A Theoretical Prediction of the Existence and Properties of the Lithium Hydride Dimer

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Abstract: Accurate electronic structure calculations are used to predict the existence and properties of the lithium hydride dimer. The vibrational frequencies, quadrupole moment, and thermodynamic functions for the dimer have been computed; the dimer is computed to be bound by 44 kcal/mol relative to two monomers at 1000 K. An analysis of geometry, charge redistribution, and molecular orbital energy shifts in the linear and cyclic LiH dimer reveals interesting similarities to previous theoretical (H-bonded and Li-bonded complexes) and experimental (structural studies of alkali halide dimers) work. The possibility of detecting other alkali hydride dimers and polymers is discussed.

One of the functions of a theoretical chemist is to be predictive, *e.g.*, to predict the existence and properties of new compounds before they are discovered. Historically, one of the most famous examples of this was the theoretical prediction[2] of the existence of noble gas compounds more than 30 years prior to their synthesis.

More recently, using electronic structure techniques, there have been two notable studies of previously undiscovered compounds: Clementi[3] predicted the existence of gas-phase NH_4Cl and Bertoncini, *et al.*,[4] the existence of gas-phase LiNa. In this paper, we present a theoretical study of the heretofore undiscovered lithium hydride dimer $(LiH)_2$. This is the first time that very accurate molecular orbital, configuration interaction (CI), *and* thermodynamic calculations have been carried out prior to experimental characterization of a polyatomic molecule.

Computational Details

The basis set[5] used in these calculations consisted of (9s, 5p) Gaussian functions contracted to (4s, 2p) on lithium and (5s, 2p) Gaussians contracted to (2s, 1p) on hydrogen. The contraction coefficients used were determined by SCF calculations on the atoms (^2S and ^2P Li and H). The exponents and coefficients of the basis set are listed in Table I, along with a number of SCF determined properties for the lithium hydride monomer. As one can see this basis set gives an SCF energy only 0.0047 au from the Hartree–Fock limit;[6] this difference in energy is small compared to the dimerization energies calculated below.

Table I. Basis Set and Monomer Properties

Li	Exponent	Coefficient	H	Exponent	Coefficient
s	921.271	0.00136717	s	33.6444	0.00611802
s	138.73	0.01041992	s	5.05796	0.04575355
s	31.9415	0.4984382	s	1.1416	0.20571928
s	9.35328	0.16064382	s	0.321144	0.50821497
s	3.15789	0.34454778	s	0.101309	1.0
s	1.15685	0.42504546	p	0.1393	0.32557181
s	0.44462	1.0	p	0.0324	0.78545888
s	0.076663	1.0			
s	0.028643	1.0			
p	0.07650	0.04277500			
p	0.1480	0.3538991			
p	0.0285	1.0			

LiH Properties[a]

$E_T = -7.98262$ au (SCF limit[b] = 7.9867)
$r_{eq} = 1.633$ Å (1.595)
$\mu = 5.48$ D (5.882)
$K = 1.055 \times 10^5$ dyn/cm (1.026)
POP (Li)[c] = 2.662
POP (H)[c] = 1.338
OPOP[d] = 0.739
Orbital energies (au) = −2.4561, −0.2986

[a] Experimental values in parentheses. [b] Reference 6. [c] Mulliken atomic population. [d] Mulliken overlap population.

The Dimer Potential Surface

The results of the SCF–MO dimer calculations are listed in Table II. The surface search was carried out in three stages. First, the molecules approached in a collinear arrangement and the minimum energy linear geometry was found near R(Li–Li) = 3.45 Å; r_1(Li–H) = 1.62 Å, and r_2(Li–H) = 1.67 Å.

Next, a dimer with a center of inversion was studied, varying the Li–Li distance (R), the HLiLi angle (θ), and the LiH distance (r). Finally, a centrosymmetric (D_{2h}) dimer was assumed, varying both the H (r_H) and Li (r_{Li}) distances from the center of inversion. The minimum energy for the dimer was found to be E_T = −16.03894 au;[7] the minimum energy geometry is

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(1) (a) University of California; (b) Lawrence Livermore Laboratory; (c) Information Systems Design.

(2) See J. H. Holloway, "Noble Gas Chemistry," Methuen, London, 1968; the earliest prediction appears to be that of von Antropoff, *Z. Angew. Chem.*, 37, 217 (1924).

