rameters of six-membered ring compounds from observed endocyclic vicinal proton-proton coupling constants. It is demonstrated that the computational procedures devised for this purpose lead to a consistent and quantitative conformational interpretation of a wide variety of six-membered ring compounds in solution. The latter interpretations are shown to correspond well to conformational data obtained for these compounds by other techniques such as X-ray crystallography and/or molecular mechanics. Moreover, the present analysis can detect whether the six-membered ring occurs in a fast two-state conformational equilibrium and, if so, describe that equilibrium quantitatively. It is therefore concluded that conformational analyses performed along the lines of the methods presented in this paper are capable of increasing our detailed and *quantitative* understanding of the conformational behavior of six-membered rings in solution to a level not heretofore attained.

Polarizability and Nuclear Shielding for the Sodium Anion in Condensed Phases

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Abstract: The environmental modifications of the polarizability, the diamagnetic contribution to the susceptibility, and the nuclear shielding of the sodium anion (Na^-) in the cryptand salt $Na^-{\cdot}Na^+C_{222}$ (C_{222} = cryptand 222) are deduced from ab-initio quantum chemistry computations. The point charge electrostatic contribution to the anion environment in the cryptand reduces to 643 au, the free anion polarizability of 1090 au predicted taking account of electron correlation using the coupled electron pair approximation. This polarizability is found to be further diminished to around 400 au on introducing a realistic model of the full environment in the cryptand. The electron correlation contribution to the polarizability is largely suppressed on entering the condensed phase. The diamagnetic contribution to the susceptibility is found to be reduced in magnitude by 32% on introducing a model for the full environment in the cryptand. This result, combined with an average energy approximation analysis of the ab-initio polarizabilities, shows that environmental modifications of the ground-state wave functions are responsible for about one-third of the polarizability reductions, with two-thirds arising from environmental modifications of the excited states and their excitation energies. The contribution of the two 3s electrons to the diamagnetic part of the nuclear shielding is found to be enhanced by 9% when the free anion experiences the present model for the environment in the cryptand, the core contribution remaining essentially unchanged. The nucleus in the cryptated anion is predicted to be shielded by 3.58 ppm relative to that in an isolated gaseous sodium atom, compared with the 2.88 ppm nuclear shielding in the free anion relative to that in the free atom. This comparative insensitivity of the shielding is consistent with the experimental observation that the Na^- shielding (uncorrected for bulk susceptibility) almost always lies within ±1 ppm of a 1.5 ppm shielding relative to the free sodium atom. This explains how the nuclear shielding can be so comparatively environment insensitive in a species interacting sufficiently strongly with its surroundings as to experience a reduction in polarizability by a factor of 2.7.

I. Introduction

The singly charged anion of an alkali metal is described, in the orbital model of the electronic structure of an atom, as containing two spin-paired electrons in its *ns* valence orbital, thus having the configuration ns^2. The anions of all the alkali metals have been prepared in the gas phase and their ionization potentials measured by photodetachment.[1] The result that an energy in the range of 0.5 eV is required to ionize any alkali metal anion (M^-) to produce the neutral atom (M) shows that these anions exist as stable species in the gas phase, having infinite lifetimes if left unperturbed. In 1953, many years before these experiments, it was suggested[2] that alkali anions might also exist in the condensed phase. Roughly contemporaneously with the photodetachment measurements, this possibility was unambiguously realized by Dye and co-workers. They both identified the sodium anion (Na^-) in solutions prepared by dissolving sodium metal in a mixture of ethylamine and a cryptand[3] as well as synthesized a crystalline salt containing Na^- ions whose structure was determined by X-ray crystallography.[4,5] The sodium anion has subsequently been identified in a wide range of solutions produced by dissolving sodium in other solvents containing added cryptands as well as in solutions of sodium in amines or crown ethers. The anions of K, Rb, and Cs were subsequently identified in solutions prepared by dissolving the appropriate metal in such solvents. Furthermore, the structures of several salts containing either the Rb^- or the Cs^- ion have been determined by X-ray crystallography. Any of three reviews[6-8] of this work contain references to the original literature.

Solutions containing alkali anions have been studied using a variety of techniques such as pulse radiolysis[9] and ultraviolet,[10] EPR,[11] and NMR[6-8] spectroscopy, of which the latter has been used most widely. The frequency of the nuclear resonance signal originating from the sodium anion is found not only to be almost independent of both temperature and concentration but also to be independent of solvent. Furthermore, this signal occurs at almost the same frequency in the crystalline salts containing Na^- as it does in solution. Each of these NMR experiments yields the shielding of the nucleus in Na^- relative to that of the ^{23}Na nucleus in hydrated sodium cations at infinite dilution. These

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results have been combined[3,12,13] with those from a variety of optical pumping, EPR, and NMR experiments to obtain experimental values for the shielding of the Na^- ion in solution relative to that in an isolated gaseous sodium atom. However, the nuclear shielding in gaseous Na^- relative to that in a gaseous sodium atom has been accurately predicted[12] by combining the results of atomic Hartree–Fock computations with the reliably known value for the contribution arising from electron correlation. The latter term was derived from experimental ionization potentials by using an argument[14] based on the Hellmann–Feynman theorem. It was found that, to within ±1 ppm, the nuclear shielding in an Na^- ion in any of these condensed-phase environments is identical to that in the gaseous anion. This result contrasts with that of any other commonly occurring anion or cation in solution where the shielding is found to depend markedly on the solvent. For example, the resonance of the aquated sodium cation at infinite dilution is deshielded relative to that of the gaseous atom by as much as 60.5 ppm,[15] corresponding to a deshielding of 55.3 ppm relative to the gaseous cation, this free cation being deshielded by 5.2 ppm[14] relative to the gaseous atom. The extremely close similarity between the Na^- shielding in the gaseous and dissolved states has been taken as evidence that this anion interacts only minimally with its environment in the solutions prepared by dissolving sodium metal in organic solvents.[3,6–8,16]

Further evidence for the weakness of the interaction of Na^- with its environment in solution is provided by the observation[7,8,10,13,16] that the NMR line widths of the Na^- signal are usually only a few hertz being as small as a single hertz in some instances,[17] despite the presence in these solutions of paramagnetic species detected by EPR spectroscopy.[17,18] The weakness of the interaction between Na^- and its solution environment has been further highlighted by an extensive series of measurements[17] of the rates of ^{23}Na spin–lattice relaxation in solutions prepared by dissolving sodium metal in the crown ether 12C4. Not only was it deduced that the spin–lattice relaxation in Na^- occurred by the quadrupolar mechanism with the necessary fluctuating electric field gradients originating from the independent translational or rotational motion of the 12C4 solvent molecules but also these relaxation rates were found to be remarkably slow. Thus a comparison of these rates with the rates of quadrupolar spin–lattice relaxation in other centrosymmetric ions in other solutions showed,[16] after taking account of differences in nuclear spin, nuclear electric quadrupole moment, Sternheimer antishielding factor, and solvent viscosity, that the interaction of the sodium anion with its environment in 12C4 is much less than that of any other commonly occurring ion with its typical environments. Indeed it was concluded[16] from all the evidence just presented that the Na^- ion exists in solution in 12C4 as an almost gas-like entity.

The extensive NMR studies of the Na^- ion have conclusively shown that the nucleus in this species is only coupled to its environment extremely weakly. However, one cannot necessarily conclude from this that the entire species interacts only minimally with its environment. The possibility that there are other ways in which this species could interact significantly with its surroundings without affecting the nuclear spin is strongly suggested by the size of the electric dipole polarizability of Na^-. Thus the ab-initio quantum chemistry computations to be presented here agree with the result of the more reliable of two other calculations[19] that the polarizability of an isolated Na^- ion is slightly in excess of 1000 au. The enormous size of this polarizability is best appreciated by comparing it with that of 165.0 au[20] for the free sodium atom and of 1.002 au for the free sodium cation.[21] Even the polarizabilities of the alkali atoms are very large compared with those of most commonly occurring ions. The polarizabilities of anions tend to be larger than those of cations. Accurate ab-initio quantum chemistry computations taking account of electron correlation predict that free fluoride and free chloride ions have polarizabilities of 15.1 au[22] and 38.1 au,[23] respectively, while an essentially exact calculation shows that the polarizability of a free hydride ion is 206 au.[24] A value of about 51 au has been suggested[25] for the polarizability of a free bromide ion by combining the ab-initio coupled Hartree–Fock result[26] with an estimate of the contribution arising from electron correlation. Examination of experimental refractive index data shows that anion polarizabilities are reduced very significantly on entering the condensed phase, those of the F^-, Cl^-, and Br^- ions being 9.2, 24.4, and 32.3 au in the solid cesium salts and 8.8, 25.4, and 34.2 au in aqueous solution at infinite dilution.[25] These are the condensed-phase environments which least affect the anion polarizabilities, those of F^-, Cl^-, and Br^- being still further reduced to 6.0 au,[28] 19.4 au,[21] and 26.9 au[27] in their solid lithium salts. Although the ab-initio prediction of 10.5 au for the polarizability of the hydride ion in LiH differs[21] from that of 12.6 au derived by subtracting the known polarizability of Li^+ from the experimentally determined molar polarizability, it is nevertheless quite clear that the polarizability of this anion is greatly reduced on entering the crystal.

