characteristics, these materials perform remarkably straightforwardly. Our observations suggest that the electronic properties of the phthalocyanines will be important to catalytic studies involving them either as bulk solids or as films of thickness greater than ~100 Å.

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Molecular Beam Electric Deflection Behavior and Polarity of Hydrogen-Bonded Complexes of ROH, RSH, and RNH

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Abstract: Molecular beam electric deflection experiments have been carried out for the dimers and higher polymers of CH_3OH, C_2H_5OH, H_2S, CH_3SH, CH_3NH_2, and $(CH_3)_2NH$. The dimers of these molecules are all found to be polar, in agreement with single, linear hydrogen bond structures. The electric deflection results for trimers and higher polymers are found to be consistent with cyclic structures.

Introduction

These studies are concerned with the conformation of hydrogen-bonded polymers of first-row hydrides and methyl and ethyl substituted hydrides. The structure of these small-molecule, hydrogen-bonded systems are of considerable theoretical[1,2] and experimental interest.[3-6] By understanding the nature of hydrogen bonding in these relatively simple molecules, it may be possible to understand in some detail the influence of hydrogen bonding in complicated systems such as macromolecules and condensed phases.

The alcohols, and to a lesser extent the amines and H_2S, have been the subject of a number of infrared vibrational spectroscopic studies in the gas phase, in inert gas and nitrogen matrices, and in various solvents. The interpretation of these results has not been entirely consistent. van Thiel et al.[5] suggested a cyclic and probably planar dimer, cyclic trimer, and open-chain higher polymers for methanol based on IR studies in a nitrogen matrix. Barnes and Hallam[4] interpreted their results for methanol in an argon matrix as consistent with an open dimer, trimer, and tetramer and a cyclic tetrameric species. Bellamy and Pace[7] proposed an open dimer (and cyclic higher polymers) from methanol solution IR spectra. Inskeep et al.[8,9] suggested that IR studies of vapor-phase methanol were best interpreted with a model consisting of open dimers and cyclic tetramers, with little or no trimer being present. Considerably less work has been done on amines and mercaptans, although we note the matrix isolation work of Tursi and Nixon,[3] who proposed an open-chain structure for $(H_2S)_2$.

Molecular beam electric deflection and electric resonance experiments[10-12] and ab initio calculations[1,13,14] on HF, H_2O, and NH_3 have shown, with impressive quantitative agreement, that the dimers of these molecules have open, linear hydro-

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gen-bonded structures. In the case of higher polymers of HF, H_2O, and NH_3, the experimental[10,12,15] and theoretical results[16,17] suggest cyclic structures, albeit with less certainty than the dimer results. In particular, the molecular beam electric deflection results for water trimers and higher polymers are ambiguous and could be interpreted as either open-chain structures or nonplanar cyclic structures.

To shed further light on this question, we have examined the electric deflection behavior of molecular beams of polymers of methyl and ethyl alcohols, methylamines and mercaptans, and hydrogen sulfide. These measurements supply qualitative information about the molecular Stark effect and the presence or absence of an electric dipole moment, which can be used to decide between possible polar and nonpolar conformations of molecules. The collision-free environment of the beams ensures that isolated molecule results are being obtained. Although the moderate strength (3-5 kcal/mol) of the hydrogen bonds formed by these molecules implies that matrix or solvent effects will not totally dominate the structure of the polymers, it is also apparent that interactions considerably less than the hydrogen-bond stabilization energy may be sufficient to change the orientation of the monomers within a polymeric complex. Thus, the isolated molecule nature of the molecular beam experiments is an advantage over condensed-phase work, although differences in these studies may also be quite interesting.

Experimental Section

The chemicals used in these experiments were as follows. CH_3OH was Baker "Instra-Analyzed". C_2H_5OH was Rossville "gold shield", and CH_3OD and C_2H_5OD were from Aldrich (99% D). H_2S, CH_3SH, CH_3NH_2, $(CH_3)_2NH$, and $C_2H_5NH_2$ were all from Matheson lecture bottles of approximately 99% purity. D_2S at about 90% isotopic purity was made by hydrolyzing anhydrous Al_2S_3 with D_2O. CH_3ND_2 at about 60% isotopic purity was made by bubbling methylamine through a solution of D_2O saturated with Na_2CO_3.

