the case. One possibility is that the photochemical products are formed in a radiationless transition from the $^3(\pi,\pi^*)$ state with a planar enone chromophore to the ground state of the products with a very different geometry. This, however, seems unlikely for two reasons. First, the Franck–Condon factors for such a radiationless transition would be very unfavorable. Second, chemical evidence suggests that the photochemistry proceeds on a nanosecond time scale and if this were occurring from the zeroth vibrational level of the lowest triplet, then the phosphorescence would have a very short lifetime and a very low quantum yield; in fact, it would be unobservable. The more likely possibility is that geometry changes leading to products occur along pathways that are inaccessible at 77 or 4 K, where strong phosphorescence is observed, but which are thermally activated at room temperature, where the photochemistry is observed.

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References and Notes

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(2) (a) K. Schaffner, *Pure Appl. Chem.* **33**, 329 (1973); (b) *ibid.*, **16**, 75 (1968).
(3) O. Jeger and K. Schaffner, *Pure Appl. Chem.*, **21**, 247 (1970).
(4) W. A. Noyes, Jr., G. S. Hammond, J. N. Pitts. Jr., and K. Schaffner, *Adv. Photochem.* **4**, 81 (1966).
(5) H. E. Zimmerman, *Science*, **153**, 837 (1966).
(6) H. E. Zimmerman and R. D. Little, *J. Chem. Soc., Chem. Commun.*, 689 (1972).
(7) S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 677 (1970).
(8) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, 2436 (1969).
(9) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).
(10) G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).
(11) P. Keller, F. G. Eggart, H. Wehrili, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **50**, 2259 (1967).
(12) H. E. Zimmerman and N. Lewin, *J. Am. Chem. Soc.*, **91**, 879 (1969).
(13) H. E. Zimmerman and D. R. Amick, *J. Am. Chem. Soc.*, **95**, 3977 (1973).
(14) R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Am. Chem. Soc.*, **95**, 4346 (1973).
(15) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972).
(16) W. C. Agosta and A. B. Smith, III, *J. Am. Chem. Soc.*, **93**, 5513 (1971).
(17) L. E. Friedrich and G. B. Schuster, *J. Am. Chem. Soc.*, **94**, 1193 (1972).
(18) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **91**, 5091 (1969).
(19) R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 2023 (1967).
(20) P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971).
(21) D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **90**, 5137 (1968).
(22) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Am. Chem. Soc.*, **92**, 1786 (1970).
(23) G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, **93**, 3129 (1971).
(24) C. R. Jones, D. R. Kearns, and R. M. Wing, *J. Chem. Phys.*, **58**, 1370 (1973).
(25) C. R. Jones, F. Pappano, A. H. Maki, and D. R. Kearns, *Chem. Phys. Lett.*, **13**, 521 (1972).
(26) C. R. Jones, A. H. Maki, and D. R. Kearns, *J. Chem. Phys.*, **59**, 873 (1973).
(27) R. M. Hochstrasser, *J. Chem. Phys.*, **39**, 3153 (1963).
(28) A. Nakahara, M. Koyanagi, and Y. Kanda, *J. Chem. Phys.*, **50**, 552 (1969).
(29) S. Dym, R. M. Hochstrasser, and M. Schafer, *J. Chem. Phys.*, **48**, 646 (1968).
(30) J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, **35**, 184 (1963).
(31) R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Am. Chem. Soc.*, **93**, 6715 (1971).
(32) J. Laane, private communication.
(33) P. Petelenz and B. Petelenz, *J. Chem. Phys.*, **62**, 3482 (1975).
(34) R. N. Jones, F. Herling, and E. Katzenellenbogen, *J. Am. Chem. Soc.*, **77**, 651 (1955).
(35) R. N. Jones, B. Nolin, and G. Roberts, *J. Am. Chem. Soc.*, **77**, 6331 (1955).
(36) S. Weinmann and J. Weinmann, *C. R. Acad. Sci.*, **256**, 2578 (1963).
(37) A. Devaquet, *J. Am. Chem. Soc.*, **94**, 3160 (1972).
(38) W. A. Case and D. R. Kearns, *J. Chem. Phys.*, **52**, 2175 (1970).
(39) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 966 (1975).
(40) R. Hochstrasser and P. Prased, *J. Chem. Phys.*, **56**, 2814 (1972).