All of the evidence just discussed suggests very strongly that on entering a condensed phase the polarizability of an Na^- ion would be considerably reduced from that of the free ion. If this were the case, it is clear that the Na^- ion would have significantly interacted with its environment. Furthermore, even the environmentally reduced Na^- polarizability would be expected to be sufficiently large that it might be difficult to imagine that the ion is decoupled from its surroundings. This reasoning appears to directly contradict the powerful NMR evidence that this anion does not interact strongly with its environment. This paper has two principal objectives. The first is to use ab-initio quantum chemistry computations to elucidate the essential features of the environmentally induced modifications of the Na^- polarizability. The second is to reconcile the apparently contradictory evidence from the NMR experiments and the polarizability considerations concerning the strength of the interaction between an Na^- ion and its surroundings. A third result of this research, produced as a byproduct, is the elucidation of the influence of the environment on the diamagnetic contribution to the magnetic susceptibility, thereby manifesting the clear chain along which the environmental sensitivity decreases on passing from the polarizability to the nuclear shielding.

II. Mechanisms for Environmental Modifications of Anion Polarizabilities

In an ionic crystal, the modification of the polarizability of an anion by its environment can be considered to consist of two different contributions.[21,28–31] The first of these, which would be the only contribution if the wave functions of the ion overlapped only negligibly with those of neighboring ions, is the modification caused by the purely electrostatic fields generated by all the other ions in the crystal. This contribution is identical to that generated by an infinite lattice of point charges. The second contribution is the further polarizability modification that arises because the

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wave functions of the ion overlap with those of neighboring ions.

The first contribution to the environmentally induced modification of the polarizability of an anion can be evaluated[21,28,32] by comparing the ab-initio quantum chemistry prediction for the polarizability of the isolated ion with that computed when the ion is placed at the center of a lattice of point charges with the outermost charges adjusted so as to produce the correct Madelung potential at the anion site. Such calculations have invariably predicted not only that the anion polarizability is reduced on entering the ionic crystal but also that the anion becomes compressed, as manifested by reduction in both the mean radius and mean square radius of its outermost orbital. These compressions cannot be readily understood on the basis of pairwise interactions between the ion and the surrounding lattice because this approach might lead one to expect that the anion electron density would expand on account of the attraction between the anion electrons and the closest neighbors which are cations. The key to understanding these contractions is to expand the potential energy ($F_{\text{env}}(\mathbf{r}_a;R)$) experienced by an anion electron having a position vector $\mathbf{r}_a$ relative to the anion nucleus into a series in which the angular variation is described using spherical harmonics:

$$F_{\text{env}}(\mathbf{r}_a;R) = F^{(0)}{}_{\text{env}}(r_a;R) + \sum_{L=1}^{\infty} F^{(L)}{}_{\text{env}}(\mathbf{r}_a;R) \qquad (1)$$

Here R is the parameter defining the geometry of the crystal. This parameter becomes just the distance between the anion and its closest cation neighbors for the case of cubic crystals, which are those for which these environmental effects on anions have been almost exclusively studied. The first term in the expansion (eq 1) is independent of any angular variables and thus depends only on the radial distance r_a of the electron from the anion nucleus and constitutes the spherically symmetric part of the potential, as designated by the supercript 0. The sum of all the remaining terms in eq 1 describes the angular variation of $F_{\text{env}}(\mathbf{r}_a;R)$, that of the term $F^{(L)}{}_{\text{env}}(\mathbf{r}_a;R)$ being the same as that of a spherical harmonic of rank L. Both the contraction of an anion as well the reduction in its polarizability on entering the point charge representation of an ionic crystal lattice are readily understood if the potential energy function (eq 1) is dominated by its spherically symmetric part. This portion ($F^{(0)}{}_{\text{env}}(r_a;R)$), depicted in Figure 1, is the same as that produced by the charge distribution generated by the following averaging procedure. For all distances r_a from the anion nucleus, all the point charges present at the distance r_a are averaged over the surface of a sphere of radius r_a. The resulting potential is constant from the nucleus of the anion ($r_a = 0$) to the distance R equal to the closest cation–anion separation because, for these distances, the electron is inside all the spherical shells of charge, the potential inside a spherical shell of charge being constant. This constant potential is attractive for an anion electron because the closest shell contains the positive charge generated by averaging the positions of the closest neighboring point charge cations. For distances r_a greater than R, the magnitude of $F^{(0)}{}_{\text{env}}(r_a;R)$ decreases because the potential outside a spherical shell of charge is the same as if all the charge were placed at the center ($r_a = 0$). The smaller oscillations in the potential at larger distances r_a are associated with distances corresponding to non-nearest neighbor separations. Clearly the charge distribution of an anion electron subject to a potential of this form, shown in Figure 1, will be contracted compared with that of the free ion. Furthermore, an electron subject to such an additional potential will be more strongly bound than that in the free ion, this effect reinforcing[29] the effect of the contraction in reducing an anion polarizability because the polarizability is determined by a combination of the properties of the ground and excited states, including especially the excitation energies. For an anion having a closed-shell electronic structure, the dominance of the spherically symmetric part of eq 1 becomes readily understandable if it is remembered that none of the non-spherically symmetric terms affect the total energy of the ion[33] if, in an orbital model of its electronic structure, it is demanded that all the orbitals in the crystal have the same angular parts as those in the free ion. This should be expected to be a good approximation for an anion in a cubic lattice because here parity considerations eliminate all terms in eq 1 containing spherical harmonics of odd orders, while the terms having second-order spherical harmonics ($L = 2$) also vanish. Hence the leading correction to $F^{(0)}{}_{\text{env}}(r_a;R)$ is a term containing fourth-rank spherical harmonics ($L = 4$) whose effect on an orbital of s or p symmetry would be expected to be small.

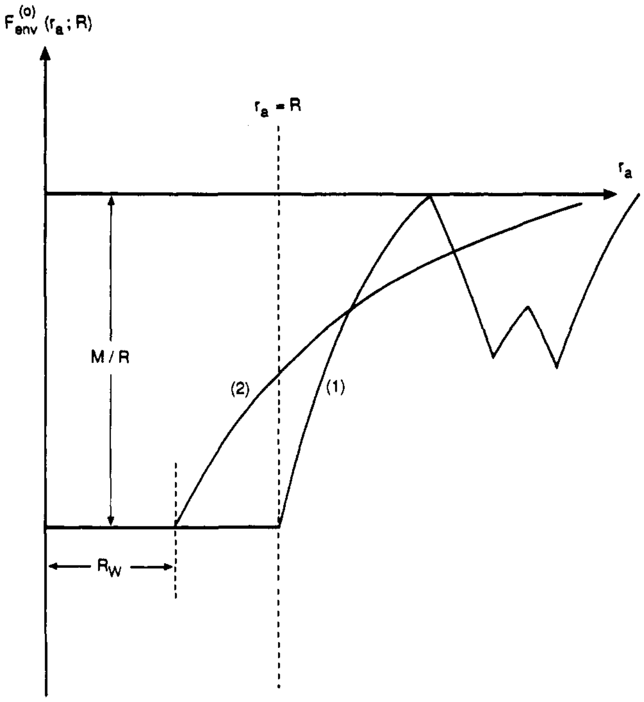

Figure 1. The spherically symmetric part ($F^{(0)}{}_{\text{env}}(r_a;R)$) of the environmental potential energy experienced by an anion electron. The curve labeled (1) is for a point charge lattice, and that labeled (2) is a realistic local model for the full potential.

The second contribution to the in-crystal modification of an anion polarizability, namely, that caused by overlap with filled orbitals on neighboring ions, can be derived[21,28,32] from ab-initio calculations in which the nearest point charges in the array used to compute the first contribution are replaced by introducing explicitly all the electrons and orbitals on these nearest neighbor ions as well as their full nuclear charges. The ab-initio computation for such a cluster of ions embedded in a point charge lattice naturally yields the polarizability of the cluster, from which that of the anion has to be extracted by subtracting both the polarizabilities of the neighboring cations as well as the dipole-induced dipole corrections.[28] The required cation polarizabilities can be taken to be equal to those predicted from ab-initio computations for the free cations, because not only have the polarizabilities of light cations been shown to be essentialy independent of their environment but also these polarizabilities are much smaller than those of the anion.[21,28,32] Such calculations have always shown that the overlap with the filled orbitals on neighboring cations both causes the outermost anion orbitals to contract still further and causes the anion polarizability to be further diminished compared with its behavior in the point charge representation of the crystal lattice. Since these overlap effects are of short range, unlike the coulomb forces acting in a point charge lattice, these contractions can be understood simply as a readjustment of the anion electron density away from the spatial regions in which cation orbitals have large amplitudes. In such spatial regions an anion electron is subject to repulsive forces[33] that originate ultimately from the Pauli principle. Since the range of this repulsion is short, all of the terms generated by expanding it in spherical harmonics according to eq 1 would be destabilizing, and so the outermost anion orbitals would still contract even if this expansion was not dominated by the spherically symmetic term. Figure 1

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shows a schematic representation of the spherically symmetric part of the full environmental potential including both the point charge electrostatic and repulsive short range overlap contributions.

III. Polarizability of the Sodium Anion

A. The Free Sodium Anion. All the polarizability calculations were performed using the CADPAC program.[34] Such calculations are performed by expanding the electronic wave function in a set of basis functions; the Appendix describes the contruction of a basis sufficiently large as to describe accurately the polarizability of an Na^- ion. The polarizability of an isolated Na^- ion was first computed using coupled Hartree–Fock (CHF) theory. The result of such a calculation is automatically free from any hyperpolarizability effects which can be present when the polarizability is computed using the finite field perturbation method.[35,36] In the latter approach the wave function is first computed either at the Hartree–Fock level or using a more sophisticated approach and the calculation then repeated including the additional terms which describe the interaction with a uniform electric field of strength F. Then either the polarizability (α) is calculated as μ/F, where μ is the dipole moment computed as the expectation value of the dipole moment operator, or the polarizability is derived by equating to $\alpha F^2/2$ the energy lowering on introducing the external field.[36] For Hartree–Fock wave functions, the results of either of these two methods will agree with those of the corresponding CHF computation, provided that F is sufficiently small for hyperpolarizability effects to be negligible.[36,37] A finite field perturbation computation using Hartree–Fock wave functions with a field strength (F) of 0.0001 au yields a free Na^- polarizability of 1457.8 au, in excellent agreement with the CHF prediction of 1455.7 au. This shows that hyperpolarizability effects will be negligible in finite field computations using this field strength and more accurate wave functions for which the analogue of the CHF approach is not available.

