Notes and References

(1) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); S. Iwata and K. Morokuma, *Chem. Phys., Lett.*, **19**, 94 (1973); *J. Am. Chem. Soc.*, **95**, 7563 (1973); **97**, 966 (1975).
(2) A. Johansson and P. A. Kollman, *J. Am. Chem. Soc.*, **94**, 6196 (1972); A. Johansson, P. Kollman, S. Rothenberg, and J. McKelvey, *ibid.*, **96**, 3794 (1974).
(3) J. E. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973); *Chem. Phys. Lett.*, **24**, 203 (1974).
(4) A. Pullman, G. Alagona, and J. Tomasi, *Theor. Chim. Acta*, **33**, 87 (1974), and previous papers in that series.
(5) E. Clementi, J. Mehl, and W. von Niessen, *J. Chem. Phys.*, **54**, 508 (1971).
(6) E. Ady and J. Brickman, *Chem. Phys. Lett.*, **11**, 302 (1971).
(7) J. E. Del Bene, *J. Chem. Phys.*, **62**, 1961 (1975).
(8) R. Bonaccorsi, A. Pullman, E. Scrocco, and J. Tomasi, *Chem. Phys. Lett.*, **12**, 622 (1972).
(9) A. Pullman, "Chemical and Biochemical Reactivity", Israel Academy of Sciences and Humanities, Jerusalem, 1975, pp 1–11.
(10) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **52**, 1784 (1970); A. C. Hopkinson and I. G. Csizmadia, *Can. J. Chem.*, **51**, 1432 (1973); *Theor. Chim. Acta*, **31**, 83 (1973).
(11) J. E. Del Bene, *J. Chem. Phys.*, **62**, 1314 (1975).
(12) J. E. Del Bene, *J. Chem. Phys.*, **63**, 4666 (1975).
(13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(14) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(16) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
(17) J. E. Del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, **36**, 195 (1975).
(18) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(19) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971).
(20) A. Pullman and A. M. Armbruster, *Int. J. Quantum Chem., Symp.*, **No. 8**, 169 (1974).
(21) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
(22) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(23) P. A. Kollman and C. F. Bender, *Chem. Phys. Lett.*, **21**, 271 (1973).
(24) The 4-31G basis set tends to flatten pyramidal angles, as in this case.
(25) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
(26) R. Ditchfield, J. E. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 703 (1972).
(27) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(28) T. R. Dyke and J. S. Muenter, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., 1974, Abstract No. PHYS 113.
(29) T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, **54**, 2442 (1972).
(30) L. C. Allen, *J. Am. Chem. Soc.*, **97**, 6921 (1975).
(31) J. E. Del Bene, *J. Am. Chem. Soc.*, **95**, 5460 (1973); *Chem. Phys.*, **15**, 463 (1976).
(32) P. A. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg, *J. Am. Chem. Soc.*, **97**, 955 (1975).
(33) A. Johansson, P. A. Kollman, J. F. Liebman, and S. Rothenberg, *J. Am. Chem. Soc.*, **96**, 3750 (1974).
(34) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(35) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(36) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).

Π and Σ States of the *N*-Formamido Radical: An ab Initio Molecular Orbital Study[1]

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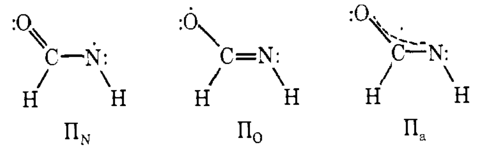
Abstract: Ab initio molecular orbital calculations are reported for the *N*-formamido free radical in its low-lying states. Geometry searches using an STO-3G basis set predict that both Σ and Π states each have at least two potential minima in their planar conformations, corresponding to localization of the unpaired electron at oxygen and at nitrogen. The energies of the different minima in the two states are all rather similar according to 4-31G basis set calculations. Both "allylic" and "twisted" geometries for the lowest Π state were also considered. Unpaired spin densities calculated by the restricted Roothaan open-shell method are reported for the various potential minima.

