Theoret. Chim. Acta (Berl.) 60, 327-337 (1981)

THEORETICA CHIMICA ACTA

The Effect of Solvent on the Internal Rotation of Formamide: A CNDO/2-Solvaton Method Study*

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The effect of solvent on the barrier to internal rotation of formamide had been studied using a solvaton method within the CNDO/2 parameterization. The experimental trend of increasing rotational barrier with increasing solvent dielectric constant has been reproduced. A critical examination of the manner in which interactions between solute and solvent were allowed to modify solute energies and the polarization of the solute wavefunction was performed.

Key words: Solvation – CNDO – Solvaton – Formamide.

1. Introduction

The prediction of the geometrical conformations of molecules has been a goal of quantum chemistry for a long time. An important group of problems in this area have been those associated with the structure of polypeptides. The formamide molecule is the simplest representative of this class of compounds. Study of the properties of the amide bond in this molecule, particularly the rotational barrier, may help in developing a better understanding of the properties of more complicated oligo- and polypeptides in which deformation of the amide linkage may occur.

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* Work performed while A.J.D. was a visting scientist at the Polymer Institute of the Slovak Academy of Sciences sponsored under the exchange program between the U.S. National Academy of Sciences and the Czechoslovak Academy of Sciences during the summer of 1980.

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0040-5744/81/0060/0327/$02.20

Table 1. Experimental barrier to internal rotation in formamide by NMR [1]

Solvent	Barrier (kJ/mole)	Dielectric constant[a]
Neat	79.1 ± 4.2	109 (20°C)
Water	89.2 ± 5.4	78.54 (25°C)
Acetone	79.7 ± 8.0	20.7 (25°C)
Dioxane	70.3 ± 4.2	2.209 (25°C)

[a] Taken from the CRC Handbook of Chemistry and Physics

The barrier to internal rotation is a function of its environment. NMR experiments [1] indicate that the barrier to internal rotation increases with increasing dielectric constant of the medium. A set of barriers and media are given in Table 1. Extrapolation to $\varepsilon = 1$ for vacuum suggests that the isolated molecule should have a rotational barrier of approximately 70 kJ/mole with an error of approximately 5 kJ/mole. The barrier of an isolated molecule, and other properties of an isolated molecule, are not of the greatest importance in a theoretical study in this problem area. The structural properties of amide containing compounds that have biological significance are properties of the molecule in aqueous solution. Theoretical methods should provide a means of incorporating the solvent in the technique or for correcting the calculated values for the presence of solvent.

Theoretical calculations seeking to reproduce the rotational barrier of an isolated formamide molecule have not been particularly successful. A sample of calculations of the barrier is presented in Table 2. Only those of Peters and Peters [3] returned low estimates. These calculations employed an STO-3G basis set with a flat geometry. Full geometry optimization including angles (not done in the partially optimized calculation) predicted a bent molecule in the lowest energy conformation [7]. A calculation of the barrier to internal rotation using a flat molecule and an STO-3G wave function fails to include the energy of stabilization of the bent form. Coincidentally, the Peters' calculation of the rotational barrier happens to be close to the experimental barrier. The GVB calculation of Harding

Table 2. Calculated barrier to internal rotation of formamide

Barrier (kJ/mole)	Type of calculation	Reference
83.3, 85.5	Multiple zeta SCF without *d* functions	2
81.2, 91.0	Multiple zeta SCF with *d* functions	2
78.2	STO-3G SCF frozen geometry	3
62.1	STO-3G SCF partial geometry optimization	3
76.2	Generalized valence bond (GVB)	4
82.5	FSGO Molecular fragment	5
97.1	4-31G Geometry optimized 270° twist	6, 7
84.2	4-31G Geometry optimized 90° twist	6, 7
103.4	4-31G Frozen geometry	8

and Goddard [4] is also close to the experimental value. Since the GVB technique partially correlates the wavefunction in the bonding regions, it does not yield a simple single configurational SCF wavefunction like those used in the other calculations mentioned in Table 2.

