

Is 9-acridinamine anion a dispersion-bound anion?

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(Received 30 July 2001; accepted 28 September 2001)

The possibility of electron binding to 9-acridinamine (9-AA) was studied at the second order Møller–Plesset perturbation theory level with the aug-cc-pVDZ basis set augmented with a diffuse $6s6p4d$ set that has proven appropriate in earlier studies of weakly bound anions. It was found that both the amino and imino tautomers of 9-AA bind an excess electron to form stable anions. The vertical electron attachment energies corresponding to the amino and imino form were calculated to be 20 and 41 cm^{-1} , respectively. It was found that while the imino 9-AA tautomer forms a typical dipole-bound anion, the electron binding energy for the amino tautomer calculated at the electrostatic Koopmans' theorem level appears to be cancelled when the correlation correction to the dipole moment of the neutral is taken into account at the MP2 level. Therefore, the stability of the latter anion may be caused only by additional electron correlation effects, which are dominated by dispersion interactions. For this reason, we suggest that this anion may be termed a dispersion-bound anion. © 2001 American Institute of Physics. [DOI: 10.1063/1.1419059]

I. INTRODUCTION

A. 9-acridinamine tautomers

9-acridinamine (9-AA) is a member of the class of compounds known as heterocycles (see Fig. 1).^{1–3} Its relatively high quantum yield for fluorescence causes 9-AA to be used as a fluorescent probe in biologically important systems.^{4–11} Moreover, 9-AA and its derivatives possess a quite broad spectrum of biological activity including bacteriostatic, tranquilizing, analeptic, and antihistaminic behavior.¹² We also note the photodynamic properties (i.e., bacteriostatic and virucidal activity appearing in the presence of the light and oxygen) of certain 9-AA derivatives. It has been demonstrated that this type of behavior is connected to the capability of a compound to intercalate with DNA and simultaneously sensitize formation of singlet oxygen.^{13–15} The most spectacular property, however, is undoubtedly the anticancer activity of 9-AA derivatives,^{16–18} which is probably related to the intercalating ability of 9-AA itself.^{19–25}

Because the biological features of a compound are strongly connected to its structural characteristics, its propensity to exist in several tautomeric forms may account for the presence or lack of biological activity. It has been shown, for instance, that nitracrine (a 9-AA derivative) exhibiting anticancer activity²⁶ crystallizes in its imino form,^{27,28} whereas its 2-nitro isomer, lacking antitumor properties, exists, in the solid phase, as a planar amino tautomer.^{29,30} Thus,

the long lasting interest in the tautomerism of 9-AA is quite understandable. Depending on the experimental technique employed, investigations that tried to determine which tautomer of 9-AA appears in experimental conditions can be interpreted as suggesting either the imino^{31–34} or amino^{35–40} form. On the other hand, the outcome of theoretical calculations carried out at the semiempirical^{41,42} as well as Hartree–Fock (HF) and density functional theory (DFT) levels suggests the possibility of coexistence of the amino and imino tautomers both in the gas phase (at least at elevated temperatures) and in polar solvents solutions.⁴³

As indicated by earlier DFT calculations,⁴³ both tautomeric forms of 9-AA possess dipole moments of similar magnitude [i.e., 3.4 and 3.8 Debye for the amino (**A**) and imino (**I**) tautomer, respectively]. Interestingly, proton transfer in the amino–imino tautomerization produces an inversion in the direction of the dipole moment.⁴¹ Thus, despite the similar magnitudes of these dipoles, the tautomers have very different electrostatic potentials, which may be important for molecular recognition at the cellular level.

The values of the dipole moments of the **A** and **I** tautomers are larger than the value of 2.5 Debye^{44,45} that seems to be necessary to form experimentally detectable dipole-bound anions. However, to the best of our knowledge, the propensity of 9-AA to support dipole-bound or other weakly bound anionic states has not been discussed so far. Moreover, due to the larger value of its dipole moment, the imino tautomer should be more strongly stabilized by electron binding, thus reducing its instability⁴³ relative to the amino form.