The polarizability predicted using Hartree–Fock theory will differ from the true value because such a calculation neglects the contribution, called the correlation polarizability, which arises from electron correlation. Here the correlation contribution has been computed using the finite field method with wave functions derived both from Moller–Plesset perturbation theory taken to second order (MP2)[37] and from the coupled electron pair approach (CEPA).[35,38] It is the MP2 method which has been most widely applied to investigate environmental modifications of ion polarizabilities.[21,25,26,28,32,39] Although this approach is more than adequate for describing the polarizabilities of cations and anions in crystals, it only treats the correlation to lowest order in perturbation theory and therefore may well be inadequate for loosely bound free anions, where the correlation contribution is a sizable fraction of the total polarizability. The CEPA approach is nonperturbative and treats the correlation to much greater accuracy, this approach predicting the polarizabilities of small atoms and molecules to an accuracy of better than 2%.[20,35]. The MP2 method, applying the perturbation treatment of all the electrons including those in the 1s and 2s orbitals, predicts the free Na^- polarizability to be 1245.0 au when derived from the computed dipole moment (the MP2D method) calculated as the expectation value of the dipole moment operator. This agrees well with the MP2 prediction of 1235.2 au derived by equating the energy lowering in the field to $\alpha F^2/2$ (the MP2E method). However, the inadequacy of the MP2 method for this system is shown by the CEPA prediction of 1090.2 au derived from the energy lowering in the electric field. The motions of all the electrons were correlated excepting those in the 1s and 2s orbitals. These two orbitals make only very small contributions to the CHF polarizability, their orbital polarizabilities being only −0.0007 and −0.071 au, respectively, compared with 1458.2 au for the 3s orbital. Hence the additional contribution from the correlation of the 1s and 2s electrons will be negligible. A program for computing the dipole moment from the CEPA wave function was not available. However, the polarizability calculated from such a dipole would be expected to differ only insignificantly from that derived from the energy lowering, because polarizabilities predicted from the two methods become identical for exact wave functions, and the CEPA function is of much greater accuracy than the MP2 one, for which the MP2D and MP2E polarizabilities are very similar.

There is no evidence that the CEPA prediction of 1090.2 au is not the most accurate currently available for the polarizability of free Na^-. The evidence presented in the Appendix shows that the only prediction of comparable accuracy is that of 1058 au derived from a photodetachment calculation[19] using the dipole-velocity form for the oscillator strength. This result only differs from the CEPA prediction by about 3%, which is not outside the accuracy that might be expected from the latter approach. Comparison of the CHF and CEPA predictions shows that correlation reduces the polarizability, the magnitude of the correlation contribution being some 33% of the total. The negative sign of the correlation polarizability is a reflection of the dominance of angular over radial correlation.[20,35] This would be expected for the Na^- ion because of the presence of the 3p orbitals lying low in energy. By comparison, the exact polarizability of the hydride ion of 206 au[24] is enhanced by some 55% over the CHF value of 93 au,[40] which shows that radial correlation is more important than angular correlation for this system. For Na^-, the fractional contribution of the correlation term is greater than for either the free fluoride or free chloride ions for which this term constitutes respectively some 29% and 17% of the total polarizability. For these halide ions, the CHF polarizabilities[41] of 10.7 au and 31.6 au should be compared with the values of 15.1 au[22] and 38.1 au[23] derived from the most accurate treatments of the correlation presently available.

B. Polarizability Modification from a Point Charge Lattice. All the crystals containing the Na^- ion which have so far been prepared[4,5,7,42–44] also contain as counter cation a complex species in which the cation is coordinated by either a crown ether or a cryptand such as 2,2,2 cryptand (C_{222}). It is the energy release on the complexation of the cation which provides the driving force for the reactions through which such crystals are prepared. Most of these crystals have noncubic structures. However, the structure of the crystal $Na^-{\cdot}Na^+C_{222}$ can be described[7] as consisting of essentially close-packed cryptated cations with sodium anions occupying the octahedral holes. Consequently, to a first approximation, in the point charge representation of all the lattice excepting the one selected Na^- ion, this anion will occupy an octahedral site in a cubic NaCl lattice having closest-cation ion separation (R) equal to the distance between the nucleus of the Na^- ion and that of its closest Na^+ neighbor. Throughout the present study, the distance R was taken to be 13.3 au, equal to the experimentally determined Na^-–Na^+ separation in $Na^-{\cdot}Na^+{}_{222}$.[7] An ab-initio quantum chemistry computation of the polarizability of an Na^- ion embedded in such a point charge lattice will yield the first contribution to the environmental modification of the anion polarizability discussed in the last section. The second contribution to the environmental modification of the Na^- polarizability, namely, that caused by overlap of Na^- orbitals with filled orbitals on neighboring species, originates largely from interaction with the CH_2 groups on the cryptand[43] as discussed in the next subsection.

The first contribution to the environmental modification of the Na^- polarizability in $Na^-{\cdot}Na^+C_{222}$ was modeled by placing the anion at the center of a 5 × 5 × 5 fragment of a point charge NaCl lattice having R = 13.3 au and the outermost charges adjusted so as to reproduce the correct Madelung potential at the

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Table I. Predicted Environmental Modifications of the Sodium Anion Polarizability (au)[a,b]

environment	CHF	MP2D	MP2E	CEPA
free ion	1455.7	1245.0	1235.1	1090.2
point NaCl lattice, R = 13.3[c]	719.1	654.6	639.1	643.2
point NaCl lattice + $2CH_4$[d]	391.1	376.1	381.6	
point NaCl lattice + 12He[e]	475.2	423.3	401.7	

[a] The environment in the second row of results models the point charge lattice, and those in the third and fourth rows model the full environment experienced by a sodium anion in $Na^-{\cdot}Na^+C_{222}$, as discussed in section IIIB,C. [b] For a description of the CHF, MP2D, MP2E, and CEPA methods, see section IIIA. [c] Point charges of unit magnitude were positioned at each point in the 5 × 5 × 5 fragment of NaCl lattice except for none at the central site containing the anion and for the outermost charges, which were adjusted so as to produce the correct Madelung potential at the central site. R is the closest cation–anion separation, measured in au. [d] The same point NaCl lattice as in the second row with the addition of 2 CH_4 molecules with the geometry shown in Figure 2. Results are for the zz component of the Na^- polarizability tensor derived by subtracting the CH_4 polarizabilities and dipole-induced dipole corrections. [e] The same point NaCl lattice as in the second row with the addition of 12 helium atoms positioned as discussed in section IIIC, with the distance R_{HA} = 10.5 au as shown in Figure 2. Results are for the zz component of the Na^- polarizability tensor.

anion site. The CHF, MP2, and CEPA predictions for the polarizability in this point lattice are compared with their free ion counterparts in Table I. The CEPA results predict that this point lattice reduces the Na^- polarizability to 59% of its value in the free state. At first sight this reduction appears to be comparable with those of the F^- and Cl^- ions when they are placed in point charge lattices having spacings equal to the experimental values for their lithium salts, where CHF plus MP2E calculations predict[21] polarizabilities of 9.1 au and 25.4 au, reduced to some 60% and 67%, respectively, of their free ion values of 15.1 au[22] and 38.1 au.[23] However, the interionic spacings of 3.8 and 4.9 au, respectively, in these two lithium salts are very much less than the 13.3 au in $Na^-{\cdot}Na^+C_{222}$. The true sensitivity of the Na^- polarizability to its environment becomes apparent when the reduction of its polarizability to 59% of the free ion value on entering the point NaCl lattice having R = 13.3 au is compared with the result that the CHF polarizability computed for a fluoride ion in the same lattice remains identical to that of the free ion to two decimal places. The 15s10p5d/12s8p5d fluoride ion basis of ref 28 was used for this CADPAC computation. Although the fractional reduction of the Na^- polarizability is less than the 91% reduction from 206 au[24] to 18.8 au[21] when the hydride ion enters the point charge NaCl lattice having spacing equal to the experimental cation–anion distance of 3.84 au in solid LiH, this separation is so much less than that in $Na^-{\cdot}Na^+C_{222}$ that the depth of the Madelung well in the hydride is 3.5 times greater than that in the Na^- salt.

Comparison of the CHF and CEPA predictions for the Na^- polarizability shows that the magnitude of the correlation contribution has been reduced from 33% in the free ion to 12% in the point charge lattice. This reduction of the fractional contribution of the correlation polarizability parallels that already found for the F^- and Cl^- ions, where correlation contributions of 29% and 17% for the free ions are reduced to 20% and 7%[21] when these ions enter a point charge NaCl lattice having R equal to the experimental values for their lithium salts. For Na^-, even the point charge lattice environment causes the behavior of the correlation polarizability to resemble that found for a neutral or cationic species, rather than that of a free anion. Thus for both the inert gases and their isoelectronic cations, comparison of computed CHF polarizabilities[39,41] with their exact counterparts shows that the correlation polarizability is at most 10%, being moreover less than 5% in the vast majority of these cases. The most accurate values currently available for the polarizabilities needed for this comparison are taken from ref 45 for He, Kr, and Xe, from ref 35 for Ne, and from ref 20 for Ar, while those for Li^+, Na^+, and K^+ are from ref 21, those for Rb^+ are from refs 27 and 39, and those for Mg^{2+} and Ca^{2+} are from ref 33. A further consequence of the supression of the Na^- correlation polarizability on entering the lattice is that this contribution becomes sufficiently small as to be accurately predicted by Moller–Plesset perturbation theory taken to just second order. Thus Table I shows not only that the MP2D and MP2E predictions for the Na^- polarizability in the lattice are very similar but also that these MP2 predictions are essentially the same as those of the CEPA calculation. This shows that the MP2 method is fully adequate to study the polarizability of this ion in the condensed phase with the consequence that it is not necessary to perform the considerably more elaborate CEPA computations.

