isolated molecule, since this value is slightly smaller than the range of energy (ΔH) difference found to various N-acylglycine dithio derivatives in CH_3CN/H_2O solutions (2.7–4.2 kJ mol^{-1}[14]).

The main conclusions emerging from the comparison of atomic charges in different conformers are summarized below and reinforce the importance of both $NH\cdots S_{(thiono)}$ hydrogen bonding in the C_5 form and the $N\cdots S_{(thiol)}$ contact in the B form.

(i) The amide hydrogen atom in the C_5 form acquires an increased positive charge, resulting from the involvement of this atom in the $NH\cdots S_{(thiono)}$ hydrogen bond. (ii) The N and S atoms are involved in different processes of electron sharing in the various conformers (mesomerism, nonbonded contacts, and hydrogen bonding). Thus, their charge cannot be taken as a single measure of a particular effect. However, the larger negative overall charge within the CSSH group in the B conformer clearly reflects the nitrogen-to-sulfur charge release due to the $N\cdots S_{(thiol)}$ interaction.

(iii) The changes in the atomic charges within the C(=O)N fragment, going from the A to B form, relates to the greater importance of mesomerism in the A conformer, involving the $C(-O^-)=N^+$ canonical form. It should be pointed out that this increased delocalization in the A C(=O)N moiety can be considered as a factor contributing to the reduced importance of the $N\cdots S_{(thiono)}$ interaction in form A, as compared with the $N\cdots S_{(thiol)}$ interaction in form B.

Conclusion

The calculations emphasize a remarkable similarity between molecular properties of N-formylglycine dithio acid and those of N-acylglycine dithio esters in the condensed phase. In particular, in molecules possessing a $C(=O)NHCH_2CS_2$ fragment, the importance of the $N\cdots S_{(thiol)}$ contact in B forms was reinforced. The theoretical evidence for a C_5-type conformer provides support for the existence of such a species which heretofore had been inferred on the base of FTIR data alone.

The results of the calculations establish a solid theoretical support for the previously proposed nature of the $N\cdots S_{(thiol)}$ interaction, clearly indicating an electronic charge release from the N to the $S_{(thiol)}$ atom in the B conformer, which perturbs the electron distribution in the peptide and dithio ester groups. This in turn demonstrates how the $N\cdots S_{(thiol)}$ contact can act as a conduit which can transmit electronic effects from the peptide to the dithio ester group—and may provide part of the explanation for the differential rate constants of deacylation in para-substituted N-benzoylglycine dithioacyl papains.[12] An important point here is that the $N\cdots S$ contact appears to shorten and hence strengthen the C–S single bond—which is the bond which has to be broken in the deacylation step. The calculations are fully consonant with the crystallographic results that the C–S bond is slightly shorter in B conformers (N-acetylglycine,[7] N-benzoylglycines,[8] 170.0–171.1 pm) than in A conformers (N-(p-nitrobenzoyl)glycine ethyl dithio ester,[7] 172.7 pm). The issue of the stabilization of the B conformer dithioacyl papain via the $N\cdots S$ contact is taken up in ref 26 where it is used to account, at least in part, for kinetic factors in the deacylation step.

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Registry No. $OHCNHCH_2CSSH$, 131904-36-4.

Substituted Ethylene Dications: Planar or Perpendicular?

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Abstract: Neutral and doubly charged substituted ethylene dications $C_2X_2Y_2$ are theoretically studied by use of ab initio quantum theoretical methods. Planar geometries are predicted for the dications $C_2F_4^{2+}$, $C_2(OH)_4^{2+}$, $C_2H_2(NH_2)_2^{2+}$, and $C_2(OH)_2(NH_2)_2^{2+}$, while twisted structures are calculated for $C_2H_4^{2+}$, $C_2(NH_2)_4^{2+}$, and $C_2(SH)_4^{2+}$. The results are explained with molecular orbital arguments. Substituents X with lone-pair orbitals strongly donate electronic charge into the formally empty $C(\pi)$ orbital of $C_2X_4^{2+}$, yielding partial CX double bonds. If X is a first-row atom, conjugation of the resulting double bonds causes a planar geometry as energy minimum form if steric repulsion of the vicinal groups is absent. The experimentally observed twisted geometry of the bromo and chloro salts of $C_2(NH_2)_4^{2+}$ cannot be considered as validation that $C_2H_4^{2+}$ has a perpendicular energy minimum geometry.