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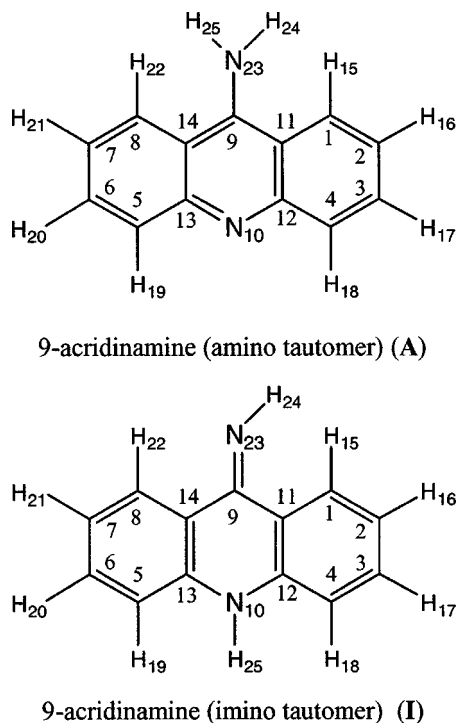


FIG. 1. Chemical structures of the amino (top) and imino (bottom) tautomers of 9-acridinamine.

B. Dipole-bound anions

The binding of electrons to polar molecules has been addressed in many theoretical^{44–62} studies. It has been shown that, within the Born–Oppenheimer (BO) approximation, a dipole moment greater than 1.625 Debye possesses an infinite number of bound anionic states,⁴⁸ although the more practical critical value to experimentally observe a dipole-bound anion bound by at least 1 cm^{-1} was found to be somewhat larger, ca. 2.5 Debye.^{44,45} In fact, it seems that this “practical” value depends strongly on the size and chemical structure of a molecule.

Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole.⁴⁹ This finding was confirmed by many more recent studies. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies much larger than the molecular rotational constants.⁵⁰

The simplest theoretical approach to estimate the electron binding energy (D) is based on Koopmans’ theorem (KT).⁶³ The KT binding energy (D^{KT}) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent-field (SCF) calculation on the neutral molecule. The orbital relaxation effects, which are neglected in the KT approximation, have been found to be quite small for a variety of dipole-bound anionic states.⁵¹ In contrast, the role of electron correlation has proven to be very significant. In fact, in many cases, the electron binding energy of a dipole-bound anion has been dominated by the contribution from electron correlation. In particular, the dispersion interaction of the excess electron with the electrons

of the neutral parent molecule has proven to be crucial for the stability of many dipole-bound anions,^{51,52,55,61} even though the binding at the electrostatic-exchange KT level was present. Moreover, correlation corrections to the dipole moment, which in the case at hand cause the dipole to decrease, are usually essential to consider.

C. The possible existence of “dispersion-bound” anionic states

Treating the dispersion interaction has been shown to be extremely important for calculating electron binding energies of dipole-bound anions within “experimental accuracy,”^{52,53} It is believed that the presence of the charge-dipole potential is necessary for excess electron binding in such species. However, one can ask if the dispersion interaction itself could be fully responsible for rendering an anion stable, for example, in cases where the correlated dipole moment is too small to bind the electron to any appreciable extent. That is, let us assume that (i) the molecule has no empty or half-filled molecular orbitals so the existence of an electronically stable valence anion is excluded, and (ii) the electrostatic and exchange interactions of the extra electron with the correlated charge density of the neutral molecule are not sufficiently attractive to form a stable dipole-bound (or quadrupole, octopole, etc.) anion. If an anionic state happens to be electronically stable under such circumstances, and if it can be proven that its stability is mainly caused by the dispersion interactions mentioned above, then we could be speaking about a new kind of anionic state—a dispersion-bound anion. While other kinds of weakly bound anions have already been discussed in the literature (e.g., dipole-, quadrupole-,^{64,65} and octopole-bound⁶⁶ states, as well as the anions bound due to polarization forces⁶⁷), to the best of our knowledge, the existence of dispersion-bound anionic states has not been confirmed in the literature thus far.

In this work, we provide results of *ab initio* calculations on the weakly bound anions formed by the amino (A) and imino (I) tautomers of 9-AA. We describe the stability of the dipole-bound I^- anionic state, and we discuss the nature of the A^- anion which we propose may be a dispersion-bound anion.