The mercaptans and amines contained small amounts of impurities, primarily other methyl and ethyl derivatives. The mass analysis of the beam was sufficient to remove the possibility of spurious refocusing from these impurities in most cases. Since dimer and polymer beam intensities are more strongly dependent on nozzle source temperature and pressure than monomers, it is possible to discriminate further against impurities by observing this dependence.

The nozzle source consisted of a 100-μm diameter hole drilled into 50-μm tantalum foil, which was sealed to a stainless steel block and inlet line with a viton O-ring. Stagnation pressures of up to about 300 Torr could be used with this nozzle. In a few cases, a 25-μm orifice was employed so that nozzle pressures of up to 2 atm were possible. The source block was in thermal contact with a Dewar, so that the nozzle temperature could be varied from 373 to 77 K if necessary. In general pure, unseeded beams were used. Although the internal temperature of molecules in these beams is not as low as in seeded, inert-gas expansions, use of the pure vapor precludes complications from polar inert-gas complexes with the molecules of interest.

The inhomogeneous electric fields (A and B fields) were 45 cm long quadrupoles, constructed from 0.635-cm diameter, polished stainless steel rods, and were of conventional design.[18] The beam source to A-field separation was 15 cm, A- to B-field 30 cm, and the B-field to detector entrance distance 40 cm. This particular geometry was chosen to be compatible with molecular beam electric resonance experiments as well as the deflection experiments discussed here. The beam molecules were detected by a Weiss-type electron bombardment ionizer[19] and 60° sector magnet mass analyzer. The mass spectral detection and analysis of the beam are particularly important in determining the polymeric composition of the beam and for discriminating against impurities.

Electric Deflection Method

In these experiments, the force exerted on a molecule by an inhomogeneous electric field can be used to discern the presence or absence of an electric dipole moment. More precisely, since this force is equal to the negative gradient of the energy, the molecular deflections give qualitative information about the sign and magnitude of the molecular Stark effect. For the quadrupole fields used in this experiment, a "stopwire" obstacle is positioned to block any straight-line trajectories from the beam source to the detector slits. When a voltage is applied to the quadrupoles, molecules diverging from the beam axis follow curved trajectories[20] around the stopwire and are detected if they have a positive Stark effect, i.e., if their energy increases with increasing electric field. Molecules with negative Stark effects follow curved trajectories away from the beam axis and no increase in detected beam signal is observed. In fact, since a small residual beam signal caused by various scattering processes is always present, even with the stopwire obstacle in place and the focusing fields off, a decrease in scattered beam is observed.

Nonpolar molecules in the electronic ground state generally have only negative Stark effects because of the electronic polarizability interaction, $-\mathbf{E}\cdot\boldsymbol{\alpha}\cdot\mathbf{E}$. Polar molecules will in general have rotational states with positive and negative Stark effects, in approximately equal numbers. Thus, in the experiment described above, an increase in beam signal implies a polar molecule, while a decrease in scattered beam implies a nonpolar molecule.[21]

In interpreting the results of a deflection experiment, some caveats must be considered. "Nonpolar" molecules with certain point-group symmetries, most noticeably T_d, have nonzero electric dipole moments in excited degenerate vibrational states.[22] Rather than give a detailed discussion of this effect,[23] we will simply note that the possible point-group symmetries for the dimers studied here are not those which can give rise to a purely vibrationally induced dipole moment. The higher polymers, which might be susceptible to these effects, did not in general show polar behavior.