Introduction

Double ionization of neutral (D_{2h}) ethylene yields $C_2H_4^{2+}$, which has a theoroetically predicted[1,2] twisted (D_{2d}) geometry. The planar form of $C_2H_4^{2+}$ is a transition state for the rotation around the CC bond, ~30 kcal/mol higher in energy than the perpendicular minimum.[1,2] The strong preference of the ethylene dication for a twisted geometry has been explained by hyperconjugation of the CH bonds.[1] $C_2H_4^{2+}$ has been observed in the gas phase,[3] but an experimental validation for the theoretically predicted twisted geometry is still missing. The high energy needed to remove two electrons from ethylene prevents the preparation of a salt compound of $C_2H_4^{2+}$ that would allow the measurement of its geometry. In order to prove the theoretical prediction that $C_2H_4^{2+}$ has a perpendicular geometry, Bock et al.[4] recently prepared the bromo and chloro salts of tetrakis(dimethylamino)ethylene dication $C_2(NMe)_4^{2+}$ and measured the geometries by X-ray diffraction. Indeed, they found that the geometry of $C_2(NMe)_4^{2+}$ exhibits twisting angles ω around the CC bond of 76° (chloro salt) and 67° (bromo salt).[4] The experimental results were supported by MNDO[5] calculations that predict a twisting angle

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Table I. Calculated Total Energies E_{tot} (in hartrees), Relative Energies E_{rel} (in Kilocalories per Mole), and Zero-Point Vibrational Energies ZPE(i) (in Kilocalories per Mole) of Structures **1–31** Using Geometries Optimized at HF/3-21G(d)[a]

$C_2X_2Y_2$			HF/3-21G(d)			HF/6-31G(d)		MP2/6-31G(d)		
			E_{tot}	E_{rel}	ZPE(i)	E_{tot}	E_{rel}	E_{tot}	E_{rel}	I_2
	neutral	**1**	−77.6010		30.1 (0)	−78.0317		−78.2841		27.5
X = H	dication (planar)	**2**	−76.5999	28.0	26.5 (1)	−77.0470	34.3	−77.2232	31.0	
Y = H	dication (perp)	**3**	−76.6445	0.0	26.3 (0)	−77.0864	0.0	−77.2726	0.0	
	neutral	**4**	−470.8554		13.0 (0)	−473.4121		−474.3393		26.2
X = F	dication (planar)	**5**	−469.8228	0.0	13.1 (0)	−472.4600	0.0	−473.3780	0.0	
Y = F	dication (perp)	**6**	−469.8150	4.9	12.8 (1)	−472.4562	2.4	−473.3736	2.8	
	neutral	**7**	−375.3654		40.8 (0)	−377.4514		−378.4144		19.4
X = OH	dication (planar)	**8**	−374.6594	0.0	41.0 (0)	−376.7594	0.0	−377.7001	0.0	
Y = OH	dication (perp)	**9**	−374.6377	13.6	40.0 (1)	−376.7467	8.0	−377.6876	7.8	
	neutral	**10**	−296.5001		70.6 (0)	−298.1451		−299.0498		15.2
X = NH_2	dication (planar)	**11**	−295.9503	9.3	73.3 (1)	−297.5864	10.9	−298.4691	11.5	
Y = NH_2	dication (perp)	**12**	−295.9651	0.0	73.6 (0)	−297.6037	0.0	−298.4875	0.0	
	neutral (1,1)	**13**	−187.0549	0.0	50.0 (0)	−188.0932	0.0	−188.6695	0.0	21.4
	neutral (trans)	**14**	−187.0369	11.3	49.9 (0)	−188.0783	9.3	−188.6565	8.2	18.2
X = H	neutral (cis)	**15**	−187.0445	6.5	50.3 (0)	−188.0822	6.9	−188.6602	5.8	18.3
Y = NH_2	dication (1,1)	**16**	−186.3034	55.7	50.4 (0)	−187.3460	54.7	−187.8849	63.4	
	dication (trans)	**17**	−186.3921	0.0	52.5 (0)	−187.4331	0.0	−187.9860	0.0	
	dication (cis)	**18**	−186.3827	5.9	52.5 (1)	−187.4223	6.8	−187.9741	7.4	
	dication (perp 1,1)	**19**	−186.2984	58.8	49.4 (1)	−187.3419	57.3	−187.8730	70.9	
	dication (perp 1,2)	**20**	−186.3888	2.1	52.2 (1)	−187.4301	1.9	−187.9814	2.8	
	neutral (1,1)	**21**	−335.9425	0.0	56.5 (0)	−337.8083	0.0	−338.7429	0.0	17.5
	neutral (trans)	**22**	−335.9392	2.1	55.9 (0)	−337.8048	2.2	−338.7409	1.3	17.1
X = OH	neutral (cis)	**23**	−335.9340	5.3	55.5 (0)	−337.8000	5.2	−338.7349	5.0	17.4
Y = NH_2	dication (1,1)	**24**	−335.3238	10.5	57.3 (0)	−337.1879	8.0	−338.0997	7.8	
	dication (trans)	**25**	−335.3405	0.0	57.8 (0)	−337.2007	0.0	−338.1122	0.0	
	dication (cis)	**26**	−335.3186	13.8	57.4 (0)	−337.1830	11.1	−338.0949	10.8	
	dication (perp 1,1)	**27**	−335.3038	23.1	56.6 (1)	−337.1792	13.5	−338.0906	13.5	
	dication (perp 1,2)	**28**	−335.3157	15.6	57.1 (1)	−337.1887	7.5	−338.0996	7.9	
	neutral	**29**	−1660.2552		29.7 (0)	−1668.0559		−1668.8027		19.1
X = SH	dication (planar)	**30**	−1659.5219	11.2	30.5 (1)	−1667.3311	11.7	−1668.0833	9.5	
Y = SH	dication (perp)	**31**	−1659.5397	0.0	30.7 (0)	−1667.3497	0.0	−1668.0985	0.0	

[a] The number of imaginary modes (i) is given in parentheses. I_2 (in electronvolts) is the energy difference between the neutral molecule and the corresponding dication. Energy differences are given relative to the most stable neutral or doubly charged molecule, as applicable.

