difference between the vertical and adiabatic values. However, neither Thrush and Zwolenik[16] nor Elder and Parr[17] observed vibrational structure in their data to support this proposal. A much larger uncertainty than the ionization potential is the heat of formation of the tropyl radical with estimates ranging from 64.8 kcal/mol[18] to 71.3 kcal/mol.[19]

In conclusion, we feel that our results confirm that the $C_7H_7^+$ ion formed at threshold for both toluene and cycloheptatriene has the tropylium structure. We also propose that the heat of formation for tropylium cation is not significantly lower than our observed value of 207 kcal/mol.

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Role of the Dispersion Energy in the Binding of the $(Cl_2)_2$ Molecule

Sir:

While the Cl_2 crystal has been the subject of many experimental and theoretical studies, the interest in the $(Cl_2)_2$ dimer is much more recent. In 1974, Klemperer et al.[1] observed that the $(Cl_2)_2$ dimer is polar, such a polarity being compatible with an "L-shaped" or a "T-shaped" structure. Two theoretical studies,[2,3] based on the use of molecular orbitals, attempted to determine the most stable configuration. Unfortunately, in both cases, either the method used or practical limitations involved in the treatment led to unconclusive results. In the first case,[2] the method used was not appropriate for the treatment of such weakly bonded molecules since the electron correlation effect is neglected. As we shall show, the dispersion energy contribution is predominant in the binding of the $(Cl_2)_2$ dimer. Thus the binding energies obtained[2] are artificial. In ref 3, the $(F_2)_2$ dimer is considered as a model, assuming a similar structure for $(F_2)_2$ and $(Cl_2)_2$. Using ab initio wave functions, the dispersion energy is added to the SCF supermolecule treatment. These calculations give a linear configuration more stable than the T-shaped one. This does not agree with the experimental observation.[1,3] As we shall show this disagreement is probably due to a bad description of the dispersion energy in ref 3, this description being better in the case of the linear configuration than in the T-shaped one.

Table I. $(Cl_2)_2$: Intermolecular Energies (kcal/mol)

Configuration	d, Å[a]	ΔE_{SCF}[b]	E_{disp}[c]	E'_{disp}[d]	E_{tot}[e]
Linear	3.175	2.10	−2.49	−1.86	−0.39
	3.440	1.10	−1.61	−1.20	−0.51
	3.969	0.45	−0.73	−0.54	−0.29
	4.763	0.19			
"T-Shaped"	3.175	1.69	−3.25	−2.44	−1.56
	3.440	0.43	−2.11	−1.58	−1.68
	3.704	−0.01	−1.40	−1.05	−1.41
	4.233	−0.11			
	4.763[f]	−0.00			

[a] See ref 3, Figure 5: in the linear case, d is the distance between the two nearest nonbounded atoms; in the "T-shaped" one, d is the distance between the middle of molecule 1 (see in the text) and the nearest atom of molecule 2. [b] $\Delta E_{SCF} = E_{SCF}(\text{dimer}) - E_{SCF}(\text{isolated molecule})$. [c] Expression 2 of ref 5. [d] Expression 1 of ref 5 and used in ref 3. [e] $E_{tot} = \Delta E_{SCF} + E_{disp}$. [f] Using a double ζ basis set.

Though our own calculations on the $(Cl_2)_2$ dimer are not yet completed, our preliminary results show the importance of the dispersion energy and explain the difficulties encountered in ref 3. In the present communication, we give the results obtained for two configurations: the linear one and the T-shaped one. As in our previous studies of the $(H_2)_2$ system,[4] a perturbation dispersion term[5] is added to the SCF supermolecule energies.[6] Two expressions of the dispersion term have been proposed,[5] corresponding to different partitions of the individual molecular hamiltonians: expression 2 is used in the present work, denoted E_{disp} in Table I; expression 1 is used in ref 3, denoted E'_{disp} in Table I.