A second point is that, although we are interested in the electric deflection of neutral molecules, the beam detector is a mass spectrometer, and it is necessary to correlate a deflection effect observed for a particular ion with the neutral precursor which is actually being deflected. In most cases, this is not difficult, but unusual fragmentation patterns can sometimes make the identification of impurities or polymeric species difficult. If mass analysis is not sufficient to identify the neutral precursor to a given ion, intensity dependence on nozzle stagnation temperature and pressure is frequently helpful, particularly in discriminating against monomeric impurities.

The electric deflection patterns observed depend on the molecular Stark effect, which in turn is affected by the internal motions of the molecules as well as the electric dipole moment. The effects of rotational motion are easily accounted for and well understood, but large amplitude tunneling motions are critically dependent on potential energy surface parameters which are not available for the polymers in this study. Such large amplitude motion can reduce the sensitivity of the experiment,[24] because the expectation value of the dipole moment over the vibrational-tunneling wave function may be less than the dipole moment of the equilibrium geometry or because the rotational and tunneling motions may be coupled in such a way as to reduce the magnitude of the Stark effect. The internal rotations of the monomers bound up in a polymer can certainly lead to the above effects. However, in the limit of very low binding energy, the deflection behavior will approach that of the free monomers, which give large refocused beams in these experiments. Thus, although it is difficult to give a precise value for the smallest dipole moment which can be detected by this method, the lower limit of around 0.3 D for rigid, asymmetric-top molecules is a reasonable estimate for the polymers studied here.

Experimental Results

The electric deflection data is given in Table I and several trends are apparent. The monomers have dipole moments of 1-2 D and show strongly polar behavior, i.e., refocused beams

Table I. Electric Deflection Data and Polarity of Hydrogen-Bonded Polymers

polymer	ion	nozzle pressure, Torr	I_{STB}[a]	% refocusing[b]	polarity
		CH_3OH at 317 K Nozzle Temperature			
CH_3OH	CH_3OH^+	100	100	230	polar
$(CH_3OD)_2$	$CH_3OD_2^+$	100	8.0	18	polar
$(CH_3OH)_2$	$(CH_3OH)_2^+$	100	4.3	15	
$(CH_3OH)_3$	$(CH_3OH)_3^+$	100	1.5	defocused	nonpolar
$(CH_3OH)_4$	$(CH_3OH)_4^+$	100	0.2	defocused	nonpolar
		C_2H_5OH at 330 K Nozzle Temperature			
(C_2H_5OH)	$C_2H_5OH^+$	90	100	286	polar
$(C_2H_5OH)_2$	$C_3H_9O_2^+$	90	0.2	5	polar
$(C_2H_5OH)_2$	$(C_2H_5OH)_2^+$	90	0.05	4	
$(C_2H_5OH)_3$	$(C_2H_5OH)_3^+$	300[c]	0.3	defocused	nonpolar
		H_2S at 235 K Nozzle Temperature[d]			
H_2S	H_2S^+	870	100	266	polar
$(H_2S)_2$	$(H_2S)_2^+$	870	2.6	37	polar
$(H_2S)_3$	$(H_2S)_3^+$	870	0.23	defocused	nonpolar
$(H_2S)_4$	$(H_2S)_4^+$	870	0.08	defocused	nonpolar
$(H_2S)_5$	$(H_2S)_5^+$	870	0.03	defocused	nonpolar
$(H_2S)_6$	$(H_2S)_6^+$	870	0.01	defocused	nonpolar
		CH_3SH at 313 K Nozzle Temperature[d]			
CH_3SH	CH_3SH^+	1750	100	196	polar
$(CH_3SH)_2$	$(CH_3SH)_2^+$	1750	1.9	17	polar
$(CH_3SH)_3$	$(CH_3SH)_3^+$	1750	0.05	0.8	(polar)
		CH_3NH_2 at 253 K Nozzle Temperature			
CH_3NH_2	$CH_3NH_2^+$	100	100	195	polar
$(CH_3ND_2)_2$	$CH_3ND_3^+$	86	3.2	29	polar
$(CH_3NH_2)_2$	$(CH_3)_2NH_2^+$	100	0.5	52	
$(CH_3NH_2)_2$	$(CH_3NH_2)_2^+$	100	1.6	0.4	
$(CH_3NH_2)_3$	$CH_3NH_2{\cdot}(CH_3)_2NH_2^+$	100	0.08	5	polar
$(CH_3NH_2)_3$	$(CH_3NH_2)_3^+$	100	0.16	0.4	
$(CH_3NH_2)_4$	$(CH_3NH_2)_4^+$	100	0.03	defocused	nonpolar
		$(CH_3)_2NH$ at 248 K			
$(CH_3)_2NH$	$(CH_3)_2NH^+$	71	100	219	polar
$[(CH_3)_2NH]_2$	$[(CH_3)_2NH]_2^+$	71	0.6	2.6	polar[e]
$[(CH_3)_2NH]_3$	$[(CH_3)_2NH]_3^+$	117	0.18	defocused	nonpolar
$[(CH_3)_2NH]_4$	$[(CH_3)_2NH]_4^+$	117	0.02	defocused	nonpolar