An ab Initio Investigation of (Formamide)$_n$ and Formamide–(H$_2$O)$_n$ Systems. Tentative Models for the Liquid State and Dilute Aqueous Solution

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Abstract: Ab initio molecular orbital calculations (STO-3G) have been made on large systems in an attempt to simulate the hydrogen bonding of formamide in the liquid state and in dilute aqueous solutions. Although the relationship between the model systems (formamide + $(H_2O)_4$ molecules representing an aqueous-formamide solution and $(\text{formamide})_5$ molecules representing the liquid state of pure formamide) and the liquid state is crude, the calculations appear to be in reasonable agreement with experimental results and provide insight into the bonding and structure of these solutions not obtainable by experiment.

The importance of hydrogen bonding in biological systems has led to a number of experimental and theoretical studies of model compounds capable of participating in the type of hydrogen bonding found in these systems. Amides have been chosen as model systems because they are the simplest molecules that exhibit peptide bonding. Information gained concerning hydrogen bonding in amide and aqueous-amide solutions, therefore, should give insight into the hydrogen-bonding mechanisms found in the more complex biological systems. Amides have also been used extensively as solvents and as solvent components in mixed solvent systems; however, the bonding and structure of these amide and aqueous-amide solutions are still not well understood.[1]

The interpretation of experimental results appears to be somewhat inconsistent with respect to the relative strength of amide and amide-water hydrogen bonds.[2-5] Nuclear magnetic resonance studies in our laboratory of amide and aqueous-amide solutions over the complete mole fraction range did not permit the determination of all of the hydrogen-bond sites on the amides or their relative importance in solution.[6-8]

Table I. Mulliken Populations and Interaction Energies of Formamide and Formamide-Water

System	C	N	H(C-H)	O	H(cis)	H(trans)	Interaction energy, kcal
F	5.7619	7.4443	0.9424	8.2917	0.7734	0.7862	
F-H_2O(1)	5.7427	7.4385	0.9248	8.3003	0.7665	0.7769	6.8
F-H_2O(1,2)	5.7240	7.4354	0.9134	8.3112	0.7465	0.7695	13.4 (14.4)[a]
F-H_2O(1,2,3)	5.7275	7.4656	0.9239	8.3406	0.7204	0.7864	28.4 (23.8)[a]
F-H_2O(1,2,3,4)	5.7357	7.4978	0.9374	8.3572	0.7332	0.7480	36.1 (31.6)[a]
F-H_2O(1,2,3,4,5)	5.7531	7.5014	0.9010	8.3701	0.7391	0.7519	40.2 (34.6)[a]

[a] The numbers in parentheses represent hydrogen bond energies obtained by adding the interaction energies of the respective dimers.

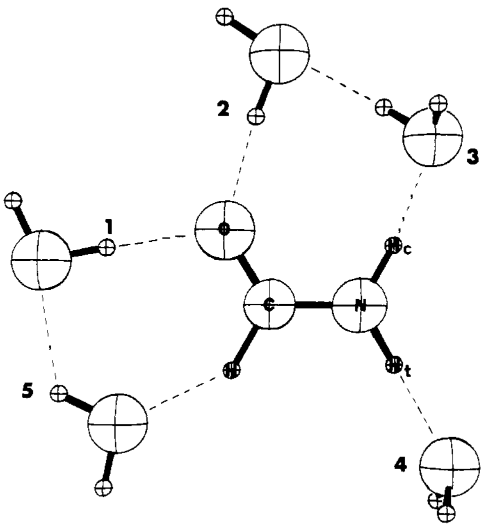

Figure 1. Calcomp drawing of formamide + $(H_2O)_5$ system.