ω for $C_2(NMe)_4{}^{2+}$ of 62°.[4] The authors concluded from their results that double ionization of $C_2H_4{}^{2+}$ and its derivatives $C_2F_4{}^{2+}$ inevitably leads to a twisting of the two halves of the molecule.[4]

We challenge the conclusion concerning the predicted twisting in $X_2C{-}CX_2{}^{2+}$. In a theoretical study published in 1986, we could already show[2] that, unlike $C_2H_4{}^{2+}$, $C_2F_4{}^{2+}$ prefers a *planar* (D_{2h}) geometry just like the neutral parent compound. This result has been explained by the conjugation of the partial CX double bonds (Figure 1) that results from the strong donation of the fluorine lone-pair orbitals into the formally empty carbon p(π) orbitals.[2] Since the nitrogen lone-pair orbital of an amino group is a *better* donor than a fluorine atom, the double bond character and thus the π-conjugation about the CC bond should be *stronger* in $C_2(NMe)_4{}^{2+}$ than in $C_2F_4{}^{2+}$. Thus, the experimentally observed[4] twisting in the former dication is surprising. Either the explanation for the planarity of $C_2F_4{}^{2+}$ is wrong[2] or the observed twisting of $C_2(NMe)_4{}^{2+}$ is caused by a different effect than stated earlier.[4] In order to give an account for the predicted and observed geometries of substituted ethylene dications, we carried out ab initio studies on $C_2X_4{}^{2+}$ dications with X = H, F, OH, SH, and NH_2 and on the corresponding neutral molecules. We also calculated neutral and doubly charged $C_2H_2(NH_2)_2$ and $C_2(OH)_2(NH_2)_2$. Our results provide an explanation for the reported data and allow predictions for still unknown substituted ethylene dications. On the basis of the results of ab initio calculations, we will show in this paper that donor groups X that are capable of strong π-donation may yield *planar* geometries for $C_2X_4{}^{2+}$.

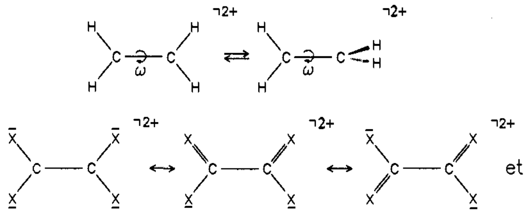

Figure 1. Schematic representation of the planar and perpendicular form of $C_2H_2{}^{2+}$ (top) and the possible resonance forms for $C_2X_4{}^{2+}$ if X has lone-pair electrons.

Theoretical Details

The calculations have been carried out by use of the CONVEX version of the GAUSSIAN 88[5] program series. Optimized geometries and theoretical vibrational frequencies have been obtained with the 3-21G(d) basis set, which has a set of d-type orbitals for third-row elements.[6] The frequencies and corresponding zero-point vibrational energies (ZPE) are scaled by a factor of 0.87 to account for deficiencies in the basis set, neglect of correlation energy, and errors due to the harmonic approximation.[7] Single-point energies of the geometry-optimized species have been calculated with the 6-31G(d) basis set.[8] Correlation energy has been estimated by use of Møller–Plesset perturbation theory[9] terminated

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at second order. Thus, the highest level of theory is denoted MP2/6-31G(d)//3-21G + ZPE. Unless otherwise noted, energy values are given at that level of theory.

Results and Discussion

Table I shows the caculated energies of the investigated molecules. The optimized geometries are shown in Figure 2.

The calculated CC distance in neutral ethylene **1** (1.315 Å) is much shorter than in the corresponding doubly charged cation $C_2H_4^{2+}$ (**2**; 1.617 Å) (Figure 2). However, the planar species **2** is a transition state and not a minimum on the potential energy hypersurface. Rotation around the CC bond yields the twisted energy minimum structure **3**, which is 31.2 kcal/mol lower in energy than **2** (MP2/6-31G(d)//3-21G + ZPE). Hyperconjugation in **3** leads to a significantly shorter CC distance (1.410 Å) than in **2**. The Mulliken population analysis[10] shows a small occupation (0.06 e) of the p(π) carbon orbitals due to hyperconjugative donation by the CH bonds (Figure 2).