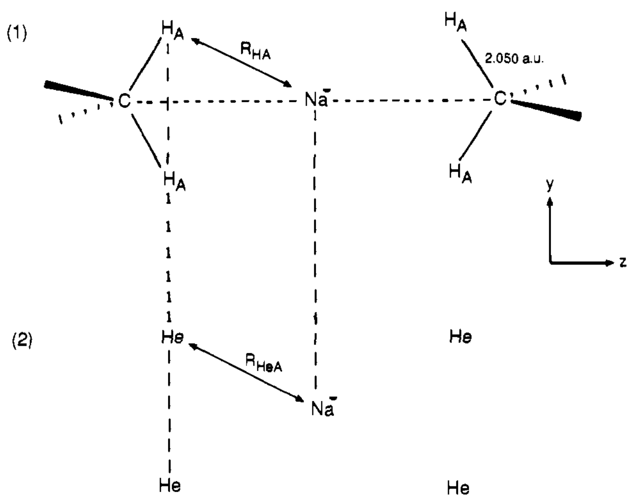

Figure 2. Diagrammatic representation of the $Na^-(CH_4)_2$ cluster model (1) and the $Na^-(He)_4$ cluster model (2) for accounting for the overlap in one plane (yz) experienced by Na^- electrons in the environment in solid crystalline $Na^-{\cdot}Na^+C_{222}$.

C. Full Polarizability Modification. An Na^- ion in a $Na^-{\cdot}Na^+C_{222}$ crystal will have its polarizability modified by the overlap of the anion wave functions with those of filled orbitals on the neighboring Na^+C_{222} cations, in addition to the modification caused by the long range electrostatic effects, which are the same as those generated by a point charge lattice. This overlap effect, which is the second of the two contributions to environmental modifications of ion polarizabilities discussed in section II, will largely originate from overlap of the Na^- orbitals with the electrons in the CH_2 groups of the cryptand since this is the dominant short range interaction experienced by the anion.[43] For five $Na^-{\cdot}M^+$ cryptand crystals, the number of CH_2 hydrogen neighbors nearest to the Na^- varies from 13 to 20, with the average anion–hydrogen internuclear separations lying between 7.43 and 7.92 au.[43] A reasonable model representation of the overlap with the two CH_2 groups lying in one plane, chosen here to be the yz plane, is provided by representing each such group by a methane molecule as shown in the top of Figure 2. Each hydrogen atom of the CH_4 molecule which is a nearest neighbor to the Na^- ion is labeled H_A, with the Na^- H_A internuclear distance (R_{HA}) taken as 7.5 au. This $Na^-(CH_4)_2$ cluster is then embedded in the 5 × 5 × 5 fragment of the point charge NaCl lattice laready described with the Na^- nucleus at the origin and the C–Na–C axis aligned along the z direction of this lattice. This embedded $Na^-(CH_4)_2$ model simulates both the long range point charge electrostatic contribution and, for the zz component of the polarizability, the short range effects arising from overlap with cryptand CH_2 groups.

The total polarizability of the $Na^-(CH_4)_2$ system embedded in the 5 × 5 × 5 point lattice fragment as shown in Figure 2 was computed at both the CHF and MP2 levels using a 6-31G basis[46] for each CH_4 molecule with the Na^- basis unchanged from that employed for both the free ion and that in just the point charge

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lattice. The CHF prediction of 476.6 au for the *zz* component α_{zz}^{TOT} of the polarizability was changed to 458.1 and 464.4 au, respectively, after using the MP2D and MP2E approaches to introduce electron correlation. Each of these results can be decomposed into the purely anionic contribution (α_A) of interest augmented by that of the two CH_4 molecules plus the dipole-induced dipole correction α_{zz}^{DID},

$$\alpha_{zz}^{TOT} = \alpha_A + 2\alpha_{zz}^{M} + \alpha_{zz}^{DID} \qquad (2)$$

with

$$\alpha_{zz}^{DID} = 8\alpha_A\alpha_{zz}^{M}R_{MA}^{-3} \qquad (3)$$

where R_{MA}, the distance between the Na^- and each carbon nucleus, is 8.487 au here for R_{HA} = 7.5 au. The result (eq 3) is derived by considering just the sum of the extra dipoles induced on each CH_4 molecule by the dipole induced on the Na^- ion by the external field, augmented by the extra dipole induced on the anion by the external field induced dipole residing on each CH_4 molecule. The polarizability (α_{zz}^{M}) of a single methane molecule can be taken to be just half of that computed for two such molecules embedded in the 5 × 5 × 5 point lattice in the absence of the anion because the dipole-induced dipole contribution, given to the lowest order by $4(\alpha_{zz}^{M})^2/(2R_{MA})^3$, is negligible. Furthermore, the methane polarizability in the $Na^-(CH_4)_2$ system can be taken to remain unchanged from that when the Na^- ion is absent, because not only is the methane contribution only a very small fraction of α_{zz}^{TOT} but also the Na^- ion will be much more sensitive to its environment than the CH_4 species. The required anion polarizability is then derived by substitution of eq 3 into eq 2 to yield an expression in which α_A is the only unknown polarizability that has not been computed ab-initio. Although the present CHF, MP2D, and MP2E predictions of 12.0, 11.9, and 11.8 au, respectively, for α_{zz}^{M} underestimate the full Hartree–Fock and exact polarizabilities of 15.8 and 16.4 au,[47] either because the 6-31G basis lacks polarization functions or because the polarizability has been reduced by the point charge lattice, this basis is fully adequate for describing the effect of overlap on the Na^- polarizability, for which only a good description of the unperturbed state of the environment is needed. The in-crystal Na^- polarizabilities presented in Table I were derived from eqs 2 and 3 by combining the predictions for α_{zz}^{TOT} with the present results for α_{zz}^{M} that were only computed to evaluate the dipole-induced dipole correction. The CHF computations as well as the MP2D and MP2E results agree in predicting that the overlap reduces the polarizability in the full environment to around 60% of its value in the point charge lattice. The final prediction that the polarizability of the Na^- ion in the $Na^-{\cdot}Na^+C_{222}$ crystal lies between 376.1 and 381.6 au shows that this property is reduced by a factor of 3 compared with that of 1090.2 au for the free anion. This reduction is greater than for the F^- and Cl^- ions in their lithium salts, where the anion polarizability is reduced by a factor of 2.5 and 1.9, respectively, compared with the free anions.[21,28] The fractional reduction of the Na^- polarizability is less than the 10-fold reduction of the hydride ion polarizability when this enters the lithium or sodium salt, although it should be remembered that the internuclear separation in these hydrides is much less than the value of *R* in $Na^-{\cdot}Na^+C_{222}$.

For the in-crystal Na^- polarizability, comparison of the respective MP2D and MP2E predictions of 376.1 and 381.6 au with the CHF result of 391.1 au shows that correlation contributes no more than 4% to α_A, compared with a 12% correlation contribution in the point charge lattice. This reduction in the fractional contribution of the correlation polarizability exactly parallels those for the fluoride, chloride, and hydride ions in their lithium salts, where correlation accounts for 10%,[28] 2.5%,[21] and 4.2%[21] of the anion polarizability, these three fractions being also reduced when compared with the corresponding fractional correlation contributions in the point charge lattice discussed in section IIIB.