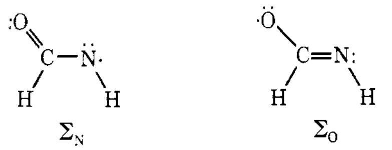
There has been considerable discussion in the literature with regard to the electronic structure of simple amido radicals.[2] For the planar *N*-formamido radical, two types of low-lying states should exist (as in the $NH_2\cdot$ free radical): so-called Π states in which the odd electron occupies a molecular orbital which is antisymmetric with respect to reflection in the molecular plane and Σ states in which the electron occupies a symmetrical orbital. The lowest-energy Π state could possess a carbon–oxygen double bond and a "single" carbon–nitrogen linkage (Π_N) as in formamide, or a carbon–nitrogen double bond and a carbon–oxygen single bond (Π_O), or exist with intermediate CN and CO bond lengths in an "allylic" form (Π_a). (Scheme I. The π electrons are indicated by dots *above* the atom symbols, whereas lone-pair electrons in the σ system are denoted by dots to the *side* of the symbol. The C, N, O, or a subscript on the state designation indicates the atom on which the unpaired electron principally is localized.)

Scheme I. Π State



The unpaired electron in the lowest-energy Σ state of the formamide radical could be localized on the nitrogen (Σ_N), giving rise to a π-bonding stiuation similar to that in formamide itself, or localized in an in-plane 2p orbital on oxygen (Σ_O), thereby yielding a carbon–nitrogen double bond (Scheme II).

Scheme II. Σ State



Since the interpretation of the ESR spectra of amido radicals has proved somewhat controversial[2] and since only semiempirical calculations regarding the energetics of the Π and Σ states have been reported,[2,3] we thought it worthwhile to reconsider the problem using ab initio calculations. Here we report the results of these computations, which used the Roothaan restricted open-shell MO method[4] together with the

Table I. Properties of $NH_2\cdot$

Method	H-N-H angle, deg In Π state	In Σ state	Π-Σ energy gap, kcal mol^{-1}
STO-3G	101	130	45.4
4-31G	108	143	26.8
Experimental[a]	103	144	~31

[a] From ref 7.

STO-3G and 4-31G basis sets (and standard molecular exponents) of Pople and co-workers.[5] Carbon-hydrogen and nitrogen-hydrogen bond distances of 1.105 and 1.013 Å, respectively, and O-C-N and N-C-H bond angles of 120° were assumed in all calculations.

To test the reliability of such calculations in dealing with different states of radicals, ab initio computations on the $NH_2\cdot$ free radical were performed, and the results are summarized in Table I. The agreement between the calculated and the experimental H-N-H bond angles is acceptable. The facts that both states are nonlinear, and that there is a substantial increase in bond angle in going from the Π state (which has an in-plane lone pair of electrons) to the Σ state (with a single electron in the nonbonding in-plane orbital and a lone pair in the π orbital on nitrogen) are both in line with considerations based upon the Gillespie-Nyholm rules and Walsh's rules. The overestimation by the 4-31G basis set calculation of the angle in the Π state is not unexpected, given a similar error in this direction for ammonia itself.[6]

Both STO-3G and 4-31G calculations predict correctly that the Π state of NH_2 is of lower energy than is the Σ state; the energy gap is well reproduced by the 4-31G basis, but is overestimated by the STO-3G minimal basis set. We conclude that the *net* error in the Π-Σ gap in NH_2 (and presumably in the corresponding states of the *N*-formamido radical) due to the lack of polarization functions *and* correlation energy differences is small if an extended sp basis set is used. (Bender and Schaefer have shown previously that the size of the energy gap in NH_2 is not affected significantly by configuration interaction.[7])