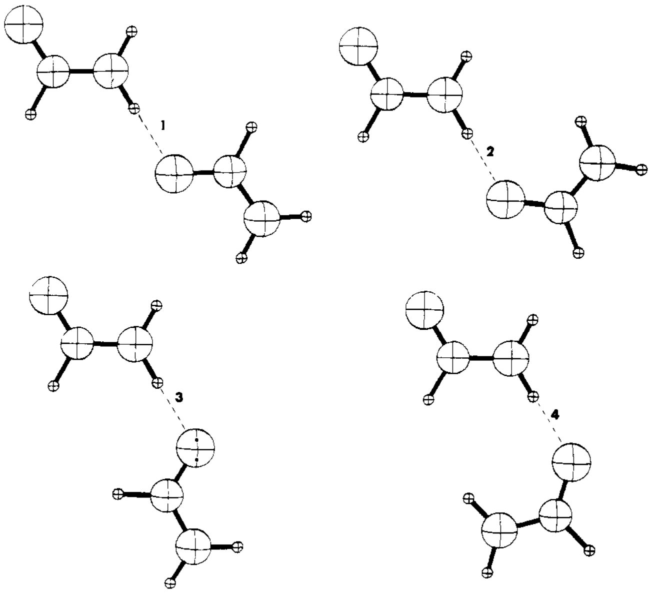

Figure 2. Calcomp drawing of trans formamide dimers.

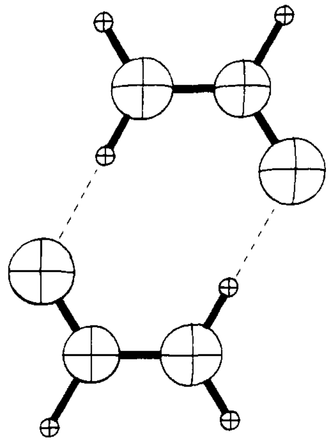

Figure 3. Calcomp drawing of cyclic formamide dimer.

Theoretical calculations have been made on amide-amide and amide-water interactions in an attempt to obtain the number of hydrogen-bond sites for the amide molecules, to determine the most stable interaction configurations, and to determine the relative strengths of these hydrogen bonds.[9-19] The ab initio calculations that have been made thus far are informative; however, they are limited to dimers, a trimer made of the addition of one water molecule to a formamide dimer, and a formamide-$(H_2O)_2$ molecule trimer. Calculations on larger molecular aggregates are needed to more nearly approximate the liquid state.

We have performed ab initio molecular orbital calculations (STO-3G) on the systems formamide + $(H_2O)_n$ and (formamide)$_n$, where $n = 1, 2, 3, 4, 5$. These systems more closely resemble an aqueous-amide or amide solution than any system previously reported.

Using the formamide geometry determined by x-ray studies[20] and the formamide-water geometries reported by Pullman[15] as a starting point, the minimum energy positions for the formamide + $(H_2O)_5$ system were obtained (Figure 1). The water molecules (1)-(5) were placed sequentially on formamide, minimum energy positions being obtained for each system (i.e., dimer, trimer, tetramer, etc.) in the process of constructing a totally hydrated formamide molecule. This involved the reoptimization of the minimum energy positions of each water molecule and the determination of any interaction between water molecules as each additional water molecule was added. It should be noted, for example, that the positions of water molecules (2) and (3) in the formamide-$(H_2O)_5$ system are different from those in the dimers, formamide-H_2O(2) and formamide-H_2O(3), because of the strong interaction between the water molecules (2) and (3) in the formamide-$(H_2O)_5$ system. Table I contains the Mulliken populations and the total interaction energies (hydrogen-bond energies) for formamide and the formamide-water species. The pertinent features for the position of each hydrogen-bonding site are: hydrogen bond length (1) = 1.725 Å, (2) = 1.715 Å, (3) = 1.670 Å, (4) = 1.700 Å, (5) = 2.015 Å, (1) (∠HOC = 112.9°), (2) (∠HOC = 113.5°), (3) (∠OHN = 171.0°), (4) (∠OHN = 178.0°), (5) (∠OHC = 145.0°), (1) (∠OHO = 3.0°), (2) (∠OHO = 5.0°). Additional information concerning the minimum energy positions may be obtained from the authors.

To obtain a comparison between amide and aqueous-amide solutions, theoretical calculations were made on formamide