The results for C_2F_4 are significantly different. Unlike **2**, the planar form of $C_2F_4^{2+}$ (**5**) is an energy minimum, while the perpendicular structure **6** is a transition state for rotation around the CC bond, 2.8 kcal/mol higher in energy than **5** (Table I). The CC distance in **6** is even slightly longer (1.597 Å) than in **5** (1.591 Å). The CF distances in **5** and **6** are clearly shorter (1.236 and 1.238 Å, respectively) than in neutral C_2F_4 (**4**) (1.330 Å). The Mulliken population analysis shows that the carbon p(π) orbitals in **5** and **6**, which are formally empty, are significantly occupied (0.51 e, Figure 2). This is a clear indication that in $C_2F_4^{2+}$ a different mechanism is operative to satisfy the electron demand of the carbon atoms than that in $C_2H_4^{2+}$. Electron donation in $C_2F_4^{2+}$ is provided by the lone-pair orbitals of the fluorine atoms. The structural data indicate that π-donation is more effective than hyperconjugation, which appears to be neglectable in $C_2F_4^{2+}$. But, π-donation by the fluorine atoms alone cannot be the cause for the planar energy minimum of $C_2F_4^{2+}$ since it is operative in the planar *and* the twisted form. Rather, weak conjugation of the partial double bonds (Figure 1) is the reason why **5** is 2.8 kcal/mol lower in energy than **6**. It follows that the stabilization in **5** due to the conjugation is worth 2.8 kcal/mol *plus* the energetic effect of the (weak) hyperconjugation by the CF bonds in **6**.

What happens when the fluorine atoms in **4**–**6** are substituted by hydroxy groups? Oxygen is a better π-donor than fluorine, and the effects resulting from π-donation should be stronger in $C_2(OH)_4^{2+}$ than in $C_2F_4^{2+}$. Our calculated results shown in Table I and Figure 2 agree with the expectation. Planar $C_2(OH)_4^{2+}$ (**8**) is a minimum, even 6.8 kcal/mol (MP2/6-31G(d)//3-21g + ZPE) lower in energy than perpendicular $C_2(OH)_4^{2+}$ (**9**), which is a transition state. Stronger π-donation in $C_2(OH)_4^{2+}$ than in $C_2F_4^{2+}$ is indicated by the computed pπ(C) populations, which are 0.66 and 0.67 e in **8** and **9**, respectively, while they are only 0.51 e in **5** and **6** (Figure 2). The CC bond in **8** is 0.013 Å shorter than in **9**, but in **5** it is only 0.06 Å shorter than in **6**. This indicates a slightly stronger conjugation of the partial CX doubly bond in **8** than in **5**, yielding for $C_2(OH)_4^{2+}$ a greater preference for the planar form **8**.

A further increase of π-donation effects, such as energy preference for the planar form, may be expected for $C_2(NH_2)_4^{2+}$. However, the calculated data shown in Table I predict that the planar structure for $C_2(NH_2)_4^{2+}$ (**11**) is a transition state and not a minimum on the potential energy surface. The energetically lowest lying form of $C_2(NH_2)_4^{2+}$ has a twisted geometry **12** with a twist angle ω around the CC bond of 53.1° (Figure 2). This agrees with the experimentally observed geometry for the $C_2(N(CH_3)_2)_4^{2+}$ salt for which torsion angles of 67° (bromo salt) and 76° (chloro salt) have been reported.[4] **12** is 11.2 kcal/mol lower in energy than **11** (MP2/6-31G(d)//3-21G + ZPE, Table I). Why does the tetraaminoethylene dication exhibit a different behavior than the fluorine and hydroxyl analogus?

An explanation is found when the calculated planar form **11** is examined. The optimized geometries shown in Figure 2 indicate that $C_2(NH_2)_4^{2+}$, unlike $C_2F_4^{2+}$ and $C_2(OH)_4^{2+}$, encounters steric repulsion by hydrogen atoms between geminal (1,1) and vicinal (1,2) amino groups. The geminal H,H repulsion is stronger since the geminal amino groups are closer to each other. Steric repulsion of the geminal amino groups could be released by rotation around the CN bonds (Figure 2), but this would weaken the π-donation of the nitrogen lone-pair electrons into the formally empty carbon p(π) orbital. The Mulliken population analysis indicates that the π-donation of the amino groups in $C_2(NH_2)_4^{2+}$ shows the expected increase compared with $C_2F_4^{2+}$ and $C_2(OH)_4^{2+}$; the carbon p(π) occupancy is 0.75 in **11** and 0.77 in **12**. Thus, the effect of π-donation by the nitrogen lone-pair electrons is stronger in $C_2(NH_2)_4^{2+}$ than the steric repulsion by the hydrogen atoms of the *geminal* amino groups. But the steric repulsion of the hydrogen atoms of the *vicinal* amino groups in planar **11** is stronger than the *conjugation* of the partial CN double bonds. This is indicated by the calculated CC distance, which is shorter in **12** than in **11**. If hyperconjugation would be the dominating force in determining the geometry of $C_2(NH_2)_4^{2+}$, **12** should have a twist angle of 90°. The theoretically predicted twist angle of 53.1° for **12** is a compromise between steric repulsion of the vicinal amino groups and the conjugation of the partial CN double bonds.