In comparisons of Π_N with Π_O and Σ_N with Σ_O, it is important to establish that the theoretical methods used do not overestimate the energy differences between double and single carbon-oxygen bonds relative to double and single carbon-nitrogen bonds. Unfortunately, this comparison is difficult to make due to the absence of experimental thermochemistry for nonconjugated C=N groups. The closest comparison possible involves the conversion of a C≡N triple bond in hydrogen cyanide to a single C-N bond in methylamine:

$$HCN + 2H_2 \rightarrow H_3CNH_2$$

For this process the 4-31G calculated energy[8] agrees very well with the experimental difference calculated using 0 K heats of formation and correcting the latter for zero-point vibrational energies:[8]

$$\Delta H(\text{exptl}) = -51.1 \text{ kcal mol}^{-1}$$

$$\Delta H(\text{4-31G}) = -52.9 \text{ kcal mol}^{-1}$$

$$\Delta H(\text{STO-3G}) = -76.5 \text{ kcal mol}^{-1}$$

Thus the STO-3G method, but not the 4-31G procedure, appears to overestimate the stability of carbon-nitrogen single bonds relative to triple bonds (and presumably relative to double bonds also). For the conversion of carbon-oxygen double bonds to single bonds, the 4-31G method again is superior:[8]

$$H_2CO + H_2 \rightarrow H_3COH$$

$$\Delta H(\text{exptl}) = -27.0 \text{ kcal mol}^{-1}$$

$$\Delta H(\text{4-31G}) = -31.6 \text{ kcal mol}^{-1}$$

$$\Delta H(\text{STO-3G}) = -46.8 \text{ kcal mol}^{-1}$$

There is some underestimation of the C=O strength relative to C-O in both cases. In summary, we can conclude that 4-31G calculations show a *slight* bias for the "O" forms over the "N" due to inherent errors in the method and that STO-3G calculations will probably be much less reliable than 4-31G computations in comparisons of the different forms.

To establish optimum geometries for the formamido free radical, STO-3G calculations were undertaken for planar Π and Σ states. (Convergence of the self-consistent field process to the state of interest required reordering of the molecular orbitals between iterations in some cases.) For both the lowest Π and Σ states, potential minima corresponding to *both* "N" and "O" forms were found; the calculated geometries are listed in Table II along with the relative energies computed by both the STO-3G and 4-31G methods.

The C-N-H angles in the Π_N and Σ_N geometries differ only slightly from the H-N-H angles in the comparable states of $NH_2\cdot$ (see Table I). For both the Π_O and Σ_O structures, the C-N-H angle is essentially tetrahedral.

Although the Π_N and Σ_N states are predicted to differ substantially in both energy and C-N-H angle, remarkably the predicted carbon-nitrogen bond length is identical in the two states as is the carbon-oxygen distance. The value of 1.218 Å for R_{CO} here is that expected for a C=O linkage (compare with 1.218 Å predicted for formamide[9]). The carbon-nitrogen distances of 1.403 Å are equal to that predicted for formamide.[9] Both basis sets agree in the prediction that the Π_N state is still lower in energy than is Σ_N, but that the gap between the states is considerably less than in $NH_2\cdot$. Presumably this differential improvement of about 16 kcal mol^{-1} by the Σ_N states is due to the conjugation of the two π electrons on the nitrogen, which can occur in the Σ_N state of the formamido radical as it does in formamide itself, but which cannot occur in $NH_2\cdot$. This interpretation is supported by the π-overlap populations involved: 0.113 for formamido (Σ_N), 0.115 for formamide, and 0.0 for $NH_2\cdot$ at the 4-31G level.

Although Σ_N is stabilized by conjugation, the computations by the two basis sets agree that it does not correspond to the global minimum in energy for a Σ state. In particular, the Σ_O form is predicted to be more stable than is Σ_N. The energy differences between the Σ minima, 10 kcal mol^{-1} according to 4-31G and 36 kcal mol^{-1} according to STO-3G, probably exceed the amounts by which the calculations inherently underestimate C=O bond strength relative to that for C-O.