The embedded $Na^-(CH_4)_2$ cluster model shown in Figure 2 cannot describe the *xx* and *yy* components of the anion polarizability tensor because there are no species containing electrons located along the *x* or *y* directions. It is not therefore surprising that the values of 709.8 and 724.1 au predicted respectively for the *xx* and *yy* components of the anion polarizability tensor by CHF theory without the dipole-induced dipole corrections differ but little from the CHF prediction of 719.1 au for the polarizability of the anion in just the point charge lattice. The dipole-induced dipole corrections are sufficiently small as not to be relevant to this observation, as shown by comparing the CHF prediction of 452.6 au for the *zz* component of the anion polarizability tensor derived by neglecting these corrections with the more accurate value of 391.1 au predicted after their inclusion. The *zz* component of the anion polarizability derived from the embedded cluster calculation can only be taken to reflect the environmental induced modification of the anion polarizability in the actual $Na^-{\cdot}Na^+C_{222}$ crystal if this *zz* component were to remain essentially unchanged on introducing further CH_4 molecules located along the *x* and *y* directions. Unfortunately the introduction of these extra CH_4 molecules produces a system ($Na^-(CH_4)_6$) of a size that was not considered practical for ab-initio computation. This difficulty was overcome by modeling each methane molecule by a pair of helium atoms located so as to reproduce the effects of the interaction between the anion and the two methane hydrogens labeled H_A. Thus the $Na^-(CH_4)_2$ cluster was modeled as Na^-He_4, as shown in the bottom of Figure 2, while the $Na^-(CH_4)_6$ system was modeled as Na^-He_{12}. Each helium atom was described by a 10s/1s contraction of a 10s basis set,[48] so that to a first approximation the helium polarizability and dipole-induced dipole corrections in the helium–anion clusters are 0. For the embedded Na^-He_4 cluster, the *xx*, *yy*, and *zz* components of the anion polarizability tensor were predicted to be 875.3, 834.7, and 269.9 au, respectively, using CHF theory when the Na–He distance remained unchanged from the 7.5-au value of R_{HA} in the $Na^-(CH_4)_2$ species. The *zz* component of the anion polarizability is much less than the CHF prediction for the embedded $Na^-(CH_4)_2$ cluster, while both the *zz* and *yy* components in Na^-He_4 are significantly greater than those predicted for $Na^-(CH_4)_2$. This shows that a helium atom located at the same distance from the anion as an H_A methane hydrogen has a much stronger interaction leading to a significantly enhanced compression of the anion along the *z* direction. Hence it follows that the Na–He distance must be optimized if the effect of a methane molecule is to be modeled by two He atoms. This was achieved by repeating the CHF computations for the embedded Na^-He_4 cluster, varying the Na–He distance by moving each pair of He atoms the same distance outward from the anion along the *z* axis, keeping unchanged the He–He distance within both pairs. The embedded Na^-He_4 cluster having the Na–He distance equal to 10.5 au was found to be an acceptable model for the embedded $Na^-(CH_4)_2$ species because the CHF predictions of 763.7, 751.5, and 433.3 au, respectively, for the *xx*, *yy*, and *zz* components of the anion polarizability tensor in this embedded Na^-He_4 cluster satisfactorily reproduce those of the embedded $Na^-(CH_4)_2$ species. For the embedded Na^-He_{12} system having the same Na–He distance of 10.5 au, the anion polarizability predicted by each of the CHF, MP2D, and MP2E methods is presented in Table I. The result that the anisotropy of the anion polarizability was less than 3%, taken in conjunction with the similarity between the CHF prediction of Table I and that for the *zz* polarizability component of the embedded Na^-He_4 system, justifies the model in which each CH_4 molecule is replaced by two helium atoms.

For the embedded Na^-He_{12} cluster, the anion polarizability predicted taking account of electron correlation by second-order Moller–Plesset perturbation theory is found (Table I) to be just slightly above 400 au. There is no essential difference between this result and that of slightly below 400 au predicted for the *zz* component of the anion polarizability in the embedded $Na^-(CH_4)_2$ cluster using the same method of treating electron correlation. It can therefore be concluded that the polarizability of the Na^- ion in the crystal cyptand $Na^-{\cdot}Na^+C_{222}$ will be around 400 au,

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reduced by some 240 au from its value in the corresponding point charge lattice.

IV. Diamagnetic Contribution to the Magnetic Susceptibility

The diamagnetic contribution (χ_{dia}) to the magnetic susceptibility of a mononuclear species is related to the mean square distance ($\langle r^2 \rangle$) of all the electrons from the nucleus by[49]

$$\chi_{\mathrm{dia}} = -\langle r^2 \rangle / (6c^2) \tag{4}$$

with all the quantities expressed in atomic units so that c, the velocity of light, equals 137.0373. The mean mth power ($\langle r^m \rangle$) of the distance of all the electrons from the nucleus is defined as the expectation value,

$$\langle r^m \rangle = \langle \psi(\mathrm{r}_1,\mathrm{r}_2,...,\mathrm{r}_N)| \sum_{i=1}^{N} r_i^{\,m} | \psi(\mathrm{r}_1,\mathrm{r}_2,...,\mathrm{r}_N) \rangle \tag{5}$$

where $|\psi(\mathrm{r}_1,\mathrm{r}_2,...,\mathrm{r}_N)\rangle$ is the electronic wave function for the system containing N electrons, with $\mathbf{r}_i$ being the coordinate of electron i relative to the nucleus. In the Hartree–Fock description, used to compute χ_{dia} as well as the diamagnetic contribution to the nuclear shielding discussed in the next section, $\langle r^m \rangle$ can be decomposed into a sum of core ($\langle r^m \rangle_c$) and valence ($\langle r^m \rangle_v$) contributions. The valence contribution is just that of the two 3s electrons. Clearly the environmentally induced modifications of the electron density of the sodium anion must affect all these expectation values (eq 5) even if the ion remains spherically symmetric.

Two sets of values of $\langle r^2 \rangle$ for the sodium anion in different environments were generated describing the electronic structure by the Hartree–Fock theory. Each result in the first set was obtained as a byproduct of the corresponding CHF computation of the polarizability. The second set was generated by computing Hartree–Fock wave functions for the sodium anion by using the Oxford atomic Dirac–Fock program,[50] with the velocity of light used in the program but not in eq 4 increased by a factor of 1000 in order to simulate a nonrelativistic computation.[51,52] The Oxford Dirac–Fock program was the only one available to us for computing the values of $\langle r^{-1} \rangle$ needed to calculate the nuclear shielding. This program, in contrast to CADPAC, does not use a basis set expansion but instead solves numerically for the radial portions of the Hartree–Fock atomic orbitals, the angular portion of each of which is just a standard spherical harmonic. Hence, for the free anion, the CADPAC results should agree exactly with those of the atomic calculation, with any discrepancies arising from inadequacies in the basis used in the CADPAC computation. The very close agreement between the CADPAC predictions of both −0.013 345 au for the 3s orbital eigenvalue and 105.33 au for $\langle r^2 \rangle$ with the corresponding results of −0.013 351 and 105.23 au from the atomic computation confirms the adequacy of the CADPAC basis. Since it has been shown[33] that only the spherically symmetric part of the environmental potential ($F_{\mathrm{env}}(\mathrm{r}_a;R)$) acting on an electron contributes to the total energy of a spherical atom if it is demanded that its atomic orbitals retain their usual central field form, the influence of the environment was introduced into the computations using the Oxford Dirac–Fock program by adding the appropriate term to the Hamiltonian acting on each electron. For a point charge lattice the spherically symmetric part ($F^{(0)}{}_{\mathrm{env}}(r_a;R)$; eq 1; Figure 1) of the environmental potential ($F_{\mathrm{env}}(\mathrm{r}_a;R)$) was readily generated exactly.[29,33] In the point lattice CADPAC computation the anion was located on a site of octahedral symmetry at which the symmetries of s, p, and d orbitals are all different. Consequently, since there were no basis functions of higher angular momentum than 2 in the CADPAC computations, each of the orbitals generated in the point charge lattice computation retained its full atomic symmetry. The CADPAC prediction of both −0.1400 au for the 3s orbital eigenvalue and 86.73 au for $\langle r^2 \rangle$ are in very close agreement with the atomic program results of −0.1401 and 86.89 au, respectively, thereby providing further evidence that the CADPAC basis is trustworthy.

In the computations with the atomic program, the environment of the Na^- ion in $\mathrm{Na}^-{\cdot}\mathrm{Na}^+\mathrm{C}_{222}$ including the overlap effects was modeled by adding to the potential experienced by each electron the potential function provided by the radius variable Madelung–Watson (RVMW) description[30,31,33] of $F^{(0)}{}_{\mathrm{env}}(\mathrm{r}_a;R)$. This model has been shown to provide a reasonable description of the environmentally induced modifications of interionic potentials involving halide ions in ionic crystals.[30,31,33] In the RVMW model, the spherically symmetric portion of $F_{\mathrm{env}}(\mathrm{r}_a;R)$, which is the only one relevant if the atomic orbitals are required to retain their full atomic symmetry, is given by

$$F^{(0)}{}_{\mathrm{env}}(r_a;R) = -k_{\mathrm{env}}/R_{\mathrm{W}} \qquad \text{for } r_a \le R_{\mathrm{W}} \tag{6a}$$

$$F^{(0)}{}_{\mathrm{env}}(r_a;R) = -k_{\mathrm{env}}/r_a \qquad \text{for } r_a \ge R_{\mathrm{W}} \tag{6b}$$

where

$$k_{\mathrm{env}}/R_{\mathrm{W}} = M/R \tag{7}$$

with M being the Madelung constant of the NaCl lattice. The curve labeled 2 in Figure 1 shows how a realistic RVMW potential differs from that, labeled 1, generated by a point charge lattice. For distances r_a sufficiently close to the anion nucleus that the electron density of neighboring species is negligible, the only contribution to $F^{(0)}{}_{\mathrm{env}}(r_a;R)$ is that arising from a point charge NaCl lattice with closest cation–anion separation R. This justifies the constant form (eq 6a) of the potential for small distances less than R_{W}, which is always less than R, the definition (eq 7) of k_{env} ensuring that the RVMW potential exactly reproduces that generated by the point NaCl lattice with spacing R. The potential form (eq 6b) is introduced because, in spatial regions where the electron density of neighboring species is non-negligible, an anion electron will experience a repulsive potential acting to reduce the constant stabilization of the point lattice. A reasonable choice for the distance R_{W}, the maximum distance r_a from the anion nucleus at which the spherical average of the electron density of neighboring species is still negligible, might be provided by subtracting the van der Waals radius (1.2 Å[53]) of a hydrogen atom from the distance between the Na^- nucleus and the closest CH_2 proton in $\mathrm{Na}^-{\cdot}\mathrm{Na}^+\mathrm{C}_{222}$. If the latter distance is taken to be 7.92,[43] R_{w} is found to be 5.65 au. The resulting predictions of −0.1167 au for the 3s orbital eigenvalue and 64.48 au for $\langle r^2 \rangle$ show, when compared to the CADPAC results of −0.1289 and 72.10 au for the embedded $\mathrm{Na}^-\mathrm{He}_{12}$ system, that this choice of R_{W} generates too repulsive an environmental potential. The CADPAC $\langle r^2 \rangle$ value was simply derived by subtracting the contribution of the helium atoms from the Hartree–Fock prediction of the total $\langle r^2 \rangle$ for the entire $\mathrm{Na}^-\mathrm{He}_{12}$ system. The potential produced by taking R_{W} to be the sodium–proton internuclear distance of 7.92 au is insufficiently repulsive, as shown by the resulting predictions of −0.1311 au for the 3s orbital eigenvalue and 74.33 au for $\langle r^2 \rangle$. The parameter R_{W} was then taken to be 7.40 au because this would exactly reproduce the value of $\langle r^2 \rangle$ predicted by the embedded $\mathrm{Na}^-\mathrm{He}_{12}$ cluster computation if $\langle r^2 \rangle$ varied linearly with R_{W}. The resulting predictions of 72.08 au for $\langle r^2 \rangle$ and −0.1287 au for the 3s orbital eigenvalue are both essentially identical to those of the cluster computation, which shows that the RVMW potential with this choice for R_{W} really does satisfactorily model the environmentally induced modifications of the properties of the Na^- ion in the solid state.