[a] Intensity of the straight-through beam normalized to the monomer parent ion intensity. [b] Maximum refocused beam as a percentage of the straight-through-beam intensity. [c] Nozzle temperature, 343 K. [d] A 25-μm diameter nozzle was used. The other experiments were done with a 100-μm diameter nozzle orifice. [e] A polar impurity at higher mass was noted, but with an order of magnitude less intensity than the dimer peak.

of 200–300% of the straight-through-beam intensity (the beam detected with the deflection fields off and stopwire obstacle removed). A refocused beam greater than 100% of the straight-through-beam is the result of the space focusing properties of the quadrupole "lenses". Since the beam source is much closer to the entrance of the quadrupole fields than to the detector entrance, the refocused beam is gathered over a much larger solid angle than the straight-through-beam and consequently can exceed 100%.

Inspection of Table I shows that in each case refocusing (polar) behavior was observed for beams detected in the dimer mass range of the mass spectrum. The trimers and higher polymers showed defocusing (nonpolar) behavior except for $(CH_3NH_2)_3$ and perhaps $(CH_3SH)_3$, although in the latter case the effect is so small that it could very easily be accounted for by an impurity.

The data in Table I indicate considerable fragmentation of the polymers by the ionizer-detector. For example, the dimers of CH_3OH and CH_3NH_2 have more abundant $(CH_3OH)H^+$ and $(CH_3NH_2)H^+$ ions than the dimer parent ions. It should be noted that the deuterated analogues of these species were studied to ensure that the results would not be complicated by contributions to the refocusing from ^{13}C or ^{14}N monomer isotopic species. These fragmentation patterns are similar to those observed for $(H_2O)_2$[11,25] and $(NH_3)_2$,[12] which form parent ions in low abundance but have relatively intense H_3O^+ and NH_4^+ ions.

The percentage refocusing observed for the dimers depended strongly on nozzle stagnation pressure, always decreasing as the nozzle pressure was increased. Since the trimers and higher polymers are quite likely to have fragment ions in the dimer mass range, this refocusing decrease can be attributed to these fragments, whose abundance should increase more rapidly than that of the dimer ions with increase in nozzle stagnation pressure but whose neutral precursors have nonpolar deflection behavior. Thus we found it useful to study each species over a range of pressures (generally 10–300 Torr, 1–2 atm for H_2S and CH_3SH) since at high pressures the large polymers will predominate and might obscure the focusing behavior of less abundant dimers and trimers. For example, the relatively low ratio of refocused beam to straight-through beam for $(CH_3)_2NH$ dimer in Table I becomes substantially larger at lower pressures because of this effect.