A few attempts have been made to study the effect of solvation on the properties of a simple amide. Germer [10] had examined N,N-dimethylformamide with his solvaton theory and found an increasing rotational barrier with increasing solvent dielectric constant. It is surprising that this had occurred since the signs he placed before the solvaton interaction terms were the opposite of those used in the present calculations [12]. McCreery, et al. [15] studied the hydration of formamide using a point charge model based on FSGO calculations. They did not attempt to calculate the rotational barrier. The Sinanoglu solvation theory had been used with the solute treated as if it were a point dipole in a continuum model of the solvent [16], and it was demonstrated that within this model solvation increased the magnitude of the rotational barrier of formamide. A supermolecule calculation within a PCILO treatment had also been used to study the rotational barrier of formamide [17] which was found to have increased with solvation. This last paper will be discussed more fully in a subsequent section of this report.

2. Calculations

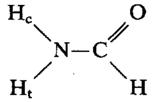
In order to calculate a barrier close to that expected on the basis of experiment, it would be desirable to include the effect of the liquid medium on the calculated barrier. A method intended to include solvent effects ought to be able to calculate barriers to internal rotation which increase with increasing solvent dielectric constant as indicated by experiment.

In this study of the rotational barrier of formamide, an approximate CNDO/2 method within the solvaton model [9–14] was applied. In order to avoid circumlocutions in the discussion to follow, the solvaton model within the CNDO/2 parameterization will be referred to as the "CNDO/2(S)" model. This model was chosen for study because it is anticipated that any future applications of theoretical methods to the properties of substances of biological interest in solution will most likely require the use of some form of semi-empirical calculation methods.

In the CNDO/2(S) method, the presence of a polarizable solvent having dielectric constant ε is represented by image charges in the continuum, the solvatons, with one solvaton for each atom in the solute model. The charge of the solvaton is equal in magnitude and opposite in sign to the net charge on the atom with which it is associated. The γ-integral formalism of CNDO is used to estimate solvaton-electron and solvaton-core interactions. In the calculations reported here, the γ-integrals took the values $\gamma_{\mu\mu}$ for the interaction of an atom μ with its own solvaton and $\gamma_{\mu\nu}$ for the interaction of atom μ with the solvaton associated with atom ν, $\mu \neq \nu$ [12]. A second set of calculations within the CNDO/2(S) model was attempted in which the γ between an atom and its own solvaton was evaluated by considering them to be separated by the van der Waals radius of the atom; the γ between an atom and the solvaton of another atom was evaluated using the separation of the interatomic distance of the two atoms in the molecule plus the van der Waals radius of the atom associated with the solvaton [13, 14]. This second model will be referred to as "CNDO/2(S–R)".

The geometries chosen were those obtained with the 4-31G wavefunctions including geometry optimixation [7, 8]. Three geometries were considered: the flat molecule, the unrelaxed twist in which all geometrical parameters were retained from the flat molecule except for rotating the —NH_2 group so that it became perpendicular to the —CHO plane, and the relaxed twist based on a 270° rotation. The 270° rotation has the higher barrier in the 4-31G basis. Bond lengths and angles for each geometry are recorded in Table 3. These values were chosen because there is disagreement concerning whether the flat conformation is really flat and because the STO-3G geometry optimized calculation for the lowest energy conformation predicts an excessively bent molecule [7]. The molecule appears to be flat with a rather low force constant for an —NH_2 wag deformation. Geometry optimized calculations on formamide in the CNDO approximation predict an even more extraordinarily twisted molecule [18]. In contrast, geometry optimized INDO calculations predict a flat geometry.

Table 3. Geometrical parameters of formamide conformations



Parameter	Flat[a]	Relaxed twist[b]
r(C—O), Angstroms	1.216	1.196
r(C—N), Angstroms	1.346	1.412
r(C—H), Angstroms	1.081	1.084
r(N—H_t), Angstroms	0.990	0.998
r(N—H_c), Angstroms	0.993	0.998
<NCO	124.7°	121.4°
<NCH	113.7°	117.9°
<H_cNC	119.5°	115.8°
<H_tNC	118.6°	114.0°
<H_cNCO, dihedral	0.0°	68.7°

[a] The geometrical parameters for the unrelaxed twist are identical to those for the flat molecule with the exception that the dihedral angle <H_cNCO is 90°.