Remarkably, the geometries calculated by the STO-3G basis set for the Π_O and the Σ_O states are virtually identical (see Table II). The carbon-nitrogen lengths are close to that expected for a purely double C=N bond (compare to 1.26 Å predicted[10] for $H_2C{=}NH$) and the carbon-oxygen bonds of 1.41 Å are long, as expected for essentially single bonds (compare to 1.386 Å predicted[9] for the O-C distance in $HO\text{-}CONH_2\cdot$). The predicted CNH angles are very close to that of 109° predicted[10] for $H_2C{=}NH$. The energies for the Π_O and Σ_O forms calculated by the 4-31G method are identical to within 0.2 kcal mol^{-1}, whereas the STO-3G basis set places the Σ_O form lower by 2.9 kcal mol^{-1}. Interestingly, the 4-31G energy for these two forms places them less than 2 kcal mol^{-1} above the global minimum for the radical, which is the Π_N form (Table II).

The near equality in energy between Σ_O and Π_O is consistent with the agreement in π-orbital overlap populations in the two forms:

Table II. Results for Formamido Radical

State designations	R_{CN}, Å	R_{CO}, Å	Angle C–N–H, deg	Relative energy,[a] kcal mol^{-1} By STO-3G	By 4-31G
Π_N	1.40_3	1.21_8	103	0.0	0.0
Π_O	1.28_0	1.41_0	108	−5.3	1.8
Π_a	(1.34)[b]	(1.30)[b]	(103)[b]	2.5	8.4
Σ_N	1.40_3	1.21_8	130	28.2	11.3
Σ_O	1.27_0	1.41_0	109	−8.2	1.6
50° twisted Π_N	(1.40_3)	(1.21_8)	(117)[c]		−1.1

[a] Relative to the planar Π_N form; a negative relative energy indicates that the form is predicted to be more stable than planar Π_N. Calculated energies of planar Π_N by STO-3G and 4-31G are −166.06223 and −168.01947 au, respectively. [b] Assumed values, not optimized. [c] Assumed value; this angle is optimum for the 90° twisted species according to 4-31G calculations.

Table III. Open-Shell Spin Densities Calculated Using 4-31G Basis[a]

Atomic orbital	Atom	Spin density for Σ_O	Σ_N	Π_N	Π_O	Π_a	45° twisted "Π_N"
1s	H_C	0.009	0.001	0	0	0	0.005
	H_N	0.002	0.020	0	0	0	0.001
2s	O	0.000	−0.001[b]	0	0	0	−0.002[b]
	N	−0.003[b]	0.082	0	0	0	0.001
	C	0.002	0.007	0	0	0	0.002
2pσ	O	0.966	0.031	0	0	0	0.011
	N	0.015	0.843	0	0	0	0.587
	C	0.010	0.017	0	0	0	0.008
2pΠ	O	0	0	0.086	0.933	0.152	0.028
	N	0	0	0.906	0.071	0.839	0.354
	C	0	0	0.007	−0.004[b]	0.009	0.008

[a] All geometries are planar except where indicated otherwise. [b] Negative spin densities occur in restricted open-shell theory due to the manner in which overlap population is split between orbital pairs.

	C=N	C–O
Σ_O	0.462	0.021
Π_O	0.464	0.028

In other words, the conjugation of a single π electron on oxygen with a C=N unit is predicted to differ insignificantly from conjugation of two π electrons with C=N. Since the characters of the orbital occupied by the unpaired electron in both Σ_O and Π_O, therefore, are equivalent, the two states are almost degenerate at their common geometry. In contrast the π-overlap population of 0.113 between carbon and nitrogen due to conjugation of two electrons with C=O in the Σ_N state is almost twice as large as that of 0.059 for a single electron on nitrogen conjugating with C=O in the Π_N state.

