Exciplexes have been proposed as intermediates in photocycloadditions.[9,10] Our suggestion that an exciplex reacts with solvent seems to be without precedent, although reactions are known which may be related to the naphthalene–acrylonitrile addition. These are the addition of dimethyl acetylenedicarboxylate and naphthalene in methanol to afford naphthyl fumarates,[11] and of benzene and maleic anhydride in trifluoroacetic acid, forming phenylsuccinic acid.[12]

We are continuing this work in order both to discover further cases of the interesting substitution and obtain a more precise mechanistic interpretation.

Acknowledgments. We thank the National Research Council of Canada and the Imperial Oil Co. Ltd. for financial support.

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Received April 10, 1970

Cyclic Systems Containing Divalent Hydrogen Symmetrically Placed between sp^2 Hybridized Electron-Rich Atoms. A New Form of Chemical Bond?

Sir:

Recent experiments[1–7] and theories[8–11] relating to anomalous forms of water, alcohols, and acids, and to gas-phase hydrogen fluoride suggest the possible existence of a heretofore unrecognized type of chemical bond. The results given in this letter make direct mathematical and physical connection between Schrödinger's equation and the above-noted research by means of *ab initio* electronic wave functions for water and hydrogen fluoride cyclic polymers constructed with a high-accuracy basis set. Present ability to provide an *a priori* answer to the question posed by this letter's title is essentially pushed to the technical limit by our calculations. In addition to the *ab initio* results, we have made estimates of further corrections beyond the range of directly computable wave functions.

Molecular orbital calculations augmented by configuration interaction were computed on the Princeton University IBM 360/91 digital computer with programs developed in this laboratory. The exact nonrelativistic Hamiltonian with clamped nuclei was used and proved to be valid because the charge distributions found are not enough different from known bond types to invoke relativistic effects or a break down of the Born–Oppenheimer approximation. Choice of orbital basis set and estimation of the instantaneous electron–electron correlation energy are the key problems. The orbital basis set employed was sufficient to span the Hartree–Fock atomic limit and this set was used with the molecular Hamiltonian both in LCAO and in a more flexible (extended) representation that lowers the total energy slightly and accommodates the molecular environment by more linear variation coefficients. Previous research on conventional hydrogen-bonded dimers[12] shows that for this type of basis set one can be assured of obtaining the correct relative stability ordering among different geometrical arrangements. (This has likewise been proved *not* to be so for cyclic hexamers with some simpler basis sets.[13]) The question of absolute binding energies for the polymers relative to separated H_2O molecules is more difficult. Although it has long been known that binding energies for strong ordinary bonds computed from molecular orbital solutions close to the Hartree–Fock limit are considerably less than experimental values, a similar rule has not yet been widely established for hydrogen bonding. However, there now exist some very high-accuracy molecular orbital water dimer wave functions for conventional hydrogen bonds[12,14,15] and the evidence is that hydrogen bond energies follow roughly the same rule as for ordinary bonds and also that radial and angular polarization effects produced on the basis set by the molecular environment largely cancel as far as binding energy estimates are concerned. Thus when used with Hartree–Fock atomic orbitals, the LCAO approximation produces a properly conservative estimate of the binding energy. For hydrogen bonding it underestimates binding energies by perhaps 10–40%. The LC(Hartree–Fock)AO approximation has the further virtues of providing the most meaningful reference point for carrying out configuration interaction and for decomposing the molecular charge distribution into atomic constituents.

We have carried our *ab initio* treatment beyond the molecular orbital level by configuration interaction through the usual and very slowly convergent procedure of adding determinants made from the four lowest lying virtual orbitals. In accord with similar results found for a wide range of molecular systems studied by numerous investigators, the correlation introduced in this manner yields an almost meaninglessly small energy lowering, but it is essentially the limit that can be handled directly by present day computers for the systems considered here.