Ab initio calculations are then performed, using molecular orbitals which are linear combinations of gaussian functions centered on each atom. For the SCF supermolecule treatment a large basis set is used: 11s and 7p uncontracted functions taken from ref 7 and a d function chosen to optimize the energy of the Cl_2 molecule. The energy of the Cl_2 molecule is 918.9077 hartrees for an optimized distance of 2.011 Å. This distance can be compared with the experimental value of 1.988 Å. For the calculation of the dispersion energy, the previous basis set is contracted into one function for each shell of the core (1s, 2s, 2p) and two functions for the valence shells (3s, 3p). The d polarization function is now optimized in order to obtain the largest value of the dispersion energy, as previously described for other systems.[4,5] In the calculation of the dispersion energy, the core shells are not taken into account. The molecular distances are not varied in the calculations.

For the linear configuration ΔE_{SCF} (Table I) is repulsive at intermediate intermolecular distances ($d \lesssim 4.763$ Å) and very probably replusive at larger distances. For the T-shaped configuration ΔE_{SCF} becomes attractive around $d = 3.7$ Å, the attractive energy being −0.113 kcal/mol for $d = 4.233$ Å. We have not tried to determine the SCF minimum with more accuracy since the van der Waals minimum is located at shorter distances. Our results are in disagreement with the study of the $(F_2)_2$ system which exhibits an SCF minimum for the two configurations.[3] However, a smaller basis set gives less repulsive energies for both configurations of $(Cl_2)_2$. Also the intermolecular SCF energy is very sensitive to the optimization of the molecular distance. Thus we may wonder whether both dimers have a different behavior or if a larger basis set would give an attractive SCF intermolecular energy for the linear configuration of the $(F_2)_2$ system.

We can see from Table I that the values of E'_{disp} are about 75% of those of E_{disp}. An analysis of the contribution due to the different molecular orbitals shows the importance of d orbitals. Let us consider the T-shaped configuration: the first molecule lies along the z axis and the second molecule lies along the intermolecular y axis. The most important contribution to the dispersion energy involves a pure $d_{x^2-y^2}$ virtual orbital of the first molecule. The d_{xy} orbital of the first molecule is also important. Other important virtual orbitals of the first molecule generally have a large coefficient corresponding to some d components. The d functions are of less interest when the molecule lies along the intermolecular y axis. For instance in the linear case, the largest contribution involves the first δ_u virtual orbital of each molecule. In this orbital the coefficient corresponding to the d_{yy} component is only 0.27. Other important virtual orbitals are of the type p_{xu} or p_{zu}, the coefficient corresponding to a d component (d_{xy} or d_{yz}, respectively) being not very large in such orbitals. Thus, though the importance of the d functions may not be negligible in the linear case, it is obviously of less importance than in the T-shaped configuration. This probably explains why the linear configuration is more stable than the "T" configuration in ref 3. Since the stability of the $(Cl_2)_2$ dimer is due mainly to the dispersion energy, a bad description of this dispersion energy may lead to misleading results.

Finally, we can see from the total energy E_{tot} (Table I) that the T-shaped configuration exhibits a much deeper van der Waals minimum (about −1.68 kcal/mol) than the linear configuration (about −0.511 kcal/mol). The corresponding intermolecular distance is about 3.44 Å. This is compatible with the observed polar character of this dimer.[1,3] Work on the L-shaped configuration is in progress. From our preliminary results, it seems that the L-shaped configuration is slightly more stable than the T-shaped one.

Acknowledgment. The calculations have been performed on the Univac 1110 of the Centre de Calcul de Strasbourg-Cronenbourg (Centre de Recherches Nucléaires du CNRS).