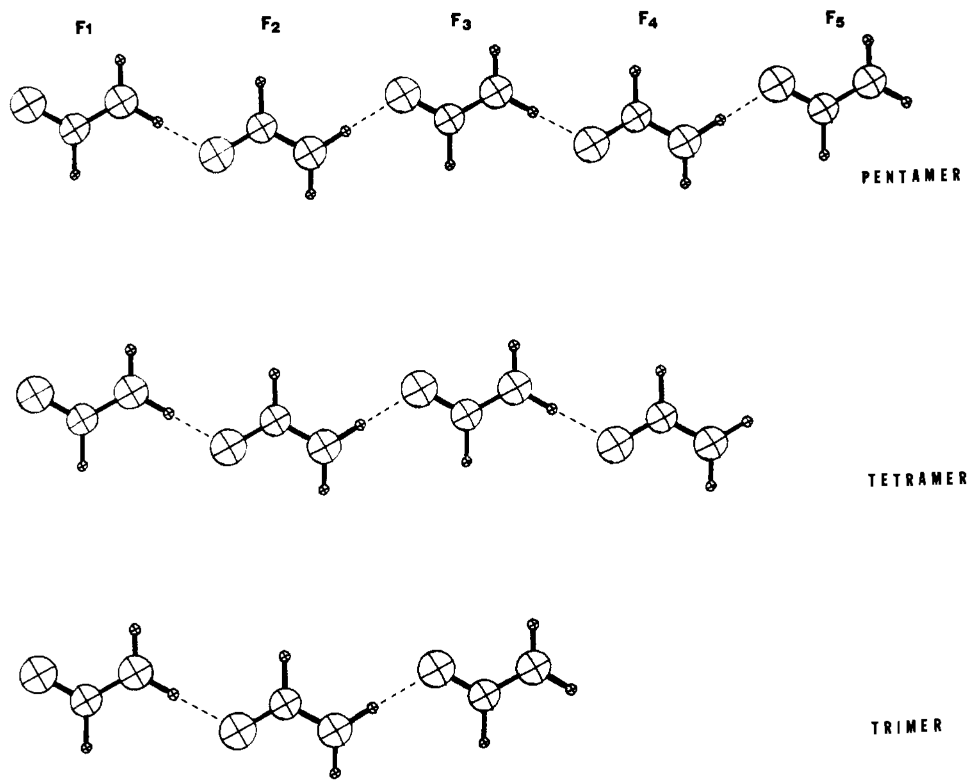

Figure 4. Calcomp drawing of formamide trimer, tetramer, and pentamer.

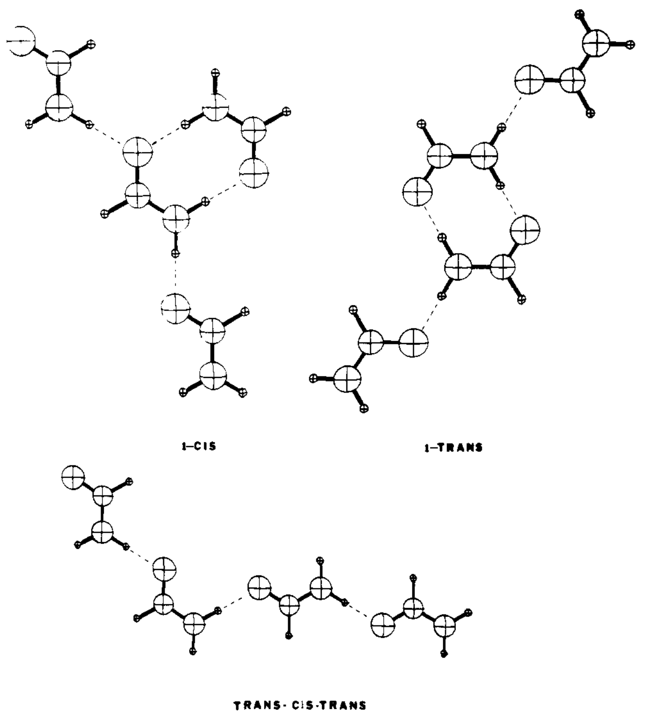

Figure 5. Calcomp drawing of mixed linear-cyclic formamide tetramers and the trans-cis-trans tetramer.

Table II

System	Interaction energy, kcal	Energy per H bond, kcal
F_t-F_t	8.28	8.28
F_t-F_t-F_t	18.49	9.25
F_t-F_t-F_t-F_t	30.00	10.00
F_t-F_t-F_t-F_t-F_t	41.69	10.42
$(F\text{-}F)_{\text{cyclic}}$	19.81	9.91
$(F\text{-}F\text{-}F\text{-}F)_{\text{TCT}}$	21.22	7.07
$(F\text{-}F\text{-}F\text{-}F)_{\text{l-trans}}$	15.00	3.75
$(F\text{-}F\text{-}F\text{-}F)_{\text{l-cis}}$	18.59	4.65

dimers, trimers, tetramers and a pentamer. The four minimum energy configurations for the linear trans formamide dimers are shown in Figure 2. The interaction energies (hydrogen-bond energies) are (1) = 8.3 kcal, (2) = 7.4 kcal, (3) = 8.2 kcal, and (4) = 7.2 kcal. Calculations were also made on the cyclic dimer shown in Figure 3.