Our *ab initio* computations are summarized in Table I (for the hydrogen fluoride tetramer an extensive geometry search for the various levels of wave functions was carried out and only the optimized values are

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Table I. *Ab Initio* Energies

System	Wave function	Conformation	R,[f] Å	r, Å	Total E, au	Stabilization E rel to monomers, kcal/mol
HF	LCAO			0.92	−99.99767	
	LCAO CI[a]			0.92	−100.01362	
	Extended			0.92	−100.01463	
$(HF)_2$	LCAO	A,[b] linear	2.88	0.92	−200.00264	4.4[c]
	LCAO + CI	A,[b] linear	2.88	0.92	−200.01845	
$(HF)_4$	LCAO	S,[b] planar	2.50	1.25	−399.88743	
	LCAO + CI	S, planar	2.50	1.25	−399.89571	
	LCAO	S, planar (0.3)[d]	2.50	1.25	−399.91023	
	LCAO	A, planar (0.6)	2.50	0.92	−400.01699	
	LCAO + CI	A, planar (0.6)	2.50	0.92	−400.02176	
	LCAO	A, planar (0.63)	2.74	0.92	−400.02386	21
	Extended	S, planar (0.36)	2.25	1.125	−400.05128	
	Extended	A, planar (0.63)	2.74	0.92	−400.11319	37
	Extended	A, planar (0)	2.5	0.92	−400.07303	
	Extended + CI	A, planar (0)	2.5	0.92	−400.07583	
$(HF)_6$	LCAO	S, planar	2.5	1.25	−599.89976	
	LCAO	S, planar	2.25	1.125	−599.95619[e]	−19
	LCAO	A, planar	2.5	0.92	−600.02739	
	LCAO	A, sp^3 chair	2.7	0.92	−600.02955	
	LCAO	A, planar	2.7	0.92	−600.03717	32
H_2O	LCAO	$\theta = 105°$	2.7	0.957	−75.97638	
$(H_2O)_2$	LCAO	A, linear	3.0	0.957	−151.9577	5.3
$(H_2O)_6$	LCAO	S, planar	2.5	1.25	−455.80186	
	LCAO	S, planar	2.35	1.175	−455.83392	−15

[a] CI ≡ configuration interaction. [b] S ≡ symmetrically placed hydrogens, A ≡ asymmetric hydrogens. [c] A more complete optimization of *r*, the F–H distance, in monomers and asymmetric polymers will have two effects. First, the minimum energy F···F distance will probably be slightly decreased, and secondly the stabilization energy increased. However, these effects are extremely small in the HF dimer [P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970)] where the stabilization energy is increased by 0.1 kcal and the F–F minimum decreased by less than 0.05 Å. In the hexamer, since the minimum F–F distance is smaller, one would expect an increase in stabilization by 2–3 kcal and a decrease in F–F minimum by 0.1–0.15 Å. [d] Distance of hydrogens from F···F line of centers. [e] Value extrapolated from the extensive geometry search carried out for the hydrogen fluoride tetramer. [f] F–F or O–O internuclear separation.

tabulated). Symmetric hydrogen bonding shows the same principal features for both fluorine and oxygen systems, and we chose to study the fluorine polymers more intensively for two important reasons. Our calculations are obviously most applicable to gas-phase molecules, and only cyclic fluoro polymers are observable in the gas phase at room temperature. Second, fluoro polymers are the only cyclic systems for which direct heat of formation measurements have been obtained. The results directly obtained from our *ab initio* molecular orbital calculations are the following.

(1) Hydrogen bond binding energies obtained from LC(Hartree–Fock)AO MO wave functions parallel the well-known rule for ordinary bonds; *i.e.*, they are systematically underestimated. (This rule often does not hold for cruder basis sets[13] or for some more elaborate sets, *e.g.*, the extended asymmetric planar (0.63) calculation in Table I.)

(2) Cyclic systems with asymmetrically placed hydrogens are lower in internal energy at $T = 0°K$ than those with symmetrical hydrogens.

(3) Rings with asymmetric hydrogens are stable with respect to their monomers, while rings with symmetric hydrogens are not. (The asymmetric water cycles are simply one possible geometrical arrangement of water molecules held together by conventional hydrogen bonds.)