II. METHODS

Since the ground-state potential energy surface of the neutral 9-AA has been recently studied,⁴³ we used the previously optimized [at the HF/6-31G(*d,p*) level] geometries of the amino and imino tautomers. Therefore, in this work we discuss neither the geometrical parameters nor vibrational frequencies of these two neutral species. However, we recall that both A and I possess C_s symmetry, but only the latter is planar. For the A tautomer, the symmetry plane is perpendicular to the conjugated aromatic rings and contains C_9 and both the exocyclic and endocyclic N atoms (see Fig. 1).

The geometry relaxation upon excess electron attachment has proven to be negligible for all dipole-bound anions formed by rigid molecules,^{46,47,51,60} yet significant for van der Waals complexes and systems containing hydrogen bonds.^{51,53–55} Hence, we expected the geometrical param-

eters of the 9-AA tautomers to change only slightly upon forming anionic states. Indeed, we checked that the SCF geometry optimization of the anion supported by the amino tautomer led to negligible changes in geometrical parameters (less than 0.0002 Å for the bond lengths and less than 0.005 deg for valence and dihedral angles). Therefore, we performed our calculations of the electron binding energies at the equilibrium geometries of the corresponding neutrals so the electron binding energies presented here are vertical electron attachment energies (VAE). Because the methods we used are based on an unrestricted Hartree–Fock starting point, it is important to make sure that little if any artificial spin contamination enters into the final wave functions. We computed the expectation value $\langle S^2 \rangle$ for the species studied in this work and found values of 0.7500 in all anion cases. Hence, we are certain that spin contamination is not large enough to significantly affect our findings.

The electron binding energies (D) were calculated using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). Since the systems studied contain 15 heavy atoms and 10 hydrogen atoms (which led to almost 500 contracted basis functions in the aug-cc-pVDZ basis set), we had to limit the level of our calculations to the second-order Møller–Plesset perturbation theory⁶⁸ (MP2) level. The values of D were analyzed within the perturbation framework described elsewhere.⁵⁴

We should emphasize that our willingness to use SCF and MP2 level treatments of the electron-molecule interaction are based on the large size of the species and the requisite basis set. It has been demonstrated in numerous studies^{69–74} that the MP n series is often not convergent and plagued by intruder states. However, it is not our intent to use the MP n series to obtain converged values for the electron binding energies. Rather, we draw on our past experience in studying weakly bound anions using KT, MP2, and higher level [e.g., CCSD and CCSD(T)] treatments to suggest how electron correlation is likely to affect the present case.

The electrostatic–exchange interactions of the excess electron with the polar neutral molecule are taken into account when D is estimated at the KT level. The polarization of the neutral host (N) by the excess electron and the effect of back polarization are taken into account when the SCF calculation is performed for the anion (An), and the accompanying induction effects on D are given by

$$\Delta D_{\text{ind}}^{\text{SCF}} = D^{\text{SCF}} - D^{\text{KT}}, \quad (1)$$

where

$$D^{\text{SCF}} = E_N^{\text{SCF}} - E_{An}^{\text{SCF}} \quad (2)$$

and E_N^{SCF} and E_{An}^{SCF} stand for the SCF energies of the neutral and the anion, respectively.

The dispersion interaction between the loosely bound electron and N is extracted from the MP2 contribution to D . The dispersion term is a second-order correction with respect to the fluctuation–interaction operator and it is approximated here by $\Delta D_{\text{disp}}^{\text{MP2}}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon_{\text{disp}}^{(02)} \approx \sum_{a \in N} \sum_{r < s} \frac{|\langle \phi_a \phi_{\text{lbe}} | | \phi_r \phi_s \rangle|^2}{e_a + e_{\text{lbe}} - e_r - e_s} = -\Delta D_{\text{disp}}^{\text{MP2}}, \quad (3)$$

where ϕ_a and ϕ_{lbe} are spin orbitals occupied in the unrestricted Hartree–Fock (UHF) anion wave function, ϕ_r and ϕ_s are unoccupied orbitals, and the e 's are the corresponding orbital energies. The subscript lbe denotes the loosely bound electron's spin orbital.

