- in the NaCN crystal and that of OH^- in $\text{Ca}(\text{OH})_2$ as given in the standard treatise of Wells.² The subject of anisotropy in ionic interactions is also of current interest in thermochemistry.⁶ Of particular interest are the statements regarding near sphericity of NH_4^+ and CN^- ions in situations where electrostatic interactions predominate. Thus, the need of a rigorous yet simple and practical definition of shapes and sizes of polyatomic anions can hardly be overemphasized.

A beginning in this direction has recently been made by Sen and Politzer,⁷ by defining the radii of *atomic anions* on the basis of the behavior of their electrostatic potential. They show that⁷ a monoatomic negative ion *must* have a negative-valued minimum in its electrostatic potential $V(r)$, at a radial distance of r_m . The value of r_m has been identified by them with the anionic radius.

It may be noted the ions F^- , Cl^- , Br^- , and I^- generally turn out to be smaller in their treatment,⁷ as compared to the respective crystal radii. It is the purpose of this note to provide a completely general yet practical treatment of anisotropies of molecular anions.

Our definition stems from general topographical features exhibited by the molecular electrostatic potential (MESP) maps of such systems. The MESP $V(\vec{r})$ at a point \vec{r} due to a molecular species (with nuclear charges $\{Z_A\}$ located at $\{\vec{r}_A\}$ and electron density $\rho(\vec{r})$) is given by (in au)

$$V(\vec{r}) = \sum_A Z_A / |\vec{r} - \vec{r}_A| - \int \rho(\vec{r}') d^3r' / |\vec{r} - \vec{r}'| \quad (1)$$

In the above equation, the first term represents the nuclear contribution and the second one corresponds to the electronic part. A reciprocal relation to (1) is furnished by the Poisson equation, viz.

$$\nabla^2 V(\vec{r}) = 4\pi\rho(\vec{r}) - 4\pi\sum_A Z_A \delta(\vec{r} - \vec{r}_A) \quad (2)$$

This relation has recently been exploited by Gadre et al.^{8,9} to explore the maximal and minimal characteristics of MESP maps. The topography of these maps is indeed very distinctive, since it can exhibit no nonnuclear maxima^{8,9} at any point in space. The minima in such maps are invariably joined via saddle points. In the same spirit, it can be readily proven that an anionic MESP must attain^{8,9} a negative-valued minimum along any ray emanating from within the nuclear framework. Thus, for every anion, there

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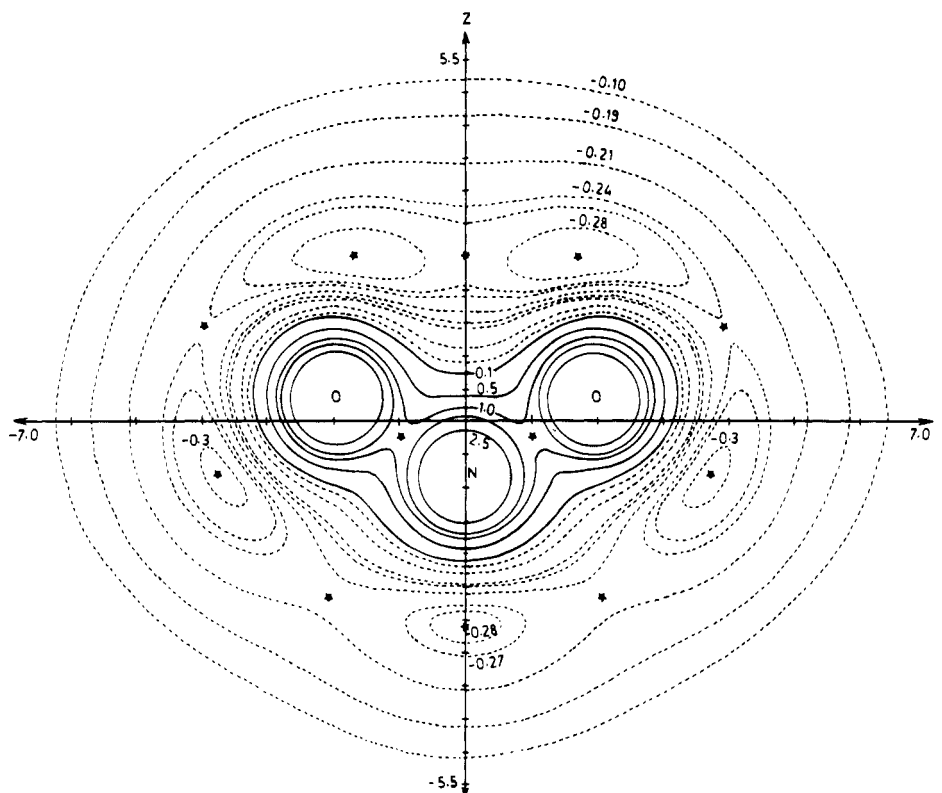


Figure 1. Contour map of the molecular electrostatic potential of the NO_2^- in the plane containing the nuclei. Nitrogen and the two oxygen nuclei are placed at (0.0, 0.0, -0.8409), (-1.9696, 0.0, 0.3680), and (1.9696, 0.0, 0.3680) (in atomic units), respectively.

exists a girdle of minima and saddle points surrounding the nuclear skeleton. An illustration of this is provided by Figure 1, which depicts a typical MESP contour map of the NO_2^- anion, in the plane containing the nuclei. The solid and dashed lines indicate positive and negative MESP values, respectively. The asterisks indicate the critical points (points at which $\nabla V(\vec{r}) = 0$) in the MESP. It is this rich topography of MESP maps that provides us with a practical method of estimating anionic shapes and sizes, based solely on their electronic charge distributions.