(3) E. Clementi and J. N. Gayles, *J. Chem. Phys.*, 47, 3837 (1967); E. Clementi, *ibid.*, 46, 3851 (1967); 47, 2323 (1967). Experimental evidence for the existence of NH_3Cl (gas phase) can be found in the work of P. Goldfinger and G. Verhaegen *ibid.*, 50, 1467 (1969).

(4) P. J. Bertoncini, G. Das, and A. C. Wahl, *ibid.*, 52, 5112 (1970).

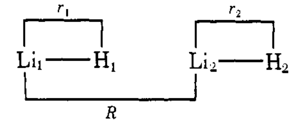
(5) The s basis used was that used by W. A. Sanders and M. Krauss, *J. Res. Nat. Bur. Stand., Sect. A*, 72, 85 (1968), in calculations on LiH. The p basis was that of I. G. Csizmadia, *J. Chem. Phys.*, 44, 1849 (1966).

(6) P. E. Cade and W. M. Huo, *ibid.*, 47, 614 (1967).

(7) A more uncontracted calculation (4s 3p (Li); 4s 2p (H)) using the same gaussians found a monomer energy of −7.98515 au (half-way to Hartree–Fock limit), a dimer energy of −16.04446 au, and a ΔE = 47.4 kcal/mol. Thus, additional basis set changes should have negligible effects on the dimerization energy.

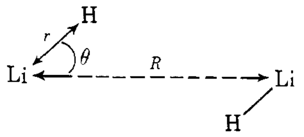
Table II. Results of SCF–MO Dimer Calculations

Linear Dimer



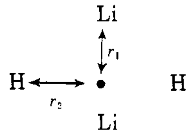
R, au	r_1, au	r_2, au	E, au
6.2	3.065	3.065	−16.00555
6.5	3.065	3.065	−16.00636
6.5	3.065	3.115	−16.00658
6.5	3.065	3.165	−16.00664
6.5	3.115	3.065	−16.00631
6.5	3.165	3.065	−16.00602
6.7	3.065	3.065	−16.00553
7.0	3.165	3.065	−16.00374
7.0	3.115	3.065	−16.00353
7.0	3.065	3.065	−16.00314
7.5	3.065	3.065	−15.99791

Cyclic Dimer



R, au	θ, deg	r, au	E, au
3.06	60	3.065	−15.99456
3.0	75	3.065	−15.98139
3.6	60	3.065	−16.02315
4.2	60	3.065	−16.03027
4.2	75	3.065	−16.00951
4.2	60	3.50	−16.02839
4.8	60	3.065	−16.02416
4.8	45	3.065	−16.02744

Centrosymmetric Dimer



r_1, au	r_2, au	E, au
2.1	2.5188	−16.03777
2.1655	2.1655	−16.02809
2.2	2.5188	−16.03879
2.2274	2.2274	−16.03215
2.25	2.5688	−16.03883
2.25	2.6688	−16.03837
2.25	2.4688	−16.03830
2.2981	2.2981	−16.03481
2.3	2.5188	−16.03826
2.3688	2.3688	−16.03565
2.4042	2.4042	−16.03551
2.4205	2.5688	−16.03586
2.4205	2.6688	−16.03511
2.475	2.475	−16.03421
2.70	2.70	−16.02341
2.23	2.58	−16.03894

r_1 = 1.18 Å and r_2 = 1.37 Å and the dimerization energy 47.2 kcal/mol (D_{2h} symmetry). The molecular orbital coefficients, orbital energies, and properties for the dimer are listed in Table III. The fact that the minimum energy geometry for the dimer is found for $r_{H-H} > r_{Li-Li}$ is not surprising since the highest occupied molecular orbital (b_{2u}) has a node between the hydrogens, but none between the lithiums; this fact is also reflected in the negative H–H overlap population and positive Li–Li overlap population. This structural principle holds for alkali halide dimers[8] as well, where halogen–halogen distances are greater than the alkali–alkali distances.

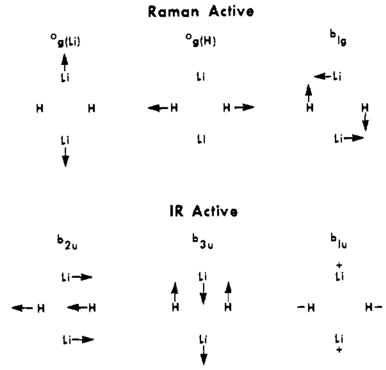


Figure 1. Vibrational modes of the LiH dimer (b_{1u} + and − refer to in and out of plane).