The total MP2 contribution to D defined as

$$\Delta D^{\text{MP2}} = D^{\text{MP2}} - D^{\text{SCF}} \quad (4)$$

is naturally split into dispersion and nondispersion terms

$$\Delta D^{\text{MP2}} = \Delta D_{\text{disp}}^{\text{MP2}} + \Delta D_{\text{no-disp}}^{\text{MP2}} \quad (5)$$

with $\Delta D_{\text{no-disp}}^{\text{MP2}}$ dominated by the correlation correction to dipole moment. Since we performed our calculation up to the MP2 level of theory, the D^{MP2} binding energies are our best estimates of the vertical electron attachment energies for the 9-AA tautomers.

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions having very low exponents.⁷⁵ In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) accurately describe the static charge distribution of the neutral and (ii) allow for polarization and dispersion stabilization of the anion upon electron attachment. The calculations of the electron binding energies presented here were performed with the aug-cc-pVDZ basis set⁷⁶ supplemented with a $6s6p4d$ set of diffuse functions centered on the exocyclic (N_{23}) and endocyclic (N_{10}) nitrogen atom, for the amino and imino tautomer, respectively (see Fig. 1 for atom numbering). This set of extra diffuse functions has proven to be very capable of treating a variety of weakly bound anions. The aug-cc-pVDZ basis set was chosen since we earlier showed its usefulness in describing weakly bound anions compared to other commonly used one-electron basis sets.⁷⁵ The extra diffuse functions do not share exponent values and we used even-tempered⁷⁷ six-term s , six-term p , and four-term d basis sets. The geometric progression ratio was equal to 5.0 since we examined earlier that such a factor is appropriate for neutral molecular hosts with dipole moments in the 3.0–4.5 Debye range.⁷⁸ For each symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in aug-cc-pVDZ basis set designed for nitrogen. As a consequence, we achieved the lowest exponents of 3.91936×10^{-6} , 3.59104×10^{-6} , and 3.68000×10^{-4} a.u., for the s , p , and d symmetries, respectively. We verified that the SCF electron binding energies of the **A** and **I** anions increase by less than 0.5 cm^{-1} if one more set of s and p diffuse functions is added.

In computing correlation energies, all orbitals except the $1s$ orbitals of carbon and nitrogen were included. All calculations were performed with the GAUSSIAN 98 program⁷⁹ on an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.⁸⁰

In order to avoid erroneous results from the default direct-SCF calculations with the basis sets with the large s , p ,

TABLE I. Dipole moments (in Debye) and N_{23} (exocyclic) Mulliken partial charges (in a.u.) of the neutral amino and imino forms of 9-acridinamine.

	Amino 9-AA	Imino 9-AA
μ^{SCF}	3.426	3.939
μ^{MP2}	3.161	3.787
$q^{\text{Mull}}(N_{23})$	+0.266	-0.522

and d sets of diffuse functions, the keyword SCF=NoVarAcc was used and the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u. We also verified that basis set near redundancies are not present by examining the lowest eigenvalue of the overlap matrix which remains larger than 5.0×10^{-5} .

III. RESULTS AND DISCUSSION

A. Neutral A and I tautomers

Even though the mechanism of the tautomerization reaction which leads from the amino to imino 9-AA and *vice versa* remains unknown, it is believed that both the **A** and **I** forms are present in the gas phase, as well as in solutions (see discussion given in Ref. 43). One of the interesting consequences of this prototropic tautomerization is a dramatic change in the electrostatic potential around the neutral molecule. Namely, as indicated by the analysis of the partial atomic charges, the positive and negative “sides” of the molecule switch places and the electrophilic region of the exocyclic N_{23} atom in the amino form becomes nucleophilic when the imino tautomer is formed. Indeed, the partial Mulliken charge of +0.266 a.u. on N_{23} in **A**, becomes strongly negative (-0.522 a.u.) in **I** (see Table I). A more detailed description is given in the electrostatic potential maps depicted in Fig. 2. It seems clear that the negative “pocket” localized near the endocyclic N_{10} atom in the amino tautomer moves to the other side of the molecule (into the vicinity of the exocyclic N_{23} atom) upon H_{25} proton transfer. Such a reverse of the electrostatic potential topology may have important consequences for interactions of 9-AA with other biologically important systems since it may affect the 9-AA recognition at the cellular level.