Some calculations were carried out on larger cyclic systems containing, for example, four formamide molecules but appeared to give systems less stable than the cyclic dimer. Because of the large amount of computational time involved for these large systems, it was felt to be prudent to consider only the most stable systems. Using the formamide dimer (1) as the basic linear structure, calculations were made on a formamide trimer, tetramer, and pentamer (Figure 4). For the large systems (i.e., tetramers and pentamer) only hydrogen bond lengths were optimized to obtain the minimum energy positions. Calculations were also performed on mixed linear-cyclic formamide tetramers and a trans-cis-trans tetramer shown in Figure 5. The data for these systems are shown in Table II.

The calculations for the formamide and aqueous-formamide systems provide important information necessary for a better understanding of the experimental results for these solutions. The large dielectric constant (117.5 at 5 °C) of formamide, IR,[13,21] and ESCA[22] data suggest that linear chain association dominates in the liquid phase of formamide. A comparison of the interaction energy for the cyclic dimer with that of the trans linear formamide dimer would suggest that the cyclic dimer should be dominant. Since only dimer calculations have been performed previously, it was important to extend the calculations to larger systems to determine if the discrepancy between

Table III. Mulliken Populations for Formamide[a]

	F_1	F_2	F_3	F_4	F_5	F_1-$(H_2O)_4$
O	8.2917					
C	5.7619					
N	7.4443					
H_c	0.7734					
H_t	0.7862					
H_{CH}	0.9424					
O	8.3147	8.3004				
C	5.7665	5.7403				
N	7.4772	7.4369				
H_c	0.7975	0.7633				
H_t	0.7486	0.7748				
H_{CH}	0.9501	0.9296				
O	8.3183	8.3234	8.3047			
C	5.7671	5.7446	5.7387			
N	7.4777	7.4686	7.4360			
H_c	0.7985	0.7870	0.7617			
H_t	0.7447	0.7384	0.7728			
H_{CH}	0.9511	0.9370	0.9289			
O	8.3244	8.3293	8.3299	8.3048		
C	5.7691	5.7421	5.7397	5.7329		
N	7.4862	7.4751	7.4733	7.4339		
H_c	0.8044	0.7916	0.7883	0.7591		
H_t	0.7374	0.7273	0.7294	0.7696		
H_{CH}	0.9542	0.9372	0.9354	0.9252		
O	8.3250	8.3294	8.3334	8.3301	8.3062	
C	5.7690	5.7430	5.7409	5.7403	5.7320	
N	7.4862	7.4756	7.4741	7.4733	7.4335	
H_c	0.8044	0.7917	0.7896	0.7876	0.7590	
H_t	0.7370	0.7262	0.7253	0.7286	0.7693	
H_{CH}	0.9543	0.9373	0.9363	0.9350	0.9252	
O						8.3572
C						5.7357
N						7.4978
H_c						0.7332
H_t						0.7480
H_{CH}						0.9374

[a] See Figure 4 for the numbering system for the formamide molecules.

the experimental results and theoretical calculations could be resolved. The calculations for a formamide trimer, tetramer, and a pentamer provide an explanation for this apparent inconsistency between the experimental data and dimer calculations. The data obtained for the linear dimer, trimer, tetramer, and pentamer show that the energy per hydrogen bond increases with chain length. Furthermore, a comparison of the data for the linear tetramer with that of the mixed linear-cyclic tetramers (1-cis and 1-trans) and the trans-cis-trans (TCT) tetramer indicates that the linear chains should be more stable than the mixed linear-cyclic systems. It has been suggested that the NH···O hydrogen bonding in associated molecules like formamide and other hydrogen-bonding systems becomes stronger as the chain of the associated molecules becomes longer.[19,21,23,24] The theoretical calculations for the linear dimer, trimer, tetramer, and pentamer strongly support this concept and the experimental evidence for the dominance of the linear chains in solution.