[b] The angles reported in Ref. 6 at the —NH_2 group are misinterpreted. The angle given as γ in this paper is actually the dihedral angle between the HN plane and the plane bisecting the H_cNH_t triangle. This means that the HNH angle *contracts* on rotation which is more realistic. The breaking of the conjugation between the N and the carbonyl pi bond should give the lone pair more sp^3 character

Since the primary objective of this study was to see whether the solvaton method of including solvent effects could be used to examine the conformational effects of solvation, an important consideration was the choice of a reasonably good set of structures to be used in all of the calculations to avoid complications in subsequent analyses.

3. Results

CNDO/2 *with Solvaton Calculations of Electrostatic and Polarization Contributions*: The CNDO/2(S) model was applied to the formamide molecule in solvents with dielectric constants 2 and 80, corresponding to dioxane and water, respectively. The flat, unrelaxed twisted, and relaxed twisted conformations were studied. In the CNDO/2(S) calculations reported here, the first approximation for the γ-integrals was used. $\gamma_{\mu\mu}$ was chosen as the appropriate γ for an atom interacting with its own solvaton. $\gamma_{\mu\nu}$ was chosen for an atom interacting with the solvaton of another atom [12]. These are the same γ-integrals used in the

Table 4. Calculations of barrier of rotation of formamide using the solvaton[a] model in the CNDO/2 parameterization

Conformation	Isolated	Dioxane ($\varepsilon = 2$)	Water ($\varepsilon = 80$)
Flat			
Electronic energy (a.u.)	−79.83453	−80.04109	−80.34040
Total energy[b] (a.u.)	−39.30066	−39.32326	−39.36486
Solvation energy[c] (a.u.)		−0.01978	−0.04815
Unrelaxed twist			
Electronic energy (a.u.)	−79.75646	−79.94991	−80.23876
Total energy[b] (a.u.)	−39.27413	−39.29290	−39.32794
Solvation energy[c] (a.u.)		−0.01642	0.04036
Barrier[b] (kJ/mole)	69.7	79.8	97.0
Barrier[c] (kJ/mole)		78.5	90.2
Relaxed twist			
Electronic energy (a.u.)	−79.41387	−79.58209	−79.83866
Total energy[b] (a.u.)	−39.28534	−39.30141	−39.33162
Solvation energy[c] (a.u.)		−0.01406	−0.05689
Barrier[b] (kJ/mole)	40.3	57.4	87.4
Barrier[c] (kJ/mole)		55.3	75.6

[a] Using $(\varepsilon - 1)/2\varepsilon$ as the weighting factor in the solvaton interaction term and choosing the gamma integrals to be $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$. This is the CNDO/2(S) model.

[b] Includes core–core repulsions and solvaton–solute interactions but excludes solvaton–solvaton interactions.

[c] Solvaton–solute electrostatic interactions are used to estimate solvaton–solvaton interactions by the relationship

$$E(\text{solvaton–solvaton}) = -(1/2)\,E(\text{solvaton–solute})\,(\varepsilon - 1)/(2\varepsilon).$$

and then the total solvation energy is given by the sum of the solvaton–solvaton energy and the solvaton–solute energy contributions. See Ref. 19 for further details

CNDO/2 calculation of the unsolvated molecule. Interactions between the solute and solvatons were weighted by the factor $k_\varepsilon = (\varepsilon - 1)/2\varepsilon$. Results of this calculation are presented in Table 4. Inspection of this table indicates that the solvaton calculation is capable of reproducing the trend of increasing rotational barrier with increasing solvent dielectric constant.

The barriers within the CNDO/2(S) model were calculated both without and with the inclusion of an estimate for the solvaton interactions among themselves. The energy of the solvent–solvent interactions, $E_{\text{sv–sv}}$, can be taken to be the negative of the solute–solvent interactions, $E_{\text{so–sv}}$, weighted by a scaling factor depending on the value of the dielectric constant of the medium. We have chosen to use

$$E_{\text{sv–sv}} = -(1/2)E_{\text{so–sv}}\frac{\varepsilon - 1}{2\varepsilon} \tag{1}$$

in order to obtain the total solvation energy including the solvaton–solvaton interaction

$$E_{\text{solv}} = E_{\text{so–sv}} + E_{\text{sv–sv}} = E_{\text{so–sv}}\left(1 - (1/2)\frac{(\varepsilon - 1)}{2\varepsilon}\right). \tag{2}$$

Estimates of the solvent–solvent interactions can also be weighted by $k_\varepsilon = 1 - (\varepsilon)^{-1}$ and $k_\varepsilon = 1 - (\varepsilon)^{-1/2}$ as suggested by Constanciel and Tapia [19]. These were also performed and will be discussed in a subsequent section.