Before continuing the discussion on the structures and energies of the dications, we would like to comment on the calculated low-energy conformation of the neutral molecules $C_2(OH)_4$ (**7**) and $C_2(NH_2)_4$ (**10**).[13] Figure 2 shows that **7** exhibits two different orientations of the hydroxyl groups. At one carbon atom, the OH groups both are planar with a syn orientation to the CC bond, while the OH groups at the other carbon atom are twisted such that the hydrogen atoms are above and below the molecular plane. The CO bonds of the OH syn to CC are significantly shorter (1.354 Å) than the "nonplanar" CO bonds (1.389 Å), which can be explained by the conjugation of the p(π) lone pair orbitals at oxygen with the CC π-bond. The same arrangement is found in **10**. The amino groups at one carbon atom are orthogonal to the molecular plane, while the other two are oriented such that the nitrogen lone pair orbitals conjugate with the CC π-bond (Figure 2). Consequently, the latter amino groups show a significantly shorter CN bond (1.382 Å) than the former NH_2 group (1.436 Å). Thus, **7** and **10** prefer a Y-shaped π-conjugation with 6 π-electrons rather than 10 π-electrons.[14] Although **7** and **10** are C_2X_4 systems with identical substituents X, the different conformations of the substituents introduce a dipole moment that is calculated as 3.21 D for **7** and 0.79 D for **10**.

In order to examine our analysis of the theoretical and experimental results for $C_2X_4^{2+}$ systems, we calculated the structures and energies of $C_2H_2(NH_2)_2^{2+}$. If our model of π-donation/conjugation is correct, then the 1,2(trans) and 1,1 isomers of $C_2H_2(NH_2)_2^{2+}$ should be planar, because steric repulsion between hydrogen atoms of geminal amino groups is absent. Our calculated results are shown in Table I and Figure 2. The neutral isomers **13** (1,1), **14** (trans), and **15** (cis) are predicted with the stability sequence **13** > **15** > **14**. The same sequence, which is opposite to what is expected from steric arguments, has been found[11] for the three isomers of $C_2H_2F_2$. The stability order of 1,1, cis, and trans isomers of $C_2H_2X_2$ has been explained on the basis of molecular orbital arguments and charge distribution.[12] We want

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[11] Jochims, H. W.; Lohr, W.; Baumgärtel, H. *Nouv. J. Chim.* **1979**, *3*, 109.

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[13] We systematically searched for conformational minima for rotation around the CO and/or CN bond of **7**, **10**, **13**–**15**, **21**–**23**, and **29**. We found several local minima that are not important for the topics discussed in this paper. The structures shown in Figure 2 are the calculated lowest energy forms.

[14] We do not think that the obvious preference for Y-shaped conjugation exhibited by **7**, **10**, **13**, **21**, and **29** is an example of the so-called "Y-aromaticity": Gund, P. *J. Chem. Educ.* **1972**, *49*, 100. Agranat, I.; Skancke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867. Rather, Y-conjugation in these molecules yields favorable charge alternation that may explain the greater stability of these conformations. Cf.: Klein, J. *Tetrahedron* **1983**, *39*, 2733. For a different interpretation, see ref 15.