The results presented in Table II show the predictions from the atomic Hartree–Fock calculations of how $\langle r^2 \rangle$ and hence the diamagnetic susceptibility are modified by the environment. As would be expected, the two electrons in the outermost (3s) atomic orbital make the dominant contribution to $\langle r^2 \rangle$ for the free anion as well as for the anion both in the point charge lattice and in the full RVMW potential. Furthermore, the core contribution

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Table II. Predicted Environmental Modifications of the Mean Square Radius ($\langle r^2 \rangle$) and Diamagnetic Shielding (χ_{dia}) of the Sodium Anion[a]

	environment		
	free	point lattice[b]	full potential[c]
$\langle r^2 \rangle_c$	6.452	6.453	6.457
$\langle r^2 \rangle_v$	98.77	80.44	65.62
$\langle r^2 \rangle$	105.23	86.89	72.08
$10^6\chi_{dia}$	−933.92	−771.15	−639.71

[a] All predictions are from Hartree–Fock computations. [b] The point charge NaCl lattice having closest cation–anion spacing equal to that of 13.3 au in $Na^-{\cdot}Na^+C_{222}$. [c] The radius variable Madelung–Watson (RVMW) model (eq 6, with $R_W = 7.40$ au) for the full environment in $Na^-{\cdot}Na^+C_{222}$. The parameter R_W is chosen as described in the text to ensure that the $\langle r^2 \rangle$ value of the CADPAC computation is reproduced.

($\langle r^2 \rangle_c$) is virtually independent of the environment, being changed by a mere 0.005 au from its free ion value on introduction of the full RVMW potential. The results in Table II show that $\langle r^2 \rangle_v$ is reduced by some 18% on entering the point charge NaCl lattice having $R = 13.3$ au. The further contraction of the electron density that arises on introduction of the full environment as modeled by the RVMW potential with $R_W = 7.40$ au causes $\langle r^2 \rangle_v$ to be diminished by another 18% compared with the point charge lattice. Although the results in Table II show that $\langle r^2 \rangle$ for the sodium anion is influenced by the environment, this property is much less sensitive to the surroundings than is the polarizability. The latter has been shown to be reduced by about 40% both on passing from the free ion to that in the point charge lattice and when passing from the latter to an environment in which the anion electrons interact with those of neighboring species.

The polarizability of an anion is proportional to the change in its energy on entering a uniform electric field. This change and hence the polarizability involve the wave function in the absence of this field as well as the first-order change in the wave function induced by the uniform electric field. The standard textbook result for the polarizability as a second-order perturbation sum results by expanding the change in the wave function as a linear combination of the excited states of the anion in the absence of the field. The work of Vinti[54] shows that if each of the excitation energies appearing as the denominator in each term in the sum is replaced by an average energy ΔE, then this expression for the mean polarizability becomes

$$\alpha = [2/(3\Delta E)][\langle r^2 \rangle + \langle \psi(\mathrm{r}_1,\mathrm{r}_2,...,\mathrm{r}_N)| \sum_{i \neq j} \mathrm{r}_i{\cdot}\mathrm{r}_j |\psi(\mathrm{r}_1,\mathrm{r}_2,...,\mathrm{r}_N)\rangle] \tag{8}$$

This shows that, within this average energy approximation, the differences between the gaseous- and condensed-phase polarizabilities can be ascribed to two different sources, namely, changes in ΔE and environmental modifications of the ground-state wave function. Since the two 3s electrons are responsible for the overwhelming contribution to the Na^- polarizability, as shown by the result that the polarizability of the sodium cation is a mere 1.0 au,[21] only the contribution of the 3s electrons should be included in the two ground-state expectation values in eq 8 while ΔE should be interpreted as a mean excitation energy for these two electrons. Furthermore, in the Hartree–Fock theory used to compute $\langle r^2 \rangle$, the second expectation value in eq 8 is 0 for an orbital containing two s electrons.[54,55] These considerations show that eq 8 can be written as

$$\alpha = 2\langle r^2 \rangle_v/(3\Delta E) \tag{9}$$

This relation taken in conjunction with the data in Table II shows that when Na^- passes from the free state into the point charge lattice, about one-third of the reduction in the anion polarizability can be ascribed to the decrease in the mean square radius $\langle r^2 \rangle_v$ of the 3s electrons. Similarly, when these electrons experience the RVMW model of the full environmental potential, the resulting further decrease of $\langle r^2 \rangle_v$ is responsible for a roughly similar fraction of the additional reduction in polarizability. Thus changes in the average energy ΔE can be held responsible for about two-thirds of each of the polarizability reductions, which explains why this property is more environment sensitive than the diamagnetic contribution to the susceptibility.

It has been deduced that, within the average energy approximation, it is changes in the mean excitation energy ΔE which are responsible for about two-thirds of the environmentally induced reductions in polarizability. This strongly suggests that, in the exact expression for the polarizability involving the ground-state wave function in the absence of a uniform electric field and the first-order correction induced by this field, it is environmentally induced changes in the first-order wave function which cause about two-thirds of the reduction in polarizability. This means that the environmentally induced compression of the ground-state wave function produces only about one-third of the total reduction (by a factor of about 2.7) in polarizability which arises when the free anion experiences the full condensed-phase environment in $Na^-{\cdot}Na^+C_{222}$. The result that this compression of the ground-state wave function is responsible for only one-third of the polarizability reduction while being the sole cause of the reduction in the magnitude of the diamagnetic susceptibility explains why the latter property is so much less sensitive to the environment than is the polarizability. The results presented in Table II show that the compression of the ground-state wave function produced when a free Na^- ion experiences the present RVMW model for the environment in $Na^-{\cdot}Na^+C_{222}$ causes the total mean square radius $\langle r^2 \rangle$ for all the electrons to be reduced by 31.5%. This causes the magnitude of the diamagnetic susceptibility to be reduced by the same percentage.

V. Environmental Modification of the Sodium Anion Nuclear Shielding

The magnetic shielding of a nucleus consists of two parts,[56] the first of these being the diamagnetic term. This is determined solely by the electronic wave function in the absence of the static external magnetic field that is necessarily present in a magnetic resonance experiment. The second contribution to the shielding, the paramagnetic term, arises because the electronic wave function is modified by the interaction of each electron with the external field. For the nucleus in any atom in an S state the paramagnetic contribution to the shielding vanishes.[57] For the alkali cations in aqueous solution, the ion–solvent interaction prevents the total orbital angular momentum (L) of the ion from being a good quantum number, thereby introducing a nonzero paramagnetic contribution to the shielding of the alkali nucleus. The orbital angular momentum carried by each of the outermost p electrons in an alkali cation causes this paramagnetic contribution to be substantial, with the result that the nucleus of such an ion in aqueous solution is significantly deshielded relative to that in the isolated gaseous cation.[8,13] In contrast, however, there is no experimental evidence for any significant paramagnetic contribution to the shielding of the nucleus of the sodium anion either in solution or in the solid state.[8,13] The smallness of this contribution might arise either because the interaction with the environment is sufficiently weak that the ion is still essentially in an S state or because in the orbital model of the electronic structure each of two outermost electrons has 0 angular momentum. In either case, the vanishing of the paramagnetic term does not require that the anion does not interact significantly with its environment. Thus the environmentally induced reductions of both the Na^- polarizability and diamagnetic susceptibility are almost certainly caused by the spherically symmetric part ($F^{(0)}{}_{env}(r_a;R)$) of the interaction between the environment and each electron. This part of the interaction ($F_{env}(\mathrm{r}_a;R)$) of each electron with the environment causes the overall electron density to contract without either removing its spherical symmetry or introducing any orbital angular momentum into the electronic wave function. Hence such

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Table III. Predicted Environmental Modifications of the Sodium Anion Nuclear Shielding (σ) and Difference ($\Delta\sigma$) from the Shielding in a Free Sodium Atom[a,b]

	environment		
	free	point lattice	full potential
σ_c	623.55	623.54	623.51
σ_v	7.93	8.16	8.67
σ	631.48	631.69	632.17
$\Delta\sigma$	2.58	2.80	3.28

[a] See footnotes to Table II. [b] All results in ppm.

contractions will not introduce any paramagnetic contribution to the Na^- nuclear shielding. Although the contractions responsible for reducing both the polarizability and the diamagnetic susceptibility of Na^- need not affect the paramagnetic contribution to the shielding, the diamagnetic contribution must in principle be modified, thus raising the question discussed in the Introduction.