It was recognized earlier that neither the amino nor imino tautomer of 9-acridinamine forms an electronically stable valence anionic state.⁴³ However, both the **A** and **I** isomers are polar and their dipole moments (μ) are larger than 2.5 Debye, which made us consider the possibility of extra electron binding due to its interaction with the charge-

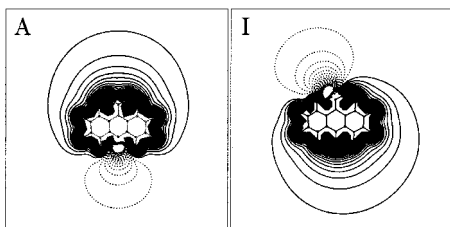


FIG. 2. Electrostatic potential maps around the neutral amino (left) and imino (right) 9-AA tautomers (depicted with the 0.003 a.u. contour spacing). The negative potential curves are indicated by the dotted lines.

TABLE II. Components of the vertical electron binding energies D (in cm^{-1}) of the anions based on the amino and imino tautomers of 9-acridinamine calculated with the aug-cc-pVDZ+6s6p4d basis set at the equilibrium geometry of the neutral.

	Amino 9-AA	Imino 9-AA
D^{KT}	5	13
$\Delta D_{\text{ind}}^{\text{SCF}}$	1	2
$\Delta D_{\text{disp}}^{\text{MP2}}$	20	31
$\Delta D_{\text{no-disp}}^{\text{MP2}}$	-6	-5
Sum (VAE)	20	41

dipole potentials. To achieve more reliable values of the corresponding dipole moments than those reported earlier on the basis of the HF/6-31G(d,p) calculations,⁴³ we estimated μ values with the aug-cc-pVDZ+6s6p4d basis set using both SCF and correlated MP2 electron densities (see Table I). Our results indicate that the imino tautomer is more polar and its SCF dipole moment is larger by 0.513 Debye than the corresponding value obtained for **A**. The correlated MP2 calculations showed that these dipole moments are overestimated at the SCF level, but the value of μ^{MP2} remains larger for **I** than for **A** (by 0.626 Debye). This suggests that the electrostatic contribution to the excess electron binding is reduced when electron correlation effects are taken into account.

B. Dipole-bound anion supported by the imino tautomer of 9-AA

We begin our discussion of the electron binding energies from the Koopmans' level which includes only electrostatic-exchange interactions of the excess electron with the uncorrelated SCF charge distribution of the neutral molecule (primarily characterized by the dipole moment, but interactions with higher permanent multipoles and penetration effects are also included). For the imino 9-AA tautomer, D^{KT} shown in Table II is very small (13 cm^{-1}) which is consistent with the magnitude of its dipole moment. The SCF binding energy includes orbital relaxation and thus takes into account static polarization of the neutral molecule by the extra electron and the secondary effect of back polarization. We found these contributions (which can be interpreted as orbital relaxation corrections to D^{KT} , denoted $\Delta D_{\text{ind}}^{\text{SCF}}$) to be extremely small for **I**⁻ and responsible for 5% of the total value of D . Although usually significant for valence-bound anions, orbital relaxation effects are often negligible and rarely responsible for more than a few percent of the total value of D for the majority of dipole-bound anions studied so far.⁵¹

The contribution denoted $\Delta D_{\text{disp}}^{\text{MP2}}$ in Table II results from dynamical correlation between the loosely bound electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations, and is the largest contribution to the total D for the anion supported by the imino tautomer. This importance of the $\Delta D_{\text{disp}}^{\text{MP2}}$ term is consistent with our earlier results for other dipole-bound anions, however, for **I**⁻ it is more than 2 times larger than the electrostatic D^{KT} stabilization, which is rather untypical.

In addition to the dispersion interaction, other electron correlation factors may also affect the charge distribution