Since the C–N π-overlap population in the Π_N state was found to be rather small, we decided to investigate the possibility that rotation of the hydrogen (on N) about the C–N bond may be quite a facile process (in contrast to that for formamide, in which the rotation barrier is[10] about 27 kcal mol^{-1}). A limited search of the rotation surface indicates that the Π_N state is *stabilized* to the extent of 1.1 kcal mol^{-1} by rotating the hydrogen 50° about the C–N bond. A study of the overlap population changes which occur upon rotation to this angle indicate that the carbon–oxygen bond is strengthened by 0.06 e as is the nitrogen–hydrogen by 0.02 e, whereas the carbon–nitrogen bond is weakened by only 0.03 e. Since the 90° twisted conformation lies only 0.7 kcal mol^{-1} and the 180° twisted lies only 5 kcal mol^{-1} in the energy above the global minimum at 50°, rotation about the C–N bond should occur in the Π_N ground state of the radical. Unfortunately a similar surface cannot be computed for the Σ_N state of the radical, since, for twist angles of other than 0 and 180°, the Π and Σ states become of identical symmetry and thus an SCF solution to the upper of these states cannot be obtained.

Finally, we explored the possibility that the allylic form Π_a is the true potential minimum for the ground state of the radical. Bond length optimization at the STO-3G level was not attempted due to the known "doublet instability" problems of minimal basis sets in dealing with the isoelectronic allyl free radical.[11] Instead, the more elaborate (and more costly) 4-31G basis set was employed. However, *no potential minimum corresponding to an "allylic" Π_a structure could be found.* In particular, holding the carbon–oxygen distance at "reasonable" allylic values of 1.31 and 1.34 Å for a range of carbon–nitrogen bond lengths yields a potential minimum only for the "single-bond" carbon–nitrogen distance of 1.39 Å in both cases. Similarly, use of an "intermediate" carbon–nitrogen bond length of 1.34 Å yields only one energy minimum when the carbon–oxygen distance is varied, that for R_{CO} = 1.22 Å, i.e., the carbon–oxygen "double bond" value. These results indicate that there exists no stable "allylic" form for the ground state of the formamido radical according to 4-31G calculations.

For comparison between different states and for possible assistance in the interpretation of the ESR spectra of such radicals, the unpaired electron spin densities for potential minima are listed in Table III. Even in the Σ forms, the unpaired electron seems highly localized on either nitrogen or oxygen and the classical valence-bond electron diagrams shown above are quite appropriate. It is interesting to note that out-of-plane rotation of the H_N in the Π_N state does not result in delocalization of the unpaired spin density away from the nitrogen, but rather increases the total $2p_N$ unpaired density total (see Table III). The experimental ESR spin density data[2] for formamido derivatives seems consistent with the Π_N values in both planar and twisted geometries, but not with the values for Σ_O or Π_O. It is difficult to decide whether the spin densities predicted for Σ_N are consistent with the experimental ESR data, since the predicted $2s_N$ unpaired electron population is rather small.

Given that the present results indicate that conjugation is far less important to the formamido free radical than it is to the parent formamide system, one would expect that the N–H bond dissociation energy in the latter should be greater than in nonconjugated amines. This expectation is substantiated by STO-3G calculations which predict that the bond energy of formamide is some 7.4 kcal mol^{-1} *greater* than calculated[12] for the reaction $CH_3NH_2 \rightarrow CH_3NH\cdot + H\cdot$. Since the difference in dissociation energies is smaller than is the difference in CN bond rotation barriers, however, there must exist energy changes in the σ bonds which occur upon dissociation and which differentially favor the conjugated over the saturated systems.