In general, the correction for interactions of solvatons among themselves increased with increasing dielectric constant of the solvent. However, the correction did not affect the overall trend of the calculated rotational barriers with solvent dielectric constant.

Within the CNDO/2(S) model, calculated barriers for the flat molecule going to the unrelaxed twist appear to be consistently closer to experimental values than the changes in energy from the flat to the relaxed twisted conformation. In the latter case, barriers are seriously underestimated. One may surmise that the low barriers may be due to the fact that the flat geometry is far from the optimized CNDO geometry while the relaxed twist might be close to the optimized CNDO geometry for that conformation. If solvaton interactions are ignored, barriers are predicted to be greater than if they were not ignored.

A small set of calculations within the CNDO/2(S) model were performed using the second set of approximations for solvaton–atom interactions [13, 14] using water as the solvent. This set of calculations corresponds to the CNDO/2(S-R) model in which the van der Waals radii were included in the calculation of the integrals. The change in the γ values led to generally smaller changes in electronic energy and other quantities related to the energy for all three conformations calculated by CNDO/2(S) model reported in Table 4.

In the CNDO/2(S-R) calculations barriers to internal rotation to the unrelaxed twisted and relaxed twisted conformations were 71.9 and 56.4 kJ/mole, respectively, ignoring solvent interactions, and 71.4 and 52.4 kJ/mole, respectively, including solvent interactions. The trend of the barrier with dielectric constant is clear for the relaxed conformation, but it is barely discernable for the unrelaxed conformation in spite of the large change in dielectric constant from one in the vacuum to 80 in water.

While retaining the inclusion of the van der Waals radii in the calculation of the γ-integrals for the solvatons, the weighting of the solvaton-solute potential energy integrals was doubled to $1-(\varepsilon)^{-1}$ and also was changed to $1-(\varepsilon)^{-1/2}$ as suggested by Constanciel and Tapia [19]. In both cases, totally unrealistic results were obtained in which the electron occupancies of the nitrogen, carbon, and the carbonyl hydrogen approached nearly complete octets (pair for hydrogen) while the carbon and the two hydrogens attached to the nitrogen were stripped of electrons. Further calculations with these weighting factors were not pursued.

In the CNDO/2(S) calculations, the net stabilization of the formamide molecule in the solvent was achieved through the lowering of the electronic energy by interaction with the solvatons. The electron–solvaton interactions became more negative as the solvent dielectric constant increased. This was reflected in both the total electronic energy and the energies of the individual molecular orbitals. On the other hand, the core–solvaton interactions became more positive as solvent dielectric constant increased.

The presence of solvatons polarized the wavefunction of the solute. In the flat molecule, the oxygen atom became more negative while the carbon and carbonyl hydrogen became more positive as dielectric constant increased. The nitrogen atom became more negative as well, but it stayed less negative than the oxygen suggesting that the oxygen would continue to be the more likely place for proton attack [20]. The nitrogen became more negative at the expense of the carbon and the amine hydrogens.

The wavefunctions obtained in the two models, the CNDO/2(S) and the CNDO/2(S-R), are polarized somewhat differently. As had been previously mentioned, changes in energy using the CNDO/2(S-R) model were smaller than those obtained in the CNDO/2(S) model. The rotational barrier was, likewise, affected only in a very small way in the CNDO/2(S-R) model. When van der

Table 5. Atomic charges in formamide

Atom	Solvent and calculation method No Solvent, CNDO/2	Water, CNDO/2(S)[a]	Water, CNDO/2(S-R)[a]
N	−0.248	−0.308	−0.321
C	0.362	0.536	0.486
O	−0.321	−0.508	−0.406
H (amine)	0.134	0.173	0.167
H (amine)	0.126	0.164	0.158
H (carbonyl)	−0.052	−0.057	−0.084