The fragmentation behavior noted above also poses the possibility that the refocusing attributed to $(CH_3NH_2)_2$ could be caused by fragmentation of $(CH_3NH_2)_3$, which was ob-

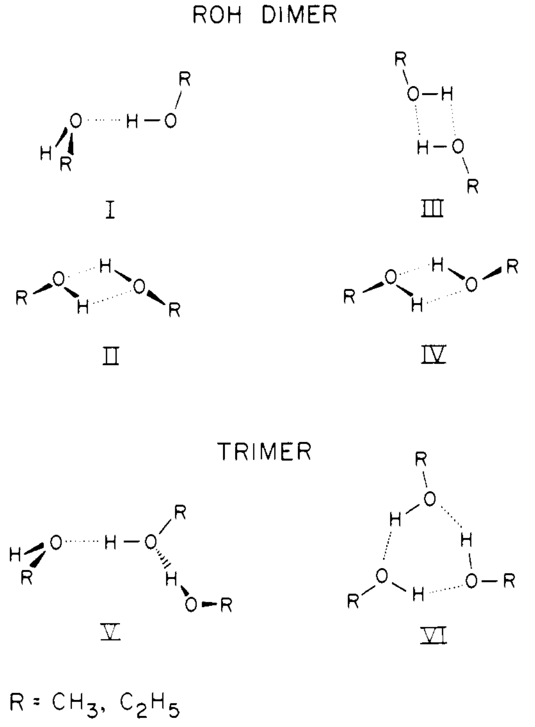

Figure 1. Alcohol dimer and trimer conformations. The triangular bonds indicate out-of-plane orientation. The dimers are polar and can have either conformation I or II, but not III or IV, with conformation I being the most likely. The higher polymers are nonpolar, eliminating open-chain structures such as V in favor of cyclic structures such as VI.

served to give refocusing. Since the refocused beams observed in the dimer mass range were generally much larger than in the trimer mass range and were observed even at low pressures when the trimer ions had negligible intensity, the more reasonable interpretation is that both the dimer and the trimer in this case are polar molecules.

Structural Implications of Deflection Results

All of the dimers in this study were observed to give beam refocusing and are polar molecules. We note at the outset that these results can be simply interpreted in terms of linear hydrogen-bonded dimer structures (Figures 1-I and 3-I) analogous to those found for $(HF)_2$[10] and $(H_2O)_2$[11] by molecular beam electric resonance spectroscopy. As discussed below, the electric deflection data strongly supports this view, but is not always unambiguous.

The observed refocusing for the alcohol dimers, $(H_2S)_2$, and $(CH_3SH)_2$ cannot be caused by cyclic dimers with zero dipole moment such as in Figures 1-III and 1-IV for the alcohols and the analogous conformations for the sulfur compounds, but is compatible with linear hydrogen-bonded structures as in Figure 1-I. In addition, nonplanar cyclic structures with both methyl groups or both non-hydrogen-bonded hydrogens on the same side of the ring (Figure 1-II) have nonzero dipole moments and could refocus. A rotation of 6° around the OH axis of each ROH molecule, measured from a planar dimer configuration, would be sufficient to generate an observable 0.3 dipole moment. For H_2S and CH_3SH dimers, 12° rotations would be sufficient.

The advantage of a nonplanar cyclic dimer conformation such as Figure 1-II over that of the planar arrangement III would presumably be a more favorable alignment of a lone pair of electrons on the electron donor with the lowest unoccupied molecular orbital of the electron pair acceptor, a σ antibonding OH orbital for the alcohols. A cyclic structure such as Figure 1-IV would retain that advantage and would have the oxygen lone pairs not involved in the bonding on opposite sides of the ring plane, further apart than in Figure 1-II, with consequent reduction in Coulombic repulsion. Since the electric deflection result eliminates Figure 1-IV as a possibility, the linear hydrogen-bond structure in Figure 1-I seems to us to be the most likely of the possible polar structures, in agreement with the known structure for $(H_2O)_2$. For similar reasons, H_2S dimer and CH_3SH dimer are also likely to have linear hydrogen-bonded structures analogous to Figure 1-I, although cyclic structures similar to Figure 1-II cannot be eliminated. In the case of $(H_2S)_2$ a "bifurcated" structure, Figure 2, is also compatible with the electric deflection results. The substantially weaker hydrogen bonding for $(H_2S)_2$ makes an analogy to the known water dimer geometry less obvious, and such bifurcated structures cannot be ruled out from the electric deflection results alone.