The Vibrational Potential of $(LiH)_2$

The normal vibrations of D_{2h} $(LiH)_2$ are $2a_{1g}$, b_{1g}, b_{2u}, b_{1u}, b_{3u}. In the four symmetry groups where there is only one normal vibrational mode, the standard constraints for movement of atoms (no translation or rotation)[9] were used to unambiguously determine the normal modes in terms of atom displacements. The SCF energy for two such displacements for each normal mode was determined, and the force constant and frequency for the modes were found by a parabolic fit. In the A_{1g} group, this procedure does not lead to unambiguous "normal modes," but because of the significant difference in mass, H–H and Li–Li "breathing" modes were separately considered and the frequency for these modes was determined. The "normal modes" and their computed frequencies are shown in Figure 1.

Configuration Interaction Calculations

The ground state electronic configuration for $(LiH)_2$ at the minimum energy geometry is $(1a_{1g})^2(1b_{3u})^2(2a_{1g})^2(1b_{2u})^2$. A complete single and double excitation configuration interaction (CI)[10] calculation from the two valence orbitals to all the 26 virtual orbitals (260 configurations) lowered the energy by 0.042468 au, compared to a lowering of the energy 0.044082 au for a complete CI from the valence orbitals of two infinitely separated monomers. The natural orbitals $3a_{1g}$, $4a_{1g}$, $2b_{2u}$, $3b_{2u}$, $2b_{3u}$, $3b_{3u}$, $1b_{1g}$, and $1b_{1u}$ were found to contribute most to the CI stabilization and a complete single and double CI excitation using these natural orbitals (39 configurations) lowered the energy by 0.039873 au; allowing all triple and quadruple excitations lowered the energy by a further 0.000942 au.

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(8) S. H. Bauer and R. F. Porter in "Molten Salt Chemistry," M. Blander, Ed., Wiley-Interscience, New York, N. Y., 1964, p 652.

(9) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955; see eq 1, 2, and 5 in Chapter 2.

(10) See, for example, S. V. O'Neill, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971), for the method used in this polyatomic CI study.

Table III. Dimer Properties, Molecular Orbital Coefficients, and Energies

AO		$\epsilon = -2.4228$ au $(1a_g)^2$	$\epsilon = -2.4214$ au $(1b_{3u})^2$	$\epsilon = -0.3676$ au $(2a_g)^2$	$\epsilon = -0.3112$ au $(1b_{2u})^2$
Li	s_1	0.6190404	0.6200296	0.1033262	0
	s_2	0.1201872	0.1204223	0.0711839	0
	s_3	0.1325915	−0.00337766	−0.2008034	0
	s_4	−0.0008681	−0.0155658	−0.0126071	0
	p_{x1}	−0.0023810	−0.0061872	−0.0943998	0
	p_{x2}	0.0005060	−0.0027443	−0.0085299	0
	p_{y1}	0	0	0	0.1311936
	p_{y2}	0	0	0	0.0670865
H	s_1	0.0035162	0	−0.3209495	0.3498665
	s_2	0.0014069	0	−0.1805420	0.3050668
	p_x	0	−0.0044261	0	0
	p_y	−0.00095092	0	−0.0264275	−0.0465577
Li	s_1	0.6190404	−0.6200296	0.1033262	0
	s_2	0.1201872	−0.1204223	0.0711839	0
	s_3	0.1325915	0.0033766	--0.2008034	0
	s_4	−0.0008681	0.0155658	−0.0126071	0
	p_{x1}	0.0023818	−0.0061872	0.0943998	0
	p_{x2}	−0.0005060	−0.0027443	0.0085299	0
	p_{y1}	0	0	0	0.1311936
	p_{y2}	0	0	0	0.0670865
H	s_1	0.0035162	0	−0.3209495	0.3498655
	s_2	0.0014069	0	−0.1805420	0.3050668
	p_x	0	−0.0044261	0	0
	p_y	0.00095092	0	0.0264275	−0.0465577

Geometry (Å)

	x	*y*	*z*
Li_1	−1.180	0	0
H_1	0	1.365	0
Li_2	1.180	0	0
H_2	0	−1.365	0

Population Analysis	Δ^a (POP monomer)
POP (Li)[b] = 2.595	−0.067
POP (H) = 1.405	0.067
OPOP (LiH)[c] = 0.353	−0.033
OPOP (LiLi) = 0.182	
OPOP (HH) = −0.237	

Quadrupole Moment (Buckinghams)

$\theta_{xx} = 18.6$ $\theta_{zz} = -0.1$

Vibrational Frequencies (cm^{-1})

$1a_g$	1150	b_{2u}	925
$2a_g$	540	b_{3u}	910
b_{1g}	790	b_{1u}	530

[a] Difference between dimer and monomer population. Negative if less electrons in the dimer. In the case of the Li–H overlap, twice the overlap population is subtracted from the monomer value. [b] Mulliken atomic populations. [c] Mulliken overlap population.