The diamagnetic contribution (σ) to the nuclear shielding of a spherically symmetric species is given by[56,57]

$$\sigma = \langle r^{-1} \rangle / (3c^2) \qquad (10)$$

If the mean inverse radii $\langle r^{-1} \rangle$ needed to evaluate σ are computed using Hartree–Fock theory, the total shielding can be decomposed into a sum of core (σ_c) and valence (σ_v) terms,

$$\sigma = \sigma_c + \sigma_v \qquad (11)$$

where the valence contribution is that arising from just the two 3s electrons. The quantities $\langle r^{-1} \rangle$ needed to calculate σ were generated in the same runs of the atomic Dirac–Fock program with the increased value of the velocity of light that were performed to derive the $\langle r^2 \rangle$ values discussed in the previous section. Naturally the value of c used in eq 10 was not increased when σ was calculated from these results for $\langle r^{-1} \rangle$.

The total shielding (σ) has not been measured, the experimentally determined quantity being the difference ($\Delta\sigma$) between the shielding in the anion and that (σ_{Na}) in an isolated gas-phase sodium atom.

$$\Delta\sigma = \sigma - \sigma_{Na} \qquad (12)$$

This isolated atom shielding has been predicted from atomic Hartree–Fock theory to be 628.89 ppm,[14] of which the single 3s electron contributes some 5.35 ppm. For an isolated sodium anion, that in a point NaCl lattice with R = 13.3 au as well as that subject to the full RVMW environmental potential having R_W = 7.40 au, Table III presents the predictions of atomic Hartree–Fock theory for both the total shieldings (σ) and the differences ($\Delta\sigma$). The results show that, although each total shielding is dominated by the core contribution σ_c, this is decreased by a mere 0.04 ppm when the free anion is introduced to the full environmental potential as described by the RVMW model. This very slight expansion of the core is a secondary effect caused by the contraction of the 3s electron density. Furthermore, the differences between the core shieldings in the anion and that in the isolated atom contribute at most 0.04 ppm to the values of $\Delta\sigma$. Thus $\Delta\sigma$ is determined almost entirely by the contributions of the 3s electrons to the shieldings. Furthermore, the only anion shielding contribution which is not almost entirely insensitive to the environment is that σ_v arising from the two 3s electrons. Table III predicts that when an isolated anion enters the point charge lattice, the resulting contraction of the valence electron density increases σ_v by only 2.9%, corresponding to an increase in the shielding of a mere 0.23 ppm, which should be compared with the Hartree–Fock prediction[12] of 2.58 ppm for $\Delta\sigma$ for the free anion. Thus the nuclear shielding is much less sensitive to the point charge lattice environment than either the diamagnetic susceptibility or the polarizability; in such an environment, the magnitude of the former is decreased by 17% and the latter reduced by 40% compared with the free ion values. Compared with the ion in the point charge lattice, the further 3s electron density contraction produced on introduction of the full environmental potential as described by the RVMW function with R_W = 7.40 au causes σ_v to be increased by a another 6.2%, or 0.51 ppm. Although this enhancement is twice that generated by the point lattice, it is still less than the modification of either the diamagnetic susceptibility or the polarizability, which are respectively decreased in magnitude by 17% and reduced by 40% on passing from the point charge lattice to the full environmental potential.

The calculations presented in Table III predict that the contribution of the 3s electrons to the nuclear shielding is increased by 0.74 ppm when an isolated sodium anion enters an ionic crystal such as $Na^-{\cdot}Na^+C_{222}$. This increase of some 9% is much less than the environmentally induced modifications of either the diamagnetic susceptibility or the polarizability. The results presented in Table II predict that, on entering the condensed phase, the magnitude of the diamagnetic susceptibility is reduced by 32% from its gas-phase value, while Table I shows the polarizability to be much more sensitive to the environment, its value in the condensed phase being smaller than that of the free anion by a factor of about 2.7. The total shielding modification arising when the free anion enters the condensed phase is the sum of the change in the valence term (σ_v) plus the very small but not quite negligible change in the core contribution (σ_c). The present RVMW model of the environment in $Na^-{\cdot}Na^+C_{222}$ predicts that, on entering the solid, the core contribution to the shielding decreases by 0.04 ppm. This, taken in conjunction with the change in the valence contribution, yields a final prediction that the shielding is greater in the solid than in the free anion by 0.70 ppm. Hence $\Delta\sigma$ for the ion in the solid is predicted to be 3.28 ppm, enhanced by the same amount from the gas-phase Hartree–Fock value of 2.58 ppm. The prediction of such a small enhancement of the shielding for an environment so greatly reducing the polarizability achieves the second objective of this paper, that of reconciling the NMR evidence for the insensitivity of the nuclear shielding in a system having a large polarizability significantly modified by the environment.

It has been shown[12] that electron correlation only contributes 0.30 ppm to the difference ($\Delta\sigma$) between the nuclear shielding in an isolated Na^- ion and that in an isolated sodium atom, thus modifying the Hartree–Fock prediction of 2.58 ppm for $\Delta\sigma$ to 2.88 ppm. This shows that the contributions to $\Delta\sigma$ from electron correlation are sufficiently small as not to modify the overall conclusions drawn from the Hartree–Fock calculations. Examination of the compilations of experimentally measured values of $\Delta\sigma$ presented in either Table 1 of ref 8 or Table II of ref 12 shows that $\Delta\sigma$ is invariably slightly less than the value of 2.88 ppm computed for a free isolated ion. If the environmental enhancement of the anion shielding is taken to be the 0.70 ppm we have predicted for solid $Na^-{\cdot}Na^+C_{222}$, then $\Delta\sigma$ is predicted to be 3.58 ppm if the small correlation contribution is assumed to be unchanged from its value in the free anion. Although such a prediction for $\Delta\sigma$ lies between 1.3 and 2.0 ppm greater than the experimental values, it should not necessarily be concluded that these discrepancies arise from a small paramagnetic contribution to the anion shielding on entering the condensed phase. Although the paramagnetic term might account for some of the small discrepancies, the experimental values of the anion shieldings were not corrected for bulk susceptibilities either of the solutions in the liquid-phase experiments or of the crystals in the solid-state measurements. For the Na^- anion in solution with hexamethylphosphoramide (HMPA) as solvent, addition of the calculated[12] bulk susceptibility correction of 1 ppm to the measured $\Delta\sigma$ value of 1.5 ppm[58] predicts $\Delta\sigma$ to be 2.5 ppm, which is the same to within experimental error as the gas-phase prediction of 2.88 ppm. The environmentally induced enhancement of the diamagnetic shielding of the anion in any solution would be expected to be less than the 0.70 ppm predicted for the ionic crystal $Na^-{\cdot}Na^+C_{222}$. Hence even after adding an estimate of this enhancement, there is no real evidence for any discrepancy with experiment whose explanation requires invoking a small envi-

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ronmentally induced paramagnetic contribution to the anion shielding.

VI. Conclusion

It has been shown how the polarizability of the sodium anion is reduced by a model environment closely approximating that in the salt $Na^-{\cdot}Na^+C_{222}$. This was considered as typifying a range of solids containing Na^- in which the charge is balanced by that of an alkali cation complexed by either a cryptand or a crown ether. The polarizability was found to be reduced by 40%, from 1090 to 643 au, on entering a point charge NaCl lattice having a closest cation–anion spacing of 13.3 au, such a lattice being the point charge representation of the environment in the cryptand $Na^-{\cdot}Na^+C_{222}$. Electron correlation reduces the polarizability of the free anion by 365 au compared with the prediction of coupled Hartree–Fock theory. The correlation contribution is largely suppressed on entering the lattice, where this term constitutes only a 76-au reduction. The great sensitivity of this anion polarizability to its environment is shown by the result that in the same point charge lattice with $R = 13.3$ au the polarizability of the fluoride ion is unchanged to two decimal places. The effect of overlap with the occupied orbitals on neighboring species was shown to reduce the polarizability of the anion in $Na^-{\cdot}Na^+C_{222}$ by a further 40% compared with its value in the point charge lattice. Thus the combined effect of point charge electrostatics and overlap compression is to reduce the polarizability of the free anion by a factor of about 2.7 to a value in the region of 400 au, which can be considered to be representative of that for the sodium anion in the solid state. However, it should be recognized that experience with other anions[21,26–28] shows that this polarizability should be expected to be affected by changes in the closest cation–anion separation.

The environmental compressions responsible for the reduction of the Na^- polarizability must, in principle, influence other properties that have nonzero values for the free anion for which the electron density is spherically symmetric. However, it has been shown that both the diamagnetic susceptibility and nuclear shielding are much less environment sensitive than is the polarizability. The diamagnetic susceptibility has been shown to be reduced by 17% in magnitude when an isolated Na^- ion enters the point charge lattice and to be reduced in magnitude by a further 17% on changing this environment to any of the models used to describe that in the $Na^-{\cdot}Na^+C_{222}$ crystal. The use of the average energy approximation to interpret the environmentally induced changes in polarizability shows that these can be decomposed into a change in the valence contribution to the mean square radius ($\langle r^2\rangle$) of all the electrons in the ground state augmented by the modification of the average energy. The result that changes in the latter are responsible for about two-thirds of the environmental reductions of the polarizability with only one-third of these decreases originating from variations in $\langle r^2\rangle$ explains why the diamagnetic susceptibility is so much less environment sensitive than the polarizability. Thus when an isolated Na^- ion is subjected to any of the models used to describe the environment in the $Na^-{\cdot}Na^+C_{222}$ crystal, the diamagnetic susceptibility is decreased in magnitude by 32% compared with the reduction in polarizability by a factor of 2.7.