Following is the outline of our algorithm for this purpose: (i) Take an arbitrary ray in a direction θ, ϕ (starting with $\theta = 0$ and $\phi = 0$) outward, from the center of mass of the system. (ii) Evaluate MESP at some points along this ray, till it attains a negative value. (iii) Locate the most outward point at which MESP is a negative minimum; store this radial distance r_m and the corresponding MESP, V_m . (iv) Repeat the steps i-iii for $\theta = 0$ to π and $\phi = 0$ to 2π in steps of $\Delta\theta$ and $\Delta\phi$ (typically $2-3^\circ$). (v) From a table of r_m and V_m , calculate the average \bar{r} , smallest of r_m , viz. $r_<$, and the largest r_m , viz. $r_>$. Also compute the root-mean-square (rms) deviation Δr as $\Delta r_i = (\sum((r_m)_i - \bar{r})^2/N)^{1/2}$ (N is the total number of r_m values). Similarly obtain \bar{V} , $V_<$, $V_>$, and ΔV .

This algorithm has been employed to evaluate the above parameters for some molecular anions. The optimized wave functions for these systems were obtained using the packages MICROMOL¹⁰ and TURBOMOLE¹¹ with a variety of Gaussian basis sets, with *dzp* or *better quality* basis sets. It should be noted that the effect of basis set (beyond dz2p quality) on the above mentioned parameters is not very pronounced. This may be because the general shape of the electrostatic potential is not affected markedly by the choice of basis set.¹² Furthermore, earlier studies by Daudel et al.¹³ show

that inclusion of CI corrections to the wave function do not much affect the MESP values, particularly in regions of chemical interest, which are generally the regions away from the nuclei. Our results, obtained by the above method, along with the respective "spherical" radii are reported in Table I. It may be noted that the literature values of radii differ from each other by about 14%. The average radius values obtained by our method agree reasonably well with the corresponding crystal-adjusted purely thermochemical ones, the notable exceptions being ClO_3^- and BrO_3^- ions. The literature values always estimate BrO_3^- to be smaller by about 0.17 Å than ClO_3^- . It is felt that relativistic effects may not shrink BrO_3^- so much so as to make it smaller than ClO_3^- . The literature values indicate that the Br-O bond length is larger than Cl-O by about 0.15 Å (1.85 and 1.50 Å, respectively).¹⁴ With these data, it is rather difficult to rationalize why BrO_3^- could be much smaller than even CN^- or SH^- and why ClO_3^- is smaller than both these species.

It is however gratifying to see an overall general agreement (barring ClO_3^- and BrO_3^-) of our radius values with the crystal-radii-adjusted thermochemical ones.³ Our values (cf. also the Sen and Politzer radii⁷ for monoatomic species) are invariably lower (except halates) than the respective thermochemical radii and could be suitably scaled. It may be borne in mind that our method is a first-ever direct theoretical one, whereas the thermochemical radii are computed *indirectly*, as fitting parameters, giving "best" lattice energy. Thus, the latter do not have a direct correspondence with the spatial extent of ions. Admittedly, our values do not incorporate relativistic and solid-state effects. However, it may be possible to incorporate these corrections in refined versions. The former are in any case not expected to be significant for the species studied here.

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Table I. Size and Potential Parameters^a of Molecular Anions