Thus triple and quadruple excitations contribute a relatively small amount to the stabilization energy of the LiH dimer. In fact, the SCF computed stabilization energy is 0.4 kcal/mol greater than that found including configuration interaction.[11]

One of the interesting contrasts between LiH dimerization and that of "weak" complexes is the fact that a CI in the latter case (which probably corresponds reasonably closely to the dispersion attraction)[12a] lowers the energy (no stabilization is found for He_2 without CI),[12b] whereas, in $(LiH)_2$, there seems to be greater "correlation energy" in the two monomers than in the dimer. One might rationalize this by noting that in the dimer, the electrons are "spread out" over a larger "box" than in the monomers, and thus instantaneous electron–electron correlation lowers their energy less. This result is not absolutely definitive because this CI has only been able to recover 0.022 of the ~0.04 correlation energy of the LiH valence orbital, but the net effect of correlation on the dimerization energy is clearly very small. This is in contrast to the conclusion of Gelus, *et al.*,[13] in their study of $2BH_3 \rightarrow B_2H_6$; these authors state that correlation energy contributes substantially ($\Delta E_{SCF} = 8$ kcal, $\Delta E_{cor} = 17$ kcal) to the stabilization energy of B_2H_6 relative to $2BH_3$, despite the fact that both are closed-shell species. Our result is more in agreement with previous assumptions in studies of association of weak complexes,[3] but there may be a difference in the contribution of correlation energy to the dimerization energy of ionic[4,14] and electron-deficient species;[13] only further more precise studies can resolve this question. An alternative ex-

[11] The stabilization from the complete single and double valence CI is 0.042468; the extra stabilization from triple and quadruple excitations is taken from the smaller basis CI and is 0.000942 au; thus the total CI stabilization is 0.043410 au for the dimer and 0.044082 for two monomers.

[12] (a) See H. Margenau and N. R. Kestner, "Theory of Intermolecular Forces," Pergamon Press, Oxford, 1969, Appendix A; (b) see, for example, P. Bertoncini and A. C. Wahl, *Phys. Rev. Lett.*, **25**, 991 (1970); H. F. Schaeffer, D. R. McLaughlin, F. E. Harris, and B. J. Alder, *ibid.*, **25**, 988 (1970).

[13] M. Gelus, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **7**, 503 (1970).

[14] P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).

planation is that the calculations of Gelus, *et al.*, were closer to the SCF limit for B_2H_6 than BH_3.

The Thermodynamics of LiH Dimerization

Using the computed vibrational frequencies, rotational constants, and electronic energies (including CI), the thermodynamic functions for LiH dimerization $2LiH(g) \rightarrow (LiH)_2(g)$ were computed at different temperatures and the results are presented in Table IV.

Table IV. Thermodynamic Functions[a]

T, K	ΔG, kcal/mol	ΔH, kcal/mol	ΔS, eu	K, atm^{-1}
300	−34.34	−44.37	−33.46	0.103×10^{26}
400	−30.91	−44.48	−33.93	0.768×10^{17}
500	−27.39	−44.46	−34.13	0.938×10^{12}
600	−23.81	−44.37	−34.26	0.469×10^{9}
700	−20.16	−44.24	−34.39	0.197×10^{7}
800	−16.47	−44.08	−34.51	0.316×10^{5}
900	−12.73	−43.91	−34.64	0.124×10^{4}
1000	−8.97	−43.74	−34.77	0.911×10^{2}
1100	−5.17	−43.55	−34.89	0.107×10^{2}
1200	−1.36	−43.37	−35.00	0.177×10
1300	2.46	−43.18	−35.11	0.385
1400	6.30	−42.98	−35.21	0.103
1500	10.15	−42.79	−35.29	0.332×10^{-1}
1600	14.00	−42.60	−35.37	0.122×10^{-1}
1700	17.85	−42.40	−35.44	0.507×10^{-2}
1800	21.71	−42.21	−35.51	0.231×10^{-2}
1900	25.56	−42.01	−35.57	0.115×10^{-2}
2000	29.42	−41.82	−35.61	0.610×10^{-3}

[a] Standard state, 1 atm.