The nuclear shielding has been shown to be even less sensitive to the environment than is the diamagnetic susceptibility. Although the results in Table III show that the total nuclear shielding changes by only 0.11% when an Na^- ion experiences our model for the environment in a $Na^-{\cdot}Na^+C_{222}$ crystal, this figure is not directly comparable with the 32% change in the diamagnetic susceptibility because the total shielding is dominated by the contribution of the core electrons, which is essentially independent of the environment. The more significant result is that, on making this change of environment, the valence contribution to the shielding is only increased by 9%. Essentially it is only the valence contribution which is responsible for any environmentally induced changes in the difference $\Delta\sigma$ between the shielding in the anion and that in an isolated gas-phase sodium atom. The contribution of the 3s electrons to the nuclear shielding is clearly less environment sensitive than that to the diamagnetic susceptibility because the largest contributions to the former involving the inverse mean radius ($\langle r^{-1}\rangle_v$) will come from the inner spatial regions, in contrast to the latter involving $\langle r^2\rangle_v$ where the more environment sensitive out spatial regions will generate the largest contributions.

The elucidation and explanation of the progressive reduction in the sensitivity to the environment along the series of properties from polarizability through diamagnetic portion of the susceptibility to nuclear shielding answers the fundamental question raised in the Introduction. This question was how the nuclear shielding could be so insensitive to the environment in a species interacting sufficiently strongly with its surroundings as to experience a great reduction in polarizability. The polarizability of an Na^- ion in any of the solutions in cryptands or crown ethers would be expected to be greater that the 400 au predicted for that in the crystalline $Na^-{\cdot}Na^+C_{222}$. Recently[25] a reliable set of values for the polarizabilities of anions in aqueous solution was deduced by combining experimental results and selected ab-initio quantum chemistry computations with previous knowledge[21,27,32] of the polarizabilities of alkali and alkaline earth cations. The results[25] showed that the polarizability of each anion in aqueous solution is much closer to the values found in ionic salts than to that of the isolated gaseous anion. This suggests that the polarizability of Na^- solution would be at most 700 au, being more probably in the range from 500 to 600 au. Although the polarizability of Na^- in the condensed phase is greatly reduced from that of the free ion, even this reduced value is still extremely large, being over twice that of either the Li or Na atoms while being at least 8 times greater than that of any halide or other ion for which a trustworthy value for the polarizability in solution is available.[25] It lies beyond the scope of this paper to elucidate the mechanisms through which the anion having a polarizability of at least 400 au almost undoubtedly interacts with its environment although in such a manner that the shielding and spin–lattice relaxation behaviors of the nuclear spin are much less affected by the surroundings than is the nuclear spin in any other ion commonly occurring in solution.[16,17]

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Appendix: Computational Methods

The basis set for the sodium anion used in the ab-initio quantum chemistry computations performed using the CADPAC program was constructed as follows. First, the contracted 12s9p/6s5p sodium atom basis of McLean and Chandler[59] was extended using a method developed by Reinsch and Meyer[20] to produce a 14s11p/8s7p set, which when used in a coupled Hartree–Fock (CHF) calculation yielded a polarizability of 750.2 au for a free sodium anion. Further s and p type functions with exponents in geometrical progression were then added to the basis until the self-consistent field energy and CHF polarizability had reached limiting values. A CHF polarizability of 1453.1 au was predicted from the resulting 16s13p/10s9p set. The quality of this basis was checked by enlarging the 19s11p set of Partridge,[60] which is known to be near the Hartree–Fock limit for the anion in the absence of terms describing the interaction with a uniform electric field. Unsurprisingly this basis, whose p functions are somewhat contracted in order to describe the 2p electrons, when used unaugmented yielded an Na^- polarizability of only 18.7 au. The lack of the diffuse p type functions needed to describe the distortion of the $3s^2$ pair that arises on introduction of the terms describing the interaction with a uniform electric field was rectified by adding two s type and six p type functions, all with exponents in geometrical progression. The close agreement between the CHF polarizability of 1449.8 au predicted using the resulting 21s17p set with the value of 1453.1 au from our 14s11p/8s7p set confirms that our basis is essentially saturated with respect to s and p symmetry functions. This basis was then enlarged by adding four d type functions with exponents derived using the method of Reinsch and Meyer[20] plus a further diffuse d type function to produce

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a final 16s13p5d/10s9p5d set yielding a CHF polarizability of 1455.7 au. Since the Na$^-$ polarizability is dominated by the contribution of the two 3s electrons which acquire a small admixture of p symmetry on introduction of the terms describing interaction with a uniform electric field, it is not surprising that the addition of d type functions hardly affects the polarizability predicted at the CHF level. However, even in the absence of the terms describing the uniform electric field, a correlated wavefunction for Na$^-$ will have mixed into the 3s^2 ground state a significant admixture of the 3p^2 configuration whose distortion by a uniform electric field will contain two electron states built from orbitals of d symmetry. This argument for the necessity of including d functions in the basis is corroborated by the result[61] that for Li$^-$ the polarizability including the important correlation contribution cannot properly be described by a basis lacking such functions.

Our best prediction for the polarizability of an isolated Na$^-$ ion is 1090.2 au, derived using the 16s13p5d/10s9p5d basis and the coupled electron pair approach,[35,38] which previous evidence has shown to be capable of predicting the polarizabilities of small atoms and molecules to within 2%.[20,35] There are only two other calculations whose accuracy might be comparable with the CEPA result, both of these being photodetachment computations[19] in which electron correlation was properly considered. These two computations differed only in whether the dipole-length or dipole-velocity forms were used for the oscillator strength, use of the former predicting an Na$^-$ polarizability of 989 au, and use of the latter, a polarizability of 1058 au. For the case of the Li$^-$ ion, where photodetatchment computations using the dipole-length and dipole-velocity forms predict[19] polarizabilities of 832 and 798 au, respectively, the reliability of the predictions can be assessed by comparing with a more trustworthy result. The best value for the Li$^-$ polarizability currently available is 798 ± 5 au predicted[61] from a computation using full configuration interaction for the two valence electrons and an extensive basis including functions of d symmetry. This result[61] is more accurate than either that of 650 au[62] from a full configuration interaction computation using a less large basis or that of 570 au derived from a variety of coupled-cluster or polarization propagator methods.[63] The extremely close agreement between the prediction of the photodetachment calculation using the dipole-velocity form of the oscillator strength with the full configuration interaction computation shows that the results derived[19] using the dipole-velocity form for the oscillator strength are to be preferred over those predicted with the dipole-length form. Hence the 989-au prediction for the Na$^-$ polarizability should be discounted compared with that of 1058 au predicted using the dipole-velocity operator. The close agreement between this result and our completely independent CEPA prediction of 1090 au provides strong evidence that both the CEPA and ipole-velocity photodetatchment results are trustworthy.

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Heteronuclear NMR Studies of Cobalt Corrinoids. 13. Amide ^{1}H and ^{15}N NMR Studies of Diastereomerism and the Base-On/Base-Off Reaction in 5′-Deoxyadenosylcobalt Corrinoids[1,2]

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Abstract: Inverse detected ^{1}H, ^{15}N HMQC spectroscopy in DMSO-d_6 has been used to observe the ^{1}H and ^{15}N NMR resonances and establish the H–N connectivities of the peripheral amides of a series of five 5′-deoxyadenosylcobalt corrinoids including the β cobalamin (i.e., coenzyme B_{12}) and its α diastereomer (in which the 5′-deoxyadenosyl ligand is in the "lower" axial ligand position), the diastereomeric α- and β-5′-deoxyadenosylcobinamides (in which the axial 5,6-dimethylbenzimidazole nucleotide has been removed by phosphodiester hydrolysis), and the base-off analogue of the coenzyme, in which the coordinating nitrogen of the axial nucleotide is methylated. The ^{15}N resonances were assigned to the various side-chain amides by observation of through-space connectivities of the amide protons with other protons on the complexes via NOESY spectra in DMSO-d_6. The latter could be completely assigned by analogy to the NOESY spectra of these complexes in D_2O since the ^{1}H spectra of the 5′-deoxyadenosylcobalt corrinoids in D_2O have been previously assigned. The ^{15}N resonances of the unsubstituted amides are found to occur in the order *d*, *b*, *e*, *g*, *c*, *a*, regardless of the nature of the axial ligands. Conversion of the β diastereomer of the cobinamide to the α diestereomer causes a 2.7-ppm upfield shift of the *c* amide resonance suggesting that this amide interacts with the 5′-deoxyadenosyl ligand in the β diastereomer. In the base-on β diastereomer of the cobalamin (i.e., coenzyme B_{12}), the syn and anti protons of the *d* amide are chemical shift equivalent. Upon conversion to the base-off species, the resonance of one of these protons shifts downfield by 0.7 ppm and the ^{15}N resonance shifts downfield by 1.7 ppm. Amide proton chemical shift thermal gradients support the possibility of an intramolecular hydrogen bond involving the *d* amide in the base-on species. Based on models, this hydrogen bond is postulated to involve the noncoordinating nitrogen of the axial 5,6-dimethylbenzimidazole nucleotide as the acceptor.

Introduction

While the α diastereomers of organocobalt corrinoids, in which the organic ligand occupies the "lower" axial ligand position (Figure 1), were once thought to be rare,[4-8] recent work[9] has shown that, in general, reductive alkylation of cobinamide,[10] and of cobalamin under appropriate conditions, leads to mixtures of

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(2) IUPAC–IUB[3] nomenclature is used throughout. Abbreviations: β-AdoCbl, β-5′-deoxyadenosylcobalamin; β-AdoCbi$^+$, β-5′-deoxyadenosylcobinamide: α-AdoCbl, α-5′-deoxyadenosylcobalamin; α-AdoCbi$^+$, α-5′-deoxyadenosylcobinamide; β-AdoMe$_3$BzmBca$^+$, Coα-(α-3,5,6-trimethylbenzimidazolyl)-Coβ-5′-deoxyadenosylcobamide; H_2OCbl$^+$, aquocobalamin; $(CN)_2$Cbl$^-$, dicyanocobalamin.

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