[a] Solvaton interactions were weighted by $(\varepsilon-1)/2\varepsilon$

Waals radii were included in the γ calculation in the CNDO/2(S-R) model, the nitrogen atom and the carbonyl hydrogen became more negative than they were calculated to be in the CNDO/2(S) model in which the γ's were unmodified from the original CNDO usage. On the other hand, the carbon and oxygen atoms have electron occupancies in the CNDO/2(S-R) model close to electrical neutrality. Atomic charges in some of the calculations are reported in Table 5. In the cases previously mentioned in which $1-(\varepsilon)^{-1}$ and $1-(\varepsilon)^{-1/2}$ had been used as the weighting of the solvaton interactions [19], the solute became so polarized that the electron occupancies became unrealistic. The electron occupancies were those associated with nearly complete ionic bonding in the molecule.

4. Discussion

4.1. Comparison with a Supermolecule Model.

The results obtained in the CNDO/2(S) calculation can be compared with those obtained using the PCILO method in the supermolecule treatment of hydration in which the supermolecule consisted of one formamide and five water molecules [17] Although the two ways of calculating the effect of solvation are quite different, they both predicted an increase in the barrier when the formamide molecule was put into water. However, the partition of the barrier energy into components attributable to the isolated formamide, formamide–solvent interactions of an electrostatic and polarization origin, and interactions entirely within the solvent leads to different values for these contributions in the two methods.

In Table 6 are reported the contributions to the barrier in water from the solute–solvent and solvent–solvent interactions by the two methods being compared. In the PCILO method, nearly equal positive contributions to the barrier from the solute–solvent and solvent–solvent interactions had been found. This was not the case in the CNDO/2(S) calculation. The contribution of the formamide–solvaton interactions is positive and nearly four times larger than the magnitude of the solvaton–solvaton contribution which is negative in sign in the CNDO/2(S) calculation. This is a direct result of using the Constanciel and Tapia formula for calculating solvaton–solvaton interactions.

Table 6. Comparison of CNDO/2(S) and PCILO/supermolecule calculations of the barrier to internal rotation of formamide

	Type of calculation	
Partitioned barrier	CNDO/2(S)	PCILO [17]
ΔE_F, Isolated molecule (kJ/mole)	69.7	66.1
$\Delta E_{F\text{-}W}$, Solute-solvent (kJ/mole)	27.3	13.0
$\Delta E_{W\text{-}W}$, Solvent-solvent (kJ/mole)	−6.8	15.9

Because of the approximate character of the methods used, it is difficult to estimate the extent to which the results reported here correspond to genuine solvation effects. One should note that the presence of five water molecules in the primary solvation shell used in the PCILO calculation is not the optimal situation. Optimization of the position of the fifth water molecule places it outside of the primary solvation shell [21]. Using an inappropriate distribution of water molecules will affect the calculation of both solute–solvent and solvent–solvent interaction energies. The CNDO/2(S) method could be subject to criticsm as well in that the representation of the solvent by charges placed outside of the molecule ignores hydrogen bonding and other aspects of solvent structure. This implies that changes attributable to the entropy of the solvent are likely to be misrepresented. The sole estimate of solvent interactions is a function of the polarization of the wavefunction and this, in turn, depends on the way that the γ-integrals are calculated and used.

4.2. Energy and Polarization Effects in the CNDO *Calculation*

The solvaton used in the CNDO calculation is a pseudoatom that has a charge equal in magnitude and opposite in sign to that of the atom in the solute with which it is associated. There charges are calculated using a Mulliken population analysis. However, it is more than merely a point charge since there is ambiguity about its position. If one considers just the atomic orbitals of the atom with which the solvaton has been associated, potential energies of the electron–solvaton interactions will depend only on the distance of the atom from the solvaton and not on the orientation. The result would be as if the potential associated with the solvaton charge were in force in every direction around the atom in question. Instead of a physically more realistic model in which the solvent charges were distributed over the surface of a region (e.g. a cavity model [22]), one obtains a situation in which the solvaton behaved as if it were of that region at every point. This can result in an excessive lowering of the energy of the electronic wave function when solvatons are introduced. The energy lowering will have its most important contribution from atoms with net negative charge and positively charged solvatons.