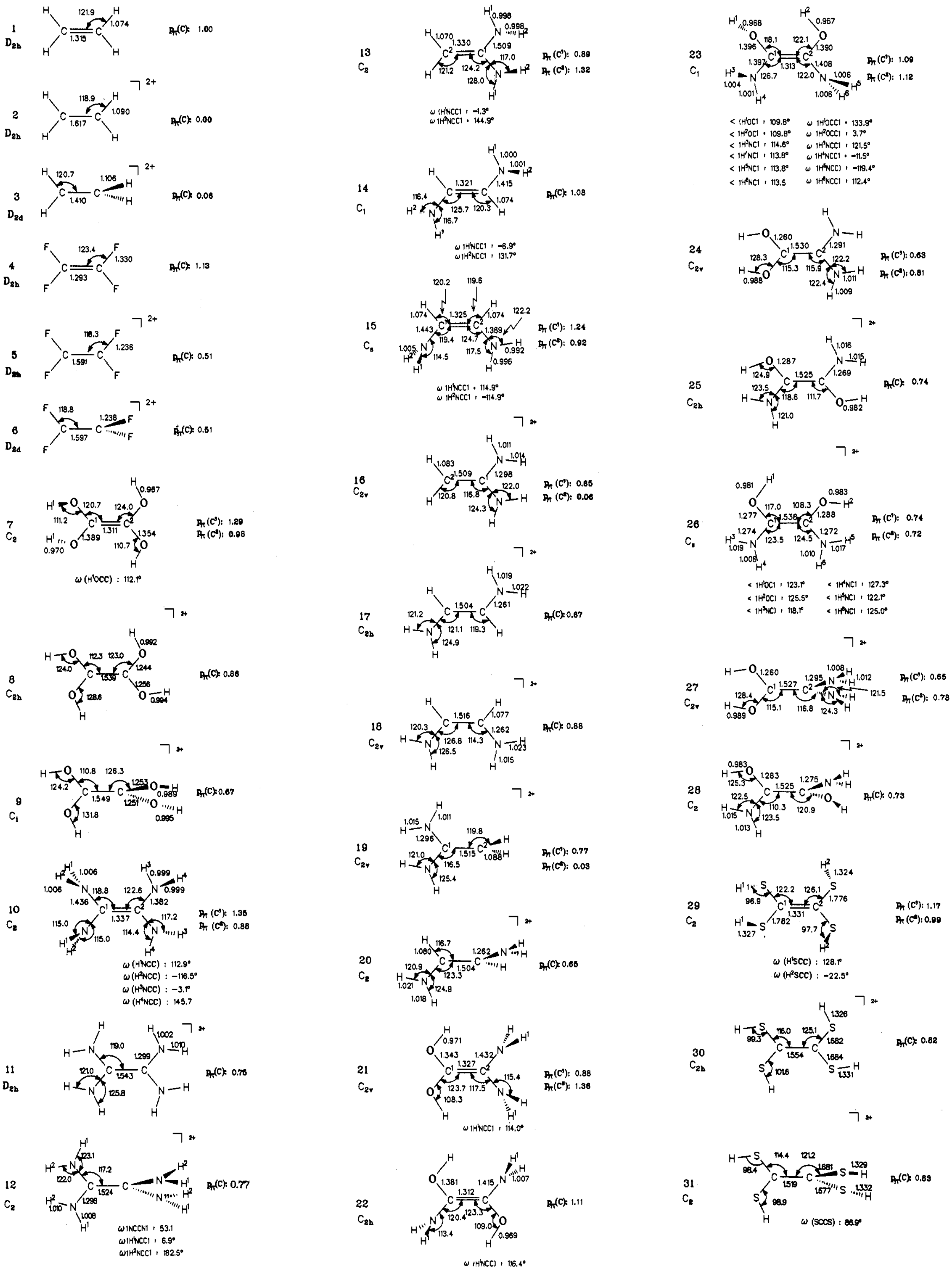

Figure 2. Calculated (3-21G(d)) geometries of structures **1**–**31**. Mulliken population of the carbon p(π) orbital. Distances are given in angstroms and angles in degrees.

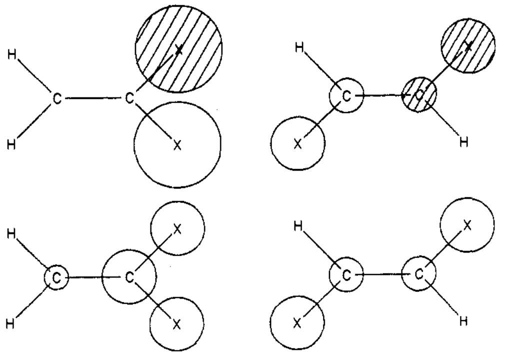

Figure 3. Schematic representation of the occupied π-orbitals of $C_2H_2X_2^{2+}$, where X is a substituent with a lone-pair orbital.

to draw attention to the calculated geometry for the cis isomer **15** (Figure 2). Unlike **13** and **14**, the amino groups of **15** are not identical; one amino group is perpendicular to the CC double bond, while the lone-pair orbital of the other amino group (which is calculated to be planar) is in resonance with the double bond. Consequently, the latter has a much shorter CN bond (1.369 Å) than the former (1.443 Å). Thus, **15** is a 4π-system that resembles an enamine and not a 6π-system. Our results may be compared with a recent study by Wiberg et al.[15] on resonance interactions in acyclic systems. Among other molecules, they studied[15b] trimethylenmethane dianion, which is isoelectronic with **13**, and found that resonance interactions in anions are small and that it is the electronegativity of the terminal atoms that determines the stability of the species.[15]

Doubly ionized $C_2H_2(NH_2)_2^{2+}$ is calculated to have only two isomers as minima on the potential energy surface, the 1,1 isomer **16** and the trans isomer **17**, which is 61.3 kcal/mol (!) (MP2/6-31G(d)//3-21G + ZPE) *lower* in energy than **16**. The cis form **18** is a transition state for the rotation of **17** about the CC bond. Also, the perpendicular geometries of the 1,1 and 1,2 isomers are not energy minima (Table I). The planar cis form **18** is subject to steric repulsion (Figure 2); rotation around the CC bond toward the twisted form **20** relieves the repulsive interaction, but further rotation toward the trans form **17** turns on conjugation about the CC bond. Because there are only two donor groups, the energy difference between the planar and perpendicular form is slightly less for $C_2H_2(NH_2)_2^{2+}$ (6.5 kcal/mol for the 1,1 isomer, 2.5 kcal/mol for the 1,2 isomer) than for $C_2(OH)_4^{2+}$ (6.8 kcal/mol), although the amino group is a better π-donor than the hydroxyl group. The significantly higher energy of the 1,1 isomer **16** than the 1,2 isomer **17** (61.3 kcal/mol), which is opposite to what is found for the neutral parent compounds, may be explained along the same line by use of the symmetry of the corresponding molecular orbitals as shown in Figure 3.