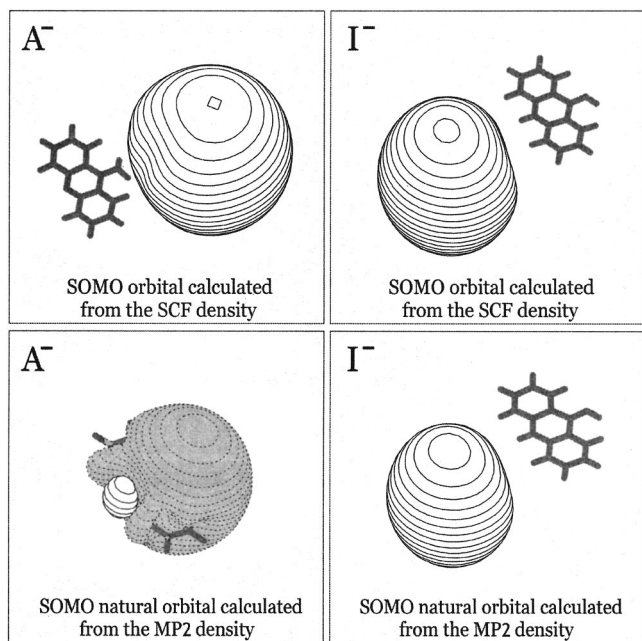


FIG. 3. Singly occupied molecular orbital in anions of the amino (left) and imino (right) tautomers of 9-acridinamine calculated from the SCF (top) and MP2 (bottom) electron densities (contour spacing $0.0017 \text{ bohr}^{-3/2}$).

(and hence the dipole moment) of the neutral molecule and thus its electrostatic interaction with the extra electron. This effect appears at the MP2 level and is denoted by $\Delta D_{\text{no-disp}}^{\text{MP2}}$. In the case of the I^- , MP2 electron correlation effects reduce the dipole moment of the neutral system as discussed earlier (by 0.15 Debye) in comparison with the SCF value, (see Table I). Therefore the value of $\Delta D_{\text{no-disp}}^{\text{MP2}}$ is destabilizing, yet the total MP2 contribution to D is substantial and stabilizing due to the dominant role of the dispersion component. In particular, the total MP2 contribution is responsible for more than 75% of D for the anion based on the imino tautomer. Combining all of these contributions produces our final prediction for the vertical electron attachment energy of 41 cm^{-1} .

The molecular orbital holding the excess electron in I^- is depicted in Fig. 3 (right column) where both the SCF and MP2 natural spinorbitals are shown. As is typical for dipole-bound anions, this orbital is very diffuse and localized mainly outside the molecular framework, near the positive centroid of the molecular host. Note that the region of space occupied by this orbital is consistent with that of the electrostatic potential of **I** shown in Fig. 2.

We consider the anionic state of I^- to be a dipole-bound state even though the dispersion contribution to the binding is the largest since: (i) the lowest nonvanishing multipole moment of the neutral molecular host **I** is the dipole moment; (ii) I^- is bound at the electrostatic KT level and remains bound even when the reduction in dipole moment caused by correlation is taken into consideration; (iii) the excess electron in I^- resides in a diffuse fully symmetric molecular orbital localized outside the molecule in the vicinity of the positive side of the dipole (see Fig. 3).

C. Anion supported by the amino tautomer of 9-AA

At first glance the anions based on the amino and imino tautomers of 9-acridinamine look quite alike, so it is tempting to label both of them as dipole-bound states (see their D values in Table II and their SCF orbitals the top part of the Fig. 3). However, we became intrigued by the observation that for A^- the sum of the binding energy calculated at the Koopmans' electrostatic-exchange level ($D^{\text{KT}} = 5 \text{ cm}^{-1}$) and the $\Delta D_{\text{ind}}^{\text{SCF}}$ (1 cm^{-1}) term is cancelled by the $\Delta D_{\text{no-disp}}^{\text{MP2}}$ term (-6 cm^{-1}). Since the second-order nondispersion correction ($\Delta D_{\text{no-disp}}^{\text{MP2}}$) is dominated by the correlation correction to the static Coulomb interaction between the loosely bound electron and the charge distribution of the neutral host, we conclude that the charge density of the neutral molecule is incorrectly reproduced at the uncorrelated level (SCF). This, in turn, leads to significant overestimation of both μ and D . The fact that $\Delta D_{\text{no-disp}}^{\text{MP2}}$ cancels $D^{\text{KT}} + \Delta D_{\text{ind}}^{\text{SCF}}$ indicates that if one used the correlated charge density for **A**, the resulting dipole moment μ is not large enough to support an anionic state.⁸¹ Moreover, even though the SCF singly occupied molecular orbital in A^- (Fig. 3 top left) exhibits a character typical for dipole-bound anions and very similar to that of I^- , the natural orbital calculated from the MP2 density looks very different (see Fig. 3, bottom left). Such is not the case for the imino tautomer of 9-AA which we consider to be a dipole-bound anionic state; for I^- the SCF and MP2-level orbitals are nearly identical (Fig. 3, right column). These data again suggest that the correlated (MP2) A^- state is qualitatively different from the correlated I^- .