The ^{13}C and ^1H NMR chemical shifts of the nuclei in formamide have been obtained as a function of the water mole fraction at 16 °C.[6,8] Although one must use caution in comparing chemical shifts to electron charge densities, it is true, however, that a number of such direct correlations are to be found in the literature for ^{13}C and ^1H nuclei.[24-41] It is of interest, therefore, to compare the theoretically determined electron charge densities for the middle formamide molecule in the pentamer and the formamide molecule completely hydrated by water to the ^{13}C and ^1H chemical shifts observed in a pure formamide solution and a very highly diluted formamide solution. Experimentally it was found that diluting formamide with water over a water mole fraction range of 0.0 to 0.91 produced a high-field shift in the CH and NH (trans) protons and a low-field shift in the ^{13}C resonance position. Even with the stabilizing effect of a hydrogen bond with the water molecule at position (1), the calculations show that the interaction energy of water (5) with the CH proton is very small and probably would not exist at all if a larger basis set were used. Consequently, a totally hydrated formamide molecule might be more accurately represented by considering only four water molecules, at positions 1-4, in the first hydration shell. Ottersen also finds that formamide molecules participate in four hydrogen bonds.[42] This does not mean that there are not water molecules around the C-H position in a real solution because there certainly are; however, it would appear that hydrogen bonding at this position is negligible. Assuming this to be correct, the theoretical charge densities (Table III) are in good agreement with the chemical shift data both in direction and relative magnitude. The charge density at the carbon atom decreases in going from the pentamer to the formamide-$(H_2O)_4$ molecule system (downfield shift) and the charge density at the CH and NH (trans) protons increases (upfield shift). It is also observed that the change in charge density is much less for the CH proton than for the NH (trans) proton. Experimentally, it was found that the high-field shift of the CH proton was less than that of the NH (trans) proton.

In conclusion, ab initio calculations have been made on very large systems in an attempt to simulate the hydrogen bonding of formamide in dilute aqueous solution and in the liquid state. These represent only the first step in the construction of a theoretical model of these solutions. To obtain a more complete picture, statistical mechanical and thermodynamic treatments of these systems would certainly have to be made. Although the relationship between the model systems and the liquid state is crude, the results of the calculations seem to be significant since they do appear to be in reasonable agreement with experimental results and provide an insight into the bonding and structure not obtainable by experiment.

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References and Notes

(1) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomena", Vol. 1, Academic Press, New York, N.Y., 1973.
(2) J. A. Schellman, *C. R. Trav. Lab. Carlsberg*, **29**, 223 (1955).
(3) W. Kauzmann, *Adv. Protein Chem.*, **14**, 1 (1959).
(4) I. M. Klotz and J. S. Franzen, *J. Am. Chem. Soc.*, **84**, 3461 (1962).
(5) A. Johansson and P. A. Kollman, *J. Am. Chem. Soc.*, **94**, 6196 (1972).
(6) J. F. Hinton and K. H. Ladner, *J. Magn. Reson.*, **6**, 568 (1972).
(7) J. F. Hinton and C. E. Westerman, *Spectrochim. Acta, Part A*, **26**, 1387 (1970).
(8) J. F. Hinton, K. H. Ladner, and W. E. Stewart, *J. Magn. Reson.*, **12**, 90 (1973)
(9) J. E. Del Bene, *J. Chem. Phys.*, **62**, 1961 (1975).
(10) M. Dreyfus and A. Pullman, *Theor. Chim. Acta*, **19**, 20 (1970).
(11) M. Dreyfus, B. Maigret, and A. Pullman, *Theor. Chim. Acta*, **17**, 109 (1970).
(12) M. Dreyfus and A. Pullman, *C. R. Hebd. Seances Acad. Sci.*, **271**, 457 (1970).
(13) R. Janoschek, *Theor. Chim. Acta*, **32**, 49 (1973).
(14) T. Ottersen and H. J. Jensen, *J. Mol. Struct.*, **26**, 365 (1975).
(15) G. Alagona, A. Pullman, E. Scrocco, and J. Tomasi, *Int. J. Pept. Protein Res.*, **5**, 251 (1973).
(16) A. Johansson, P. Kollman, S. Rothenberg, and J. McKelvey, *J. Am. Chem. Soc.*, **96**, 3794 (1974).
(17) A. S. N. Murthy and C. N. R. Rao, *J. Mol. Struct.*, **6**, 253 (1970).
(18) T. Ottersen and H. J. Jensen, *J. Mol. Struct.*, **26**, 375 (1975).
(19) G. N. Port and A. Pullman, *I.I.Q.C. Quantum Biology Symposium*, **No. 1**, 21 (1974).
(20) J. Ladell and B. Post, *Acta Crystallogr.*, **7**, 559 (1954).
(21) S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York, N.Y., 1954.
(22) H. Siegbahn, L. Asplund, P. KelFve, K. Hamrin, L. Karlsson, and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 1059 (1974).
(23) J. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970).
(24) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).
(25) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
(26) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).
(27) G. C. Levy, G. L. Nelson, and J. D. Cargioli, *Chem. Commun.*, 506 (1971).
(28) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966).
(29) R. Lazzeretti and F. Taddei, *Org. Magn. Reson.*, **3**, 283 (1971).
(30) J. F. Sebastian and J. R. Grunwell, *Can. J. Chem.*, **49**, 1779 (1971).
(31) T. Tokuhiro and G. Fraenkel, *J. Am. Chem. Soc.*, **91**, 5005 (1969).
(32) W. Adams, A. Grimison, and G. Rodriquez, *Tetrahedron*, **23**, 2513 (1967).
(33) J. E. Bloor and D. L. Breen, *J. Am. Chem. Soc.*, **89**, 6835 (1967).
(34) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975).
(35) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).
(36) T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964).
(37) A. Veillard and B. Pullman, *C. R. Hebd. Seances Acad. Sci.*, **253**, 2418 (1961).
(38) V. Škala and J. Kuthan, *Collect. Czech. Chem. Commun.*, **35**, 2378 (1970).
(39) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, **No. 34**, 18 (1962).
(40) H. Gunther, J. Prestien, and P. Joseph-Nathan, *Org. Magn. Reson.*, **7**, 339 (1975).
(41) G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, **7**, 1 (1975).
(42) T. Ottersen, *Acta Chem. Scand., Ser. A*, **29**, 939 (1975).