In **17**, both lone-pair orbitals of the nitrogen atoms donate electronic charge toward the carbon atoms. In **16**, only the (+) combination of the lone-pair orbitals can donate electronic charge while the (−) combination of the lone-pair orbitals can not interact with the CC π-orbital. Thus, π-donation in **17** is nearly twice as strong as in **16**, which leads to a stabilization of more than 60 kcal/mol (Table I). Wiberg[15b] has recently studied the resonance stabilization in Y-shaped trimethylenmethane dication and found that, despite its "Y-conjugation", the dication does not have much additional stabilization compared with the singly charge 2-methylallyl cation. For reasons outlined previously, we also find that Y-conjugation does not by itself provide additional stabilization compared with other types of conjugation.

As a further test of our π-donation/conjugation model, we calculated the structures and energies of $C_2(OH)_2(NH_2)_2$ and $C_2(OH)_2(NH_2)_2^{2+}$. The results are shown in Table I and Figure 2. For the neutral molecules, the geminal substituted isomer **21** is most stable, the trans form **22** is next, and the cis form **23** is energetically highest (Table I). Again, the structure with Y-shaped π-conjugation **21** is energetically favored. In **21** and **22**, the NH_2 groups are perpendicular and the OH groups planar. In **23**, one NH_2 and one OH group have their lone-pair orbital in conjugation with the CC π-bond while the other groups are perpendicular (Figure 2). Thus, **21**–**23** are 6π-electron systems, and **21** and **22** prefer conjugation of the CC π-bond with the *oxygen π* lone pair rather than with the nitrogen lone-pair orbital.

Nuclear repulsion between vicinal hydrogen atoms is absent in the 1,1 and trans forms of $C_2(OH)_2(NH_2)_2^{2+}$. Therefore, the corresponding isomers **24** and **25** are minima on the potential energy surface (Table I, Figure 2). Even the cis isomer **26** is calculated to be an energy minimum structure, although it is the least stable of the planar isomers **24**–**26** (Table I). The perpendicular structures **27** and **28** are calculated as transition states for rotation around the CC bond (Table I, Figure 2). The trans form **25** is the energetically lowest lying isomer of $C_2(OH)_2(NH_2)_2^{2+}$, 7.3 kcal/mol more stable than **24** and 10.4 kcal/mol lower in energy than **26**. **25** also has the shortest CC bond of the three isomers (Figure 2). Interestingly, the CN bonds in **25** are *shorter* (1.269 Å) than the CO bonds (1.287 Å).

We extended our studies of $C_2X_4^{2+}$ systems to molecules that involve groups X with donor atoms of the third-row elements. Is π-donation by sulfur as strong as by oxygen, and does $C_2(SH)_4^{2+}$ prefer a planar geometry just like $C_2(OH)_4^{2+}$? Experimental data have been reported for a tetrathiofulvalene dication that has a torsion angle ω around the $S_2C{-}CS_2$ bond of ~60°.[16] We calculated the structures and energies of neutral $C_2(SH)_4$ (**29**) and the planar **30** and perpendicular **31** forms of $C_2(SH)_4^{2+}$. The results are shown in Table I and Figure 2.

Neutral $C_2(SH)_4$ (**29**) prefers a conformation with a Y-shaped π-conjugation just like valence isoelectronic $C_2(OH)_4$ (**7**). However, the SH groups at C^2 are twisted by 22.5° out of the molecular plane, while the corresponding OH groups in **7** are perfectly planar (Figure 2). Thus, the Y-shaped π-conjugation in **29** is slightly distorted and seems to be less important than in **7**. Nevertheless, a dipole moment of 1.81 D is calculated for neutral $C_2(SH)_4$.

For $C_2(SH)_4^{2+}$, the twisted isomer **31** is predicted to be an energy minimum with a torsion angle ω of 86.9° (Figure 2). The planar form **30** is a transition state for rotation around the CC bond, 9.3 kcal/mol higher in energy than **31**. The CS bonds in **30** and **31** are significantly shorter than in **29**, and the Mulliken population analysis shows high occupancy of the carbon p(π) orbitals (Figure 2). This points toward strong π-donation by the SH groups. Two factors may explain why the twisted form is lower in energy than the planar structure, in contrast to the results obtained for $C_2(OH)_4^{2+}$. First, double bonds between carbon and third-row elements are weaker than between carbon and the corresponding second-row element; thus, conjugation of the (weaker) partial double bonds in **30** will be less effective than in **8**. Second, CS bonds are better hyperconjugative donors than CO bonds. Accordingly, **31** has a clearly shorter CC bond (1.519 Å) than **30** (1.554 Å) (cf., **8** 1.539, **9** 1.549 Å).