(4) The very small correlation energies reflect the fact that we have only been able to obtain a few terms in a slowly convergent series, and they yield no new information except for the comparison between symmetric and asymmetric cycles, where the total number of electrons is identical and the overall size of the systems similar. The only significant result is that correlation corrections may be expected to favor symmetric over asymmetric structures.

In summary, our present level of *ab initio* wave functions leads to cyclic, asymmetric hexamers[16] which are bound with respect to six isolated molecules and to cyclic symmetric hexamers which are slightly unbound with respect to the separated monomers (Table I, last column). On the other hand, it is apparent from these results that correlation energies are underestimated and that correlation effects will be greater for the symmetric bond. In the following paragraph we employ a simple and admittedly crude model for estimating correlation energies. Besides correlation, we have also made relatively rough, but straightforward, estimates of zero-point energies. It is obvious that the only satisfactory way to check the accuracy of our prescription is to test against experiment for closely related systems, and this we have done using all known data for asymmetric bonds (Table II).

The dominant electronic structure effect attendant to hydrogen bonding is the shift of charge from hydrogen to oxygen, and this is particularly striking for symmetrically placed hydrogens. Most of the correlation correction will occur in this region of negative charge

(16) We did not compute a wave function for the cyclic, asymmetric water hexamer because calculations already exist which unequivocally demonstrate its considerable stability relative to six water monomers. First, from the results reported in this work, energies for cyclic, asymmetric water polymers will parallel those for cyclic, asymmetric hydrogen fluoride polymers. Second, *ab initio* wave functions for the cyclic, asymmetric water hexamer already exist [J. Del Bene and J. A. Pople, *Chem. Phys. Lett.*, **4**, 426 (1970)]. Although these employ a simpler basis set than our work and somewhat overestimate stabilization energies, there is no question as to their qualitative conclusions.

Table II. Atomic Charges, Correlation Corrections, and Binding Energies

System	Conformation[a]	Charges on atoms (no. of electrons)	Correlation[b] correction around O or F center, kcal/mol	ΔE,[c] kcal/mol	
				Calcd[d]	Exptl
HF		F 9.44	21.8		
		H 0.56			
$(HF)_2$		F 9.46	45.6	5.3	7[e]
		H 0.54			
$(HF)_4$	Sym	F 9.53	105		
		H 0.47			
	Asym	F 9.48	95	25	28[e]
		H 0.52			
$(HF)_6$	Sym	F 9.55	163	3–8	
		H 0.45			
	Asym	F 9.49	146	40	42[e]
		H 0.51			
H_2O		O 8.72	33.1		
		H 0.64			
$(H_2O)_2$		O 8.75	69	6.4	5–7[f]
		H_{int} 0.61			
$(H_2O)_6$	Sym	O 8.85	235	11–16	
		H_{int} 0.51			
$F\text{–}F^-$			49.5[g]		
$O\text{–}O^-$			46.0[g]		