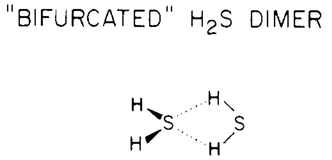

Figure 2. Possible $(H_2S)_2$ "bifurcated" structure. The polar electric deflection results for H_2S and CH_3SH dimers allow structures analogous to Figures 1-I or 1-II or, for $(H_2S)_2$, the above structure. Nonpolar cyclic structures are eliminated, however.

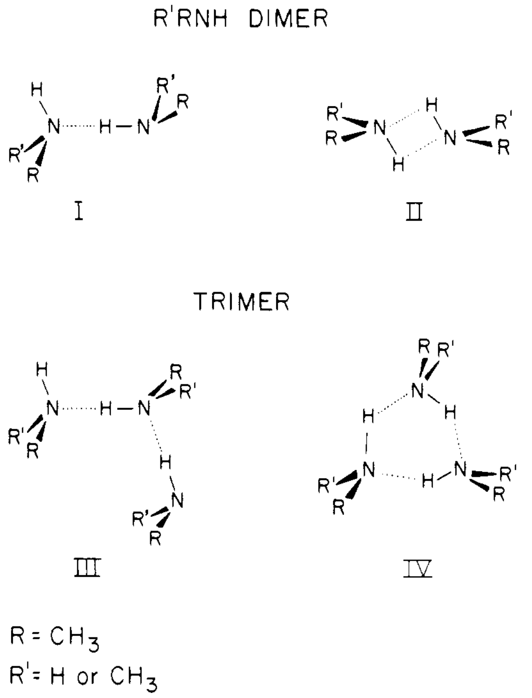

Figure 3. The electric deflection results for $(CH_3)_2NH$ polymers show that the linear hydrogen-bonded dimer (I), cyclic trimer (IV), and cyclic tetramer structures are the correct conformations for these molecules. The results for CH_3NH_2 polymers are less definitive, but arguments presented in the text favor similar structures for $(CH_3)_2NH$ and CH_3NH_2 polymers.

The refocusing behavior of dimethylamine dimer can be explained only by the linear hydrogen-bonded structure of Figure 3-I. Methylamine dimer would have a dipole moment in the cyclic conformation (Figure 3-II) with both methyl groups on the same side of the ring, as well as for the linear hydrogen-bonded conformation. The magnitude of the methylamine dipole moment and its orientation to the CNH_2 framework[26] are similar to that of NH_3, and thus the cyclic dimer would have a dipole moment of only a few tenths of a debye. Very little or no refocusing would be expected, and the observed result is more in accord with the linear hydrogen-bonded structure. This is also in agreement with the results for dimethylamine dimer and ammonia[12] dimer, which have similar structures.

It should be noted that the molecular beam experiments would not detect a nonpolar dimer in the presence of a substantial amount of polar dimers. However, the conformational temperatures of the supersonic nozzle beams used here are probably substantially less than the stagnation temperatures of 250–350 K used in this study. Since these temperatures depend on complicated relaxation processes, they cannot be accurately estimated. An experiment which sheds some light on this question was an earlier attempt[10] to make HF-DF dimers from 50% deuterated HF under nozzle conditions similar to those in the present study (pure HF at around 100 Torr and 300 K through a 100-μm orifice). Only HF···DF was observed and not DF···HF. The difference in zero-point vibrational energies of the two isotopic "conformations" is probably around 100 cm^{-1},[27] implying a conformational temperature of less than 100 K. It seems likely, then, that the electric deflection results are characteristic of the lowest energy conformation, or at least of one which is only 100 cm^{-1} or less above it.