The appropriate expressions relating electronic vibrational, rotational, and translational properties to thermodynamic functions are listed in Davidson[15] (the molecule was assumed to be in its ground electronic state).

Brewer has shown[16] that, for a liquid in equilibrium with its gas phase monomer and dimer and the heat of dissociation of dimer (calculated here to be 42 kcal/mol) less than the heat of vaporization of the monomer (47 kcal/mol),[17] the monomer will be the predominant gas-phase species at lower temperatures and the fraction of dimer will increase as the temperature increases.

The best way to detect the dimer is not obvious; it is not likely that the total pressure of dimer can be made high enough to allow an electron diffraction study. Perhaps one can take advantage of the high quadrupole moment of $(LiH)_2$ and use an electric field and field gradient to separate atoms and monomer from dimer.

An alternative method of detection for the dimer is matrix isolation. After depositing small amounts of LiH in an inert matrix (and allowing some diffusion by raising the temperature slightly), one could search for the three ir-active (b_{1u}, b_{2u}, and b_{3u}) vibrational modes of $(LiH)_2$.

The Electronic Structure of Linear $(LiH)_2$ and Hydrogen Bonds

Even though the linear $(LiH)_2$ is far less stabilized than the cyclic structure (ΔE(linear) = 26.0 kcal/mol), there are some interesting features of its charge distribution which deserve comment. First, the charge redistribution supports the previous generalization from studies on H-bonded[18] and "lithium bonded"[19] systems that the charge shifts to *increase* the already existing polarity in the monomers and thus the attraction between fragments. At the minimum energy geometry, Li_1 has lost 0.236 electron, Li_2 has lost 0.194, H_1 has gained 0.366, and H_2 has gained 0.064. In this system, hydrogen, as the more electronegative atom, gains charge on dimer formation.

The molecular orbital energy shifts follow the trend previously noted;[19] the MO's mainly centered on fragment 1 ($\epsilon_1 = -2.5160$ au, $\epsilon_2 = -0.3908$ au), which is the electron donor, decreased in energy relative to the monomer MO energies (Table I); the MO's from the electron acceptor, fragment 2, are increased in energy ($\epsilon_1 = -2.3596$, $\epsilon_2 = -0.2524$).

The charge transfer shifts seem to be different from those in H bonds, $X\!:\cdots H—Y$, where the X fragment donates some of its lone-pair electrons to H—Y. In this linear dimer, the fragment which is donating its electronegative end (Li_1–H_1) actually appears to gain 0.130 electron at the expense of Li_2–H_2 (see above Mulliken populations). If one breaks up the Mulliken atomic populations into orbital populations, one finds that all the orbitals except the longest range Li_2 s function (exponent = 0.028643) have positive orbital populations; this Li_2 s function actually has a negative population of −0.229. Such an unphysical result shows that the Mulliken populations analysis is not a suitable tool to examine charge transfer[20] effects in this system; the orbital energy shifts are indirect evidence that the "charge transfer" is actually taking place in the intuitively reasonable direction (from fragment 1 to 2).

Conclusions and Chemical Analogies

We have presented electronic structure calculations which predict the existence and characterize the properties of $(LiH)_2$. What more general conclusions can we draw from this study?

First, other alkali hydrides would probably have similar dimerization energies. However, they would probably be more difficult to detect, because the weaker M–H bond strength in the monomer makes the dissociation $2MH \rightarrow 2M + H_2$ more favored,[21] but if one works at high partial pressures of H_2, these species may also be observable. However, it might be easier to detect them in an inert matrix. Theoretical calculations at the SCF level are now underway on $(NaH)_2$ to see how its ΔE (dimerization) compares with that of $(LiH)_2$.

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[15] N. Davidson, "Statistical Mechanics," McGraw-Hill, New York, N. Y., 1962, pp 124–125.

[16] L. Brewer, Paper 7, National Nuclear Series, Vol. 19B, L. L. Quill, Ed., McGraw-Hill, New York, N. Y., 1950; G. N. Lewis and M. Randall, "Thermodynamics" (revised by K. S. Pitzer and L. Brewer), 2nd ed, McGraw-Hill, New York, N. Y., 1961, pp 537–539.