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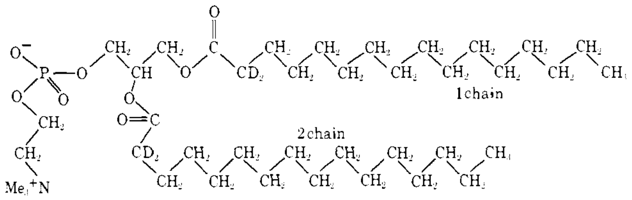
Deuterium Nuclear Magnetic Resonance Investigation of the Dipalmitoyl Lecithin–Cholesterol–Water System

Sir:

There has recently been considerable interest in using a variety of physical techniques to investigate the interactions between cholesterol and lipid membranes.[1] Early studies demonstrated that cholesterol could either increase or decrease the fluidity of lipid monolayers, depending on the initial degree of order of the hydrocarbon chains involved.[2,3] More recent investigations using differential scanning calorimetry,[4-6] x-ray diffraction,[7,8] spin-labeling,[9-11] freeze-fracture electron microscopy,[12] deuterium NMR,[13-15] carbon-13 NMR,[16-18] proton NMR,[19-20] and neutron diffraction[21,22] have been aimed at elucidating the precise nature of the phase separations induced by cholesterol in lipid bilayers, and of the effects of the bulky steroid nucleus on the segmental motion of the lipid hydrocarbon chains.

Below the chain melting temperature (T_c), spin label,[11] freeze fracture electron microscopy,[12] ^{13}C NMR,[18] and very recent calorimetric experiments[23] detect a phase boundary at a cholesterol (CHOL) mole fraction (χ_{CHOL}) of about 0.2. In contrast, earlier calorimetric data,[4-6] x-ray diffraction experiments,[8] and recent ^{13}C NMR experiments[24] detect changes at $\chi_{CHOL} \simeq 0.33$, but not at 0.2. In an attempt to understand these two groups of apparently conflicting experiments, we have undertaken a systematic study of the ^2H NMR spectra of the dipalmitoyl phosphatidylcholine (DPPC)–CHOL and dimyristoyl phosphatidylcholine (DMPC)–CHOL systems in excess water (≥50 wt % H_2O), and we present a preliminary account of our results here. We detect significant changes in our NMR spectra at both $\chi_{CHOL} \simeq 0.2$ and 0.33, and offer possible explanations as to some of the molecular changes occurring at these compositions.

The parameters we study in our experiments are the residual quadrupole splittings, $\Delta\nu_Q$, of some specifically deuterated phosphatidylcholines. These splittings, which were monitored as a function of both χ_{CHOL} and temperature, reflect the motional state of the acyl chains. While one expects discontinuities in these parameters at phase boundaries, it does not necessarily follow that abrupt changes in motional parameters imply a phase boundary. This is so because thermodynamic phases are macroscopic and it is conceivable that one can have abrupt variations in structural/motional parameters, as the concentration or temperature is varied, at the microscopic level within the same macroscopic phase. This is a difficulty inherent in many of the approaches which have been used to map the phase diagram of the lecithin–cholesterol–water system, and it may account for some of the different conclusions which have been obtained using different methods. Thus, identification of the discontinuities and breaks in our data with phase boundaries is by inference only.



Recently Seelig and Seelig[25] have shown that the ^2H spectra of pure 1,2-[2′,2′-D]DPPC (I) exhibit three major quadrupole splittings, and by selectively deuterating either the 1 or 2 chains they assigned the largest splitting to the deuterons on the 1 chain and the two smaller splittings to the deuterons on the 2 chain. We have confirmed this result. Figure 1c illustrates a typical spectrum obtained at 55 °C of pure I in excess water. In addition to the major splittings between the 1 and 2 chains mentioned above, we also observe a small splitting of the 1 chain lines not reported by Seelig and Seelig: this splitting is observed either with or without high power proton irradiation. The splittings observed in the ^2H spectra could be due to magnetic inequivalence of the two deuterons on each chain, or to two different conformations of the lipid molecules, which are interconverting at a rate slow compared to the splittings. In temperature-dependent studies on DPPC and DMPC in the absence of cholesterol, the 2-chain lines remain of approximately equal intensity over about a 40 °C range above T_c. In addition, we have observed split equal intensity lines from 2-