With the exception of methylamine trimer and perhaps methyl mercaptan trimer, all of the trimers and higher polymers observed in this study have nonpolar behavior. The refocused beam for methyl mercaptan trimer, which was only 2×10^{-6} as large as the monomer refocused beam, could easily be from an impurity and therefore will not be discussed below. These results eliminate open-chain structures such as the trimer structures of Figures 1-V and 3-III, which would have 2–4 D dipole moments, and, barring some unforeseen dynamic effect, would have readily observable refocusing. Thus cyclic structures with the monomer dipole moments coplanar (Figures 1-VI and 3-IV) are implied by the electric deflection results. For the alcohols, a rotation of 12° about the OH axis of one monomer from such a configuration would be sufficient to generate an observable 0.3 D dipole moment. Thus the cyclic trimers must have coplanar ROH units within crude limits of about 10°, or more precisely the dipole moments must be coplanar within those limits, as a puckered ring arrangement could also be imagined. A limit of 20° can be similarly calculated for $(H_2S)_3$. Cyclic tetramers could have substantial out-of-plane bending if the R groups are arranged alternately on opposite sides of the plane, which seems plausible if electric dipole–dipole interactions between monomer units are considered. A complete cancellation of dipole moment would not be possible for odd-numbered polymers, however.

Methylamine trimer had a small but readily observable refocusing, while methylamine tetramer and the dimethylamine trimer and tetramer were nonpolar. There is no symmetry restriction preventing a cyclic methylamine trimer from having a dipole moment, although it would be at most a few tenths of a debye for the trimer structure of Figure 3-IV. The chain trimer cannot be ruled out, but the small refocusing is more consistent with such a cyclic structure than with a chain trimer such as in Figure 3-III which would have a large dipole moment of about 3 D. Nonpolar results for the dimethylamine trimer and ammonia trimer[12] are less ambiguous, and the cyclic trimer structure is almost certainly the correct choice for these molecules and methylamine trimer. The nonpolar result for methylamine tetramer may imply a cyclic structure with the methyl groups alternately on opposite sides of the ring. The low amount of tetramer observed coupled with the small dipole moment of a cyclic tetramer, even with all of the methyl groups on the same side of the ring (roughly 0.3 D), does not definitively eliminate less symmetrical cyclic structures.

Conclusions

The results of this study are all consistent with dimer structures of the single, linear hydrogen-bond type which are known to hold for $(HF)_2$ and $(H_2O)_2$ from molecular beam electric resonance microwave experiments and from ab initio calculations. The electric deflection results rule out cyclic dimers with a center of symmetry. Although one can imagine cyclic dimer structures which are polar for the alcohols, H_2S, CH_3SH, and methylamine dimers, they seem unlikely for the reasons mentioned earlier. Refocused beams observed for ammonia and dimethylamine dimer eliminate cyclic dimers for those molecules. Viewing the molecular beam electric deflection and electric resonance results along with ab initio calculations for the dimers of first-row hydrides and substituted hydrides, there is no reason to doubt that their structures are all of the linear, single hydrogen-bond type. The H_2S and CH_3SH results along with earlier HCl dimer[21] and HF···HCl[28] dimer results suggest that second-row hydrides may behave similarly.

A second major trend which emerges from these results is that the trimers and higher polymers are in general nonpolar and apparently have cyclic structures. Considering the molecules in this study and previous work on HF, H_2O, and NH_3 polymers, only methylamine trimer and the water polymers show definite polar behavior. As previously mentioned, there is no symmetry restriction preventing a cyclic methylamine trimer from having a dipole moment and the weak refocusing suggests, but does not prove, that this is the case, since its dipole moment would be quite small for a reasonable cyclic structure. The water polymer results are particularly interesting, and one of the reasons for undertaking the present study. The electric deflection results are compatible with open-chain polymers, or cyclic nonplanar polymers.[29] It was originally suggested[15] that the small refocused beams were likely to come from cyclic polymers with the non-hydrogen-bonded hydrogens bent out of the plane, rather than chain polymers which would have large dipole moments and should show strong refocused beams. The nonpolar results for HF, NH_3, and the alcohol and amine trimers and higher polymers reinforce this view, and we believe that, apart from the dimers, all of the first-row hydrides and substituted hydrides have cyclic structures for the smaller polymers ($n = 3$–6).