Summary and Outlook

The calculated energy minimum structures of substituted ethylene dications $C_2X_4^{2+}$ clearly show that π-donation of lone-pair electrons of substituents X is the dominating mechanism to donate electronic charge into the formally empty carbon p(π) orbitals. This leads to significantly shorter CX bonds relative to the neutral compounds and introduces partial CX double bonds. If X is a first-row element, conjugation of the partial CX double bonds yields planar structures if steric repulsion of the vicinal groups is absent. The experimentally observed twisted geometry of the bromo and chloro salts of $C_2(N(CH_3)_2)_4^{2+}$ *cannot* be considered as validation for the theoretically predicted[1,2] perpendicular geometry of $C_2H_4^{2+}$ as proposed by Bock et al.[4] The twisted geometry of $C_2(N(CH_3)_2)_4^{2+}$ is caused by steric repulsion between the vicinal amino groups, while the perpendicular structure of

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$C_2H_4^{2+}$ results from strong hyperconjugation.

What experiments are possible to test our theoretical predictions? Table I shows the calculated ionization energies I_2 for the adiabatic removal of two electrons from substituted ethylenes. The data may serve to give an estimate if stable dications can be expected in a condensed phase. The ionization energies of C_2H_4 (**1**) and C_2F_4 (**4**) are very high (27.5 eV for **1** and 26.2 eV for **4**), too high to expect that salt compounds may be formed. The lowest I_2 value is found for $C_2(NH_2)_4$ (**10**; 15.2 eV). The I_2 values of $C_2(OH)_4$ (**7**; 19.4 eV), $C_2H_2(NH_2)_2$ (**13**–**15**; 18.2–21.4 eV), $C_2(OH)_2(NH_2)_2$ (**21**–**23**; 17.1–17.5 eV), and $C_2(SH)_4$ (**29**; 19.1 eV) are intermediate. However, since salt compounds of tetrathiofulvalen are known,[16] it seems feasible that dications of these molecules may be prepared and the geometries be measured. Our calculations indicate that $C_2(OR)_2(NR_2)_2$ may be the best candidates. In case of the ethylene diamines $C_2H_2(NR_2)_2$, the 1,2-substituted isomers should be much easier to prepare than the 1,1 isomers.

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Ion Solvation in Polarizable Water: Molecular Dynamics Simulations

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Abstract: We present the results of molecular dynamics simulations on gas-phase ion water clusters and ion solvation in liquid water using nonadditive many-body potential models. To our knowledge, this is the first simulation model that has led to very good agreement with experiment for the energies of water, ion clusters, and ionic solutions as well the coordination numbers for the aqueous solutions of Na^+ and Cl^-. We have studied the Na^+ ion gas-phase complexes with one to six water molecules. In addition to obtaining good agreement with the experimental enthalpies, the calculated Na^+–oxygen radial distribution function (RDF) for the $Na^+(H_2O)_6$ cluster displays two distinguishable zones; integrating over the first zone yields four water molecules, and the remaining two water molecules belong the second zone. In contrast to the structure of the Na^+ complex with four water molecules, the four water molecules around the Cl^- ion in $Cl^-(H_2O)_4$ are found clustered together in one hemisphere of the ion. These waters form weak hydrogen bonds with each other, resulting in an average water–water binding energy of −4.6 kcal/mol. These results indicate that the stability of the $Cl^-(H_2O)_4$ complex arises in part from water–water binding. The coordination number of the Na^+ and Cl^- ions obtained from ionic solution simulations is approximately 6, in good agreement with experimental results. We have also calculated the water–water interactions in the first hydration shell of Na^+ and Cl^- solutions to examine the effect of these ions on the water–water interactions. We found the water–water interactions in this region of the Cl^- solution are positive and ~4 kcal/mol less repulsive than the corresponding water–water interactions for the Na^+ solution. Thus, the structure in the first hydration shell of full ionic solution simulation of the anion appears to have significantly different character from that of the gas-phase anion–water cluster. In addition, we found the water molecules between the first and second hydration shells are strongly mobile. Finally, we find it to be essential to include the three-body potential (ion–water–water) in the simulation of the ionic solution to obtain quantitative agreement with the experimental solvation enthalpies and coordination numbers.

I. Introduction

The study of the thermodynamic and structural properties of ions in water by statistical mechanics or computer simulation techniques has made a significant contribution to the understanding of the chemistry and physics of solvation. To date, there have been numerous studies on this important subject.[1-11] With few exceptions,[4,5,7] however, almost all of these water–water and water–ion potential models used in these studies are pairwise additive. Consequently, these studies often overestimate the coordination numbers and the solvation enthalpies of the ions. It is now recognized that many-body or nonadditive interactions are important if one wishes to describe ionic interactions in clusters and in solution quantitatively.[4,7,11,12]

Recently, we have developed a polarizable water potential model that explicitly includes the electronic polarization energy.[13] We have carried out a molecular dynamics simulation on liquid water using this model. We have obtained good agreement with experimental results for the water dimer and the structural and the thermodynamic properties of liquid water. We have also examined complexes of Na^+ and Cl^- with one to six water molecules using the molecular mechanics method.[13] In addition to the good agreement with gas-phase experimental enthalpies, the study of

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