| ion (basis) (energy, au) | radius params, Å | | | | potential params, au | | | |
|-------------------------------------------------|------------------------------|------------------------------|------------------------------|------------|----------------------|--------|--------|------------|
| | r^b | $r_<$ | $r_>$ | Δr | \bar{V} | $V_<$ | $V_>$ | ΔV |
| BH ₄ ⁻ (tz2p) (-26.985) | 1.73 (1.79 ^b) | 1.58 | 2.29 | 0.38 | -0.249 | -0.262 | -0.217 | 0.011 |
| OH ⁻ (tz2p) (-75.376) | 1.14 (1.19 ^b) | 1.07 (1.33 ^b) | 2.03 (1.40 ^c) | 0.17 | -0.396 | -0.441 | -0.184 | 0.060 |
| CN ⁻ (tz2p) (-92.326) | 1.52 (1.77 ^b) | 1.33 (1.91 ^b) | 1.89 | 0.17 | -0.277 | -0.320 | -0.256 | 0.013 |
| N ₃ ⁻ (tz2p) (-163.313) | 1.75 (1.81 ^b) | 1.64 (1.95 ^b) | 2.38 | 0.19 | -0.233 | -0.280 | -0.205 | 0.026 |
| NO ₂ ⁻ (tz2p) (-204.132) | 1.62 (1.78 ^b) | 1.26 | 2.23 | 0.23 | -0.270 | -0.319 | -0.206 | 0.028 |
| NO ₃ ⁻ (tz2p) (-279.004) | 1.88 (1.65 ^b) | 1.75 (1.89 ^c) | 2.47 | 0.16 | -0.224 | -0.281 | -0.177 | 0.032 |
| SH ⁻ (dz2p) (-398.067) | 1.62 (1.93 ^b) | 1.53 (2.07 ^b) | 3.01 (1.95 ^c) | 0.15 | -0.286 | -0.312 | -0.171 | 0.031 |
| BF ₄ ⁻ (tz2p) (422.877) | 2.00 (2.18 ^b) | 1.84 (2.28 ^c) | 2.54 | 0.18 | -0.228 | -0.240 | -0.198 | 0.010 |
| CNS ⁻ (tzp) ^c (-489.864) | 2.27 (1.99 ^b) | 1.63 (1.95 ^c) | 3.18 | 0.53 | -0.209 | -0.249 | -0.151 | 0.025 |
| ClO ₃ ⁻ (tzp) (-683.862) | 2.09 (1.57 ^b) | 1.83 (1.71 ^b) | 2.65 (2.00 ^c) | 0.20 | -0.207 | -0.276 | -0.136 | 0.048 |
| ClO ₄ ⁻ (tzp) (-758.668) | 2.21 (2.26 ^b) | 2.10 (2.40 ^b) | 2.73 (2.36 ^c) | 0.15 | -0.210 | -0.234 | -0.172 | 0.016 |
| BrO ₃ ⁻ (G-1) (-2796.339) | 2.24 (1.40 ^b) | 1.91 (1.91 ^c) | 2.77 | 0.19 | -0.195 | -0.269 | -0.121 | 0.052 |

^a See text for details. ^b The values in parentheses denote the Huheey³ (h) and Marcus^{16a} (b), and Marcus^{16c} (c) thermochemical (spherical) radii, respectively. The values in the top line are the present (spherically averaged) ones. ^c The literature radii for the SCN⁻ ion are from refs 3 and 16c, respectively, for comparison.

It is also possible to unearth further "chemical" information from the parameters derived from MESP maps. For instance, one may make qualitative predictions of anisotropies in electrostatic interactions of these ions with interacting ions/molecules. The low values of ΔV for CN⁻ and ClO₄⁻ (cf. Table I) imply that these species would not be significantly anisotropic with respect to such interactions. This is in accordance with the recent thermodynamic studies which have led to the conclusion⁶ that "... in clusters and condensed systems, where electrostatic interactions predominate, CN⁻ may similarly behave as a spherical core ion". It may also be concluded from the potential rms parameter ΔV that OH⁻, ClO₃⁻, and BrO₃⁻ (of the species studied) are likely candidates for exhibiting anisotropies in electrostatic interactions.

The minima $V_<$ of these species are expected to show, barring solvent effects, etc., trends parallel to the respective base strengths and nucleophilicities.¹⁵ Good nucleophiles are expected, in general, to be good bases, viz. good electron donors. Thus, among the species studied, as per the $V_<$ values, OH⁻ is a "good" nucleophile and ClO₄⁻ is a relatively "bad" nucleophile. In fact, the trend in $V_<$ values, tabulated in Table I, is in overall agreement with the average nucleophilicity of the anions.¹⁵ For example, CN⁻ and OH⁻ show an average nucleophilicity of more than 1000, NO₃⁻ has a value of 1, and ClO₄⁻ is assigned a value less than 1. It may be reemphasized here that the correlation of nucleophilicity with $V_<$ in the present study, is approximate in that it does not take into consideration the solvent and experimental effects, such as temperature, concentration, etc.

MESP maps also provide us with a handle on anionic softness parameters.¹⁶ The anionic softness parameter indicates how diffuse, or "fluffy", is the electronic distribution of a given species. This implies that the greater the charge in the negative MESP region, the greater is the corresponding softness parameter (σ). For instance, the σ values for OH⁻, SH⁻, CN⁻, SCN⁻, and N₃⁻ are^{16a} 0.0, 0.63, 0.48, 0.84, and 0.78. The respective integrated electron density values (over a region where $V < 0$) are 3.72, 4.13, 4.22, 5.74, and 5.12, thereby revealing similar trends, in general,

as shown by the σ parameters above.

In summary, the MESP maps of anions thus provide us with a unifying theme for explaining and predicting various chemical properties such as size, shape, nucleophilicity, and softness of molecular anions.

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Complexes of Tetrathiomolybdate and -tungstate with Copper(I) and Silver(I): Sulfur-33 NMR Properties

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Introduction

Sulfur has a vast chemistry, but direct spectroscopic probes are conspicuously lacking. ³³S NMR is an obvious possibility, but the isotope has a low natural abundance (0.76 atom %), a small gyromagnetic ratio, and a significant electric quadrupole moment.¹ Consequently, ³³S NMR is relatively insensitive and line widths can be broad. However, careful choice of both compounds and appropriate experimental methods can provide information of structural significance.²⁻⁴

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