In conclusion, the ab initio calculations described above predict that the ground state of the formamido radical is almost doubly degenerate. The two lowest states are of identical symmetry in the nonplanar geometry (which is probably preferred by one of them at least), but of different symmetry, Σ and Π, in the planar conformations. Further, the Π state is predicted to possess two potential minima which are almost degenerate also, whereas the second geometry for the Σ state lies significantly above the first in energy. Presumably the two low-lying states would both be populated except at the lowest temperatures if the predicted energetics are close to correct. It should be emphasized that no final conclusions concerning relative stabilities of closely spaced states can be made from these calculations. More advanced calculations, which would include both polarization functions and configuration interaction, are required before definitive conclusions can be drawn. (In addition, the *relative* stability order presumably can be switched by substituting suitable groups for the hydrogen atoms.) According to present calculations, the allylic form Π_a evidently does not correspond to a potential minimum on the energy surface for the ground state. Thus Π_N and Π_O do not represent merely valence-bond structures which contribute to a resonance hybrid, but correspond closely to the dominant structures at the two geometries which are potential minima on the Π surface. The quantum-mechanical reason for this behavior is not clear.

References and Notes

(1) Research supported by the National Research Council of Canada.

(2) See (a) T. Koenig, J. A. Hoobler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russell, *J. Am. Chem. Soc.*, **96**, 4573 (1974); (b) W. C. Danen and R. W. Gellert, *ibid.*, **94**, 6853 (1972), and references cited therein.

(3) E. Evleth, P. Horowitz, and T. Lee, *J. Am. Chem. Soc.*, **95**, 7948 (1973).

(4) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(5) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(6) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).

(7) C. F. Bender and H. F. Schaefer III, *J. Chem. Phys.*, **55**, 4798 (1971).

(8) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(9) J. E. Del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, **36**, 195 (1973).

(10) N. C. Baird and H. B. Kathpal, unpublished calculations.

(11) See K. Van Der Meer and J. J. C. Mulder, *Chem. Phys. Lett.*, **34**, 189 (1975), and references cited therein.

(12) Absolute values for the dissociation energies are not quoted here, as they are likely to be quite inaccurate in calculations which do not include configuration interaction. See, for example, the results in W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).

Optical Activity of Uridylyl-(3′,5′)-adenosine. Crystal Structures and Solution Conformation

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Abstract: Circular dichroism and absorption spectra have been calculated for neutral and protonated uridylyl-(3′,5′)-adenosine (UpA) in each of the observed crystalline forms and in two model dinucleotide geometries for the purpose of assessing the importance of crystal structure contributions to the solution conformation of this dinucleotide. Comparison of the calculated optical properties with experimental spectra indicates that the crystal geometries are not the dominant structures in any distribution of conformations which the molecule assumes in aqueous neutral solution. However, one of the crystal structures may be important at low pH. The model dinucleotide geometries give spectral shapes similar to those observed experimentally, but with larger intensities. The optical activity was calculated by both the coupled oscillator and generalized susceptibility methods utilizing monomer parameters from either experimental data or theoretical π-electron calculations. These methods are compared and the geometric origin of the UpA circular dichroism is discussed.

I. Introduction

Of the three published dinucleotide crystal structures,[1-4] only that of uridylyl-(3′,5′)-adenosine (UpA) is marked by conformations distinctly different from model RNA[5] or DNA[6] dinucleotide geometries. Two UpA structures, designated UpA 1 and UpA 2, are found in the unit cell and are characterized by open conformations with a distance between bases (R_{12}) of 6.8 and 11.8 Å, respectively. By contrast, crystalline adenylyl-(3′,5′)-uridine (ApU) adopts a right-handed incipient helical conformation[3] similar to the RNA 11 form ($R_{12} \approx 4.6$ Å). It has been suggested that the UpA crystal structures are two of seven basic conformations from which the secondary structures of all polynucleotides can be generated[7] and that UpA 1 may be an important component in the structure of tRNA loops.[1,2,7] In this paper we utilize optical criteria to investigate whether the UpA conformations found in the crystal contribute to the conformation(s) inferred to be present in aqueous solution.

Comparison of the predicted optical properties of UpA 1 and UpA 2 with the solution spectra is important for several reasons. Conformational energy calculations indicate a broad