When the γ-integral calculation in the CNDO/2(S) model is changed from the original method to the modified method in which the van der Waals radii were included, the energy is affected primarily by the reduction of the magnitude of the γ-integrals used to describe intersolvaton interactions and the interactions involving an electron on one atom and the solvaton associated with another atom. The interaction between the solvaton and the electrons on the atom with which it is associated is changed to a lesser extent.

The effect of polarization on the wavefunction differs between the CNDO/2(S-R) and the CNDO/2(S) models. The effect of polarization is diminished for the C, O, and amine hydrogens when the van der Waals radii are included. However, for the nitrogen and carbonyl hydrogen, the polarization is enhanced. One may interpret this behavior as being caused by a change in the ratio between attractive interactions for an atom with its own solvaton and repulsive interactions between cores and solvatons.

The CNDO/2(S) method could develop difficulties because it does not include many of the integrals normally included in an *ab initio* study because of the application of the zero differential overlap approximation. The most important class of omitted integrals are the three-center one-electron potential energy integrals involving orbitals on two atoms and a charge in the region where the solvent is expected to be. Although these integrals are systematically excluded in the ZDO approximation, they would help in more accurately representing the electrostatic potential around a molecule, in particular that part contributed by the overlap bonding distribution of electrons. The inclusion of these integrals is a principle reason why the Giessner-Prettre and Pullman [23] approximation in which the CNDO wavefunction is deorthogonalized and all potential energy integrals are calculated has been successful in producing potential maps in good agreement with those calculated from *ab initio* STO-3G wavefunctions. Departures from rigorous application of the CNDO method, especially if they involve either relaxation of the ZDO approximation or introducing a more careful representation of the ZDO approximation or introducing a more careful representation of the solvent, are not without subtleties. These questions are under investigation in the laboratories of the authors [24].

These last points are rather important if one wishes to optimize geometries. *Ab initio* calculations can easily become prohibitively expensive. Study of the changes in optimal geometries of reasonably sized molecules, especially molecules of biological interest, under the influence of solvent will probably require approximate molecular orbital methods.

5. Conclusions

The CNDO/2 method incorporating the simple solvaton model of solvation as originally proposed [12] reproduced reasonably well the experimental trend of the barrier to internal rotation with the dielectric constant of the solvent.

The success of the CNDO/2 calculations was not complete. The polarization of the wavefunctions in the approximate method depended on the choices made for the γ-integrals between atoms and solvatons. Modification of the solute–solvent interaction by introducing van der Waals radii (in the CNDO/2(S-R) model) reduced the stabilization energy. This has helped in some cases to reproduce better experimental solvation energies [14]. However, in the present example, the effect on the rotational barrier seems to be underestimated by this model. In addition, use of the weighting factors $1-(\varepsilon)^{-1}$ and $1-(\varepsilon)^{-1/2}$ instead of $(\varepsilon-1)/2\varepsilon$ gave unrealistic results.

The polarization of the wavefunction is strongly affected by the degree of interaction between the most electronegative atoms and their positive solvatons permitted in the model chosen. These interactions are insufficiently compensated since the solvaton represents a uniform solvent charge associated with its corresponding atom in the solute and since many integrals normally included in the *ab initio* calculation were not calculated at all because of the ZDO approximation.

It is prudent to anticipate that these problems, and similar ones, will also be present in the application of solvation models in which the solvent is simulated by a more complex charge distribution than a set of simple solvatons (e.g. a cavity model [22]) to approximate wavefunctions obtained using the CNDO or INDO methods. The effects of these problems need to be accessed when the model is extended [24].

The fact that problems of this nature exist for the CNDO/2 calculations is not due to the fact that solvation is being studied. Rather, the problem seems to have arisen from the application of the ZDO approximation in order to enable one to calculate wavefunctions in an expeditious and inexpensive manner. One is confronted with the perennial problem of finding an acceptable way of avoiding the expensive calculations associated with *ab initio* work while yet obtaining a good wavefunction. This is independent of the question of solvation.

Acknowledgement. One of us (A.J.D) wishes to thank the U.S. National Academy of Sciences and the Slovak Academy of Sciences for the opportunity to participate in the exchange scientist program. Thanks also to Ing. Juraj Tkac and Ing. Pavel Majek for assistance in using the computer programs of the institute and to Dr. Ondrej Kysel for helpful discussions.

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Received April 22, 1981