[a] All planar, LCAO wave functions. [b] Relative to neutral O or F. [c] Relative to monomers. [d] The numbers in this column give the stabilization energies calculated from our wave functions corrected for both correlation energy and the difference in zero-point energy (zpe) of $(HF)_n$ and nHF. For example, in the HF hexamer, the original 6H–F stretches are shifted downfield (decrease in zpe) but there are 24 additional vibrations. The additional vibrations are all very low frequency in this weak complex (for example, the F···F stretch has a zpe of roughly 100 cm^{-1}). Assuming that the additional zpe is 100 cm^{-1} per mode and that the zpe of each HF stretch decreases by 100 cm^{-1}, one finds a zero-point correction of 1800 cm^{-1} (5.1 kcal). Similar correlations are made for other asymmetric structures. In the symmetric structures, there is a dramatic decrease in H stretching frequency (*e.g.*, the H–F stretching frequency changes from 400 cm^{-1} in hydrogen fluoride to 1500 cm^{-1} in FHF^-), but also an increase in frequency for the new vibrations (F···F stretch in FHF^- is 600 cm^{-1}), so that one can crudely estimate the zero-point energy difference between $(HF)_6$ (symmetric) and 6HF as 5–10 kcal. In infinite two- and three-dimensional solids, the zero-point energy may actually be less than that of the monomers. For additional details on this zero-point energy correction, see E. Clementi and J. N. Gayles, *J. Chem. Phys.*, **47**, 3837 (1967). It is useful to record here computed binding energies when only the correlation correction is added. These are: $(HF)_2$, 6.4 kcal/mol; $(HF)_4$, 28.8, $(HF)_6$ sym, 13; $(HF)_6$ asym, 47; $(H_2O)_2$, 8.1; $(H_2O)_6$ sym, 21. [e] E. U. Franck and F. Meyer, *Z. Electrochem.*, **63**, 571 (1959). [f] D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Clarendon Press, Oxford, 1969. [g] Correlation energies for the neutral atoms were found from the difference between the nonrelativistic total experimental energies and the calculated Hartree-Fock total energies [A. Veillard and E. Clementi, *J. Chem. Phys.*, **49**, 2415 (1968)]. The known electron affinities [C. W. Scherr, J. W. Silverman, and F. A. Matsen, *Phys. Rev.*, **127**, 830 (1962)] were added to the experimental neutral atom energies to obtain the experimental negative ion energies. Hartree-Fock negative ion total energies are given in E. Clementi, *IBM J. Res. Devel. Suppl.*, **9**, 2 (1965).

buildup around the oxygens (or fluorines) and its values can be estimated by weighting the difference in correlation energy between O and O^- (or F and F^-) with the relative charge shifts. A Mulliken population analysis of the LCAO MO wave function was used to obtain the atomic charges. This is a reasonable estimate, valid to first order, because correlation corrections do not change the charge distribution to this order, and because the arbitrary Mulliken charge separation assumption and the several effects tending to distort a true representation of the charge surrounding an oxygen (or fluorine) center do not significantly modify *relative* charge shifts of monomers and polymers. Correlation corrections computed by the above method are tabulated in Table II. The differential correlation energy between the monomer and cyclic polymer is added to the *ab initio* LC(Hartree–Fock)AO relative energies of Table I. After the further addition of differential zero-point energies (footnote *d*, Table II), the resultant energies of formation can be compared with experimental values (Table II). Assuming the approximations discussed above, we see that cyclic, symmetric, planar water hexamers are predicted to have a lower internal energy than six isolated water molecules. This implies that anomalous water can, in principle, exist as a well-defined entity with its unique and heretofore unrecognized type of chemical binding. However, it is clear that the asymmetric hexamer is considerably more stable than the symmetric hexamer, and it is believed true that symmetric hexamers will have a lower entropy than free water molecules. Thus there remains a very substantial problem in regard to the formation mechanism for a substance like anomalous water that has been in no way elucidated by this work.

Acknowledgment. We wish to thank the Chemistry Programs Section of the National Science Foundation (Grant No. GP-8907) for support of this research.

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Received March 7, 1970

Electron Spin Resonance of Free Radicals from Acetylenes and Allenes

Sir:

A number of studies have been carried out to establish the structure of free radicals derived from acetylenic compounds by hydrogen abstraction.[1,2] The principal C_3H_3 radical obtained from methylacetylene can be represented by the valence bond structures I and II which are designated propargyl and allenyl, respectively. Chemical studies[3–5] have led to divergent conclusions regarding the structure of the C_3H_3 radical.

$$\underset{\text{I}}{\dot{C}H_2\text{—}C{\equiv}CH} \longleftrightarrow \underset{\text{II}}{CH_2{=}C{=}\dot{C}H}$$

Electron spin resonance (esr) represents the most direct method for the study of the electronic structure of free radicals. An incompletely resolved and broadened esr spectrum of the C_3H_3 radical trapped in the solid state at 77°K was obtained by direct photolysis

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