[17] "JANAF Thermochemical Tables," 2nd ed, Dow Chemical Co., Midland, Mich., 1970; National Bureau of Standards, Report No. NSRDS-NBS-37.

[18] A. Johanssen, P. Kollman, and S. Rothenberg, *Chem. Phys. Lett.*, in press; P. Kollman and L. C. Allen, *Chem. Rev.*, 72, 283 (1972).

[19] P. Kollman, J. F. Liebman, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1142 (1970).

[20] A physically more meaningful way to compute polarization and charge transfer effects is through valence bond calculations, and we hope to investigate this point. See also P. Politzer and R. S. Mulliken, *J. Chem. Phys.*, 55, 5135 (1971), for a better way to examine charge redistribution effects.

[21] See M. C. Sneed and R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. 6, Van Nostrand, Princeton, N. J., 1957, p 112 ff.

Secondly, what about higher polymers of gas phase LiH? Matrix isolation techniques have been used to identify[5] a polymer of LiF. A trimer of LiH probably would be difficult to observe in the gas phase (very unfavorable entropy), but an intuitively reasonable structure would be a benzene-like hexamer with alternating lithium and hydrogen atoms. Just as in $(LiH)_2$, the three lithiums would be closer to the center of the molecule than the hydrogens because there are no valence orbital nodes between the lithiums and two between the hydrogens. Ethyllithium forms a gas-phase dimer,[22] but methyllithum appears to be predominantly a tetramer in solution studies, with the Li and methyl groups forming two interlocking tetrahedra.[23] Thus there is precedent for the existence of $(LiH)_4$ in a similar structure with H replacing CH_3.

Acknowledgments. One of us (P. A. K.) is most grateful to Leo Brewer for instruction in the thermodynamics of high-temperature species and for pointing out the role of high H_2 pressure in alkali hydride studies. P.A.K. also thanks Joe Cambre, Bill Hunt, and Lester Andrews for helpful comments.

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[22] E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, 2, 197 (1964).

[23] L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, 91, 1057 (1969).

Comparison of Semiempirical Classical and Semiempirical Quantum Mechanical Calculations on Acetylcholine

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Abstract: The results of a semiempirical classical calculation on acetylcholine, in which the conformational energy is taken to be the sum of nonbonded and electrostatic pair-wise interactions, are compared to both semiempirical quantum mechanical INDO (intermediate neglect of differential overlap) results and to experimental data for the same molecule. It is found that both the classical and quantum mechanical studies give similar results and that both correlate well with experimental data. In addition, our study points out a difficulty in the INDO method in that it allows nonbonded atoms to approach almost to bonding distances before giving repulsion.

The importance of the acetylcholine molecule in the transmission of electrical signals through the neural system has stimulated much experimental and theoretical research on its allowed conformations. The theoretical studies have included semiempirical classical calculations by Liquori, Damiani, and De Coen,[1] in which they included nonbonded interactions and torsional potentials but did not include electrostatic interactions, and a recent follow-up by Ajò, *et al.*,[2] in which electrostatic interactions were included; and semiempirical quantum mechanical calculations by Kier[3] using the extended Hückel method and by Beveridge and Radna[4] using the INDO (intermediate neglect of differential overlap) method. The principal reason that our present study was initiated was to get a more quantitative idea of the accuracy that one can achieve using classical type potential functions by comparing our results both with the above quantum mechanical results, especially the very extensive study by Beveridge and Radna, and with experimental data for acetylcholine. This purpose is especially relevant at this time due to two recent papers. The first by Pullman and coworkers[5] criticizes semiempirical classical calculations of dipeptides on the basis that such calculations failed to predict certain experimental results while their PCILO (perturbative configuration interaction using localized orbitals) method did. The second by Tonelli[6] compares experimental nmr results to theoretical results obtained from dipeptide maps generated both classically and quantum mechanically. Tonelli found that classical and extended Hückel results agreed with experiment while the PCILO method of Pullman yielded different results.

Calculation Parameters

In order to facilitate comparison of our results with the INDO results of Beveridge and Radna,[4] hereafter referred to as BR, we used exactly the same structural parameters. These were taken by BR primarily from the X-ray crystallographic results of Canepa, *et al.*,[7] except for parameters involving the hydrogen atoms which were not determined. The hydrogen–carbon bond distances were set at 1.09 Å and the H–C–C bond angles were set at 109.47°. In addition, the methyl hydrogens of the trimethylammonium group were oriented for minimal steric repulsions.

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