We therefore suggest that if the excess electron is not bound by the correlated dipole potential as appears to be the case for A^- , the corresponding anion should not be called a dipole-bound state. So what kind of state is A^- ? We suggest calling this anion dispersion bound. Again, to distinguish between I^- and A^- , if dispersion effects were absent, I^- would still be bound but A^- would not. So, the existence of A^- depends on dispersion while the existence of I^- arises from dipole binding.

We believe there could be a multitude of such anions that have yet to be discovered for which two situations are possible: (i) a dispersion-bound anion is artificially bound (as is A^-) at the KT electrostatic level due to the overestimated SCF dipole moment of the neutral molecule—or (ii) the anion is not bound at the KT level. The second case is actually more difficult for us because the LUMO of the neutral is not a good “starting point” for subsequent treatment of dispersion.

In order to test whether our values of the SCF dipole moment and KT binding energy for the A^- are stable with respect to the basis set used, we performed two additional tests.

(i) We replaced the $6s6p4d$ diffuse basis with a $7s7p5d$ basis and found that μ^{SCF} and D^{KT} changed less than 0.0001 Debye and 0.3 cm^{-1} . Then, keeping the $7s7p5d$ diffuse basis, we verified that the MP2 dipole moment changes by less than 0.00005 Debye when compared to μ^{MP2} obtained with the $6s6p4d$ basis.

(ii) We replaced the aug-cc-pVDZ+ $6s6p4d$ basis set

with the aug-cc-pVTZ+6s6p4d basis and again found that the changes in μ^{SCF} and D^{KT} were negligible (0.0001 Debye and 0.1 cm^{-1} , respectively).

These observations show no tendency for the SCF dipole moment or KT electron binding energy to increase when a bigger basis set is used, nor any tendency for $\Delta D_{\text{no-disp}}^{\text{MP2}}$ to not cancel $D^{\text{KT}} + \Delta D_{\text{ind}}^{\text{SCF}}$ as the basis is increased. Therefore, we believe the excess electron binding is indeed very small and equal to 6 cm^{-1} at the SCF level. This supports our conclusion that the artificial binding at the $\text{KT} + \text{SCF}_{\text{ind}}$ level is cancelled by $\Delta D_{\text{no-disp}}^{\text{MP2}}$, which primarily reduces the dipole moment (see Table II).

IV. SUMMARY

We studied the possibility of binding an excess electron to the amino and imino tautomers of 9-acridinamine. On the basis of our *ab initio* MP2/aug-cc-pVDZ+6s6p4d results we found that:

(i) The amino (A) tautomer binds an excess electron by 20 cm^{-1} while the imino (I) tautomer binds by 41 cm^{-1} .

(ii) I^- is bound at the electrostatic-exchange KT and SCF level and remains bound when the correlation correction to the dipole moment of the neutral molecule is taken into account. The singly occupied molecular orbital (SOMO) holding the excess electron in I^- is diffuse and localized on the positive end of the dipole moment, outside the molecular framework, which is typical for all dipole-bound anions. The character of the SOMO remains qualitatively the same when MP2 density is used instead of SCF density.

(iii) A^- is bound at the electrostatic-exchange KT and SCF level but, when the correlation correction to the dipole moment of the neutral molecule is added, it does not remain bound. Hence, the only remaining contributions to the electron binding energy are the results of electron correlation, among which the dispersion interaction has proven to be the most important. The SOMO of the A^- anion changes significantly when the SCF electron density is replaced with the correlated MP2 density.

(iv) While the I^- anion is a typical dipole-bound anion, the nature of the electron binding in the anion supported by the amino tautomer is different and we suggest calling this anion dispersion-bound because its existence depends on dispersion effects while that of I^- does not.

ACKNOWLEDGMENTS

This paper is dedicated to Professor Jerzy Blazejowski. This work was supported by the NSF Grants 9618904 and 9982420 to J.S. and the Polish State Committee for Scientific Research (KBN) Grant No. DS/8371-4-0137-1 to P.S. and J.R. The computer time provided by the Center for High Performance Computing at the University of Utah is also gratefully acknowledged.

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