The weak refocusing for water polymers and zero refocusing for the alcohol polymers higher than the dimer further suggests that the out-of-plane bending is not large, on the order of 10° or less to give the nonpolar methanol trimer results.

Given that $(HF)_2$, $(H_2O)_2$, and HF·HCl all have hydrogen bonds which are nearly linear in the equilibrium configuration and have proton acceptor molecule orientations suggestive of a hybridized lone pair of electrons collinear with the hydrogen bond axis, cyclic trimer structures and, to a lesser extent, cyclic higher polymers would appear to be surprising.

In an important paper, Janda et al.[28] have accounted for the structural features of a number of weakly bound complexes with a generalization of a molecular orbital description from Pimentel.[30] In this model, the monomers are oriented in the complex to provide the optimal interaction between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor. The observed structures of hydrogen-bonded dimers are successfully accounted for if the HOMO is taken to be a hybridized lone pair orbital of the electron donor and the LUMO a σ antibonding orbital of the electron-pair acceptor. The linearity of the hydrogen bond in the dimers is due to the cylindrical (or nearly cylindrical) symmetry of the LUMO.

At first glance, the strained ring structures of the trimer and higher polymers discussed here contradict this model. However, Janda et al.[28] have noted that the LUMO in these systems has predominantly a hydrogenic s character. The resulting lack of directionality is reflected in bending force constants for dimers such as $(HF)_2$ and HF···HCl being about 50 times smaller than for HF···ClF and about three times smaller than for Ar···ClF, despite the weaker binding in the latter two complexes. Similarly, the cyclic polymer structures found here reflect a lack of directionality, which in the HOMO-LUMO model would have its origin in the high s character of the LUMO.

There are only a small number of ab initio calculations, primarily for water, in which the question of cyclic vs. linear trimers and higher polymers has been carefully studied. Pople and Del Bene[16,17] concluded from minimal basis set LCAOSCF calculations that cyclic structures for the trimers and higher polymers of HF and H_2O are more stable than open-chain structures, in agreement with our results. Lentz and Scheraga,[31] using a more extensive basis set, concluded that water trimers would have an open-chain structure with the higher polymers being cyclic. The geometries in these latter calculations were not fully optimized, however.

Curtiss[32] has recently published a minimal basis set ab initio calculation, similar to the water polymer calculations of Del Bene and Pople, for methanol polymers. The trimer through hexamers were found to have cyclic arrangements as the lowest energy structures, in agreement with our results. However, the methyl groups are bent substantially out of the plane of the oxygens, 62° for the trimer, which would generate a 1-D dipole moment for the odd-numbered polymers. Our results suggest a more nearly planar arrangement. It would appear to us that more extensive trimer calculations for first-row hydrides would be of considerable importance.

The linear, hydrogen-bonded dimers and cyclic higher polymer structures found in this work and in related experiments show that the hydrogen bond does not have strong geometrical preferences, even when compared to weaker van der Waals complexes. It would appear to us that this lack of directionality, along with its moderate strength, may be the distinguishing features of the hydrogen bond in condensed phases and macromolecules.

It would be desirable to obtain more quantitative experimental and theoretical results for the systems discussed here. A microwave structure for dimers such as $(H_2S)_2$ or $H_2S{\cdot}HF$ with a second-row hydride as the proton acceptor would be a very useful test of the HOMO-LUMO model, since H_2S has a substantially different hybridization from H_2O. Similarly, the water trimer (and methylamine trimer) is a possible candidate for microwave spectroscopy since it is a polar molecule. However, irrespective of its point-group symmetry, it will have 96 distinct, isoenergetic conformations, differing only by permutation of identical nuclei or by inversion, which can interconvert by relatively low-barrier tunneling motions. The resulting microwave spectrum may not be pleasant to analyze. Mixed trimers such as $(HF)_2H_2O$ or $(H_2O)_2HF$ should supply similar information and may have simpler spectra.

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