Electronic Structure and Proton Affinity of Methylenephosphorane by ab Initio Methods Including Electron Correlation

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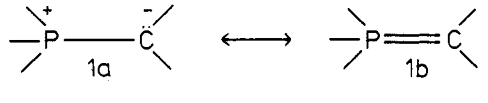
Abstract: The electronic structures of methylenephosphorane PH_3CH_2 and its protonated adduct $PH_3CH_3^+$ were computed at the SCF level and with inclusion of electron correlation in the IEPA, CEPA, and PNO-CI schemes. For the equilibrium distance R_{PC} and the force constant k_{PC} we obtained the following values: PH_3CH_2, $R_{PC}(SCF) = 3.16$ au (1.67 Å), $R_{PC}(CEPA) = 3.19$ au (1.69 Å), $k_{PC}(SCF) = 5.90$ mdyn/Å, and $k_{PC}(CEPA) = 5.53$ mdyn/Å; $PH_3CH_3^+$, $R_{PC}(SCF) = 3.42$ au (1.81 Å), $R_{PC}(CEPA) = 3.45$ au (1.83 Å), $k_{PC}(SCF) = 3.51$ mdyn/Å, and $k_{PC}(CEPA) = 3.25$ mdyn/Å. The dipole moment $\mu(SCF)$ of PH_3CH_2 is 3.18 D. The proton affinitiy of PH_3CH_2 is in the SCF approximation −272.3 kcal/mol and −263.4, −267.9, and −269.7 kcal/mol in IEPA, CEPA, and PNO-CI, respectively The energy of the highest occupied MO agrees reasonably well with the lowest ionization energy of $(CH_3)_3PCH_2$. The properties of the molecular orbitals and the total electron density were investigated by means of contour diagrams and density plots. In agreement with experimental NMR and previous theoretical results we find the carbanion character in PH_3CH_2 dominating. Artifacts of the Mulliken population analysis and the arbitrariness of defining atomic radii are discussed. From a comparison of R_{PC} and k_{PC} calculated with different basis sets we conclude that a large amount of the shift in R_{PC} and k_{PC} going from $PH_3CH_3^+$ to PH_3CH_2 is due to the carbanion character of PH_3CH_2 without participation of any d functions. The remaining effects cannot be simply explained by a d_π-p_π bond in the highest occupied MO only.

The electronic structure of phosphorus ylides or alkylidene phosphoranes is generally formulated as a resonance hybrid of two structures: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