is readily available through the use of oriented multibilayers, which facilitate the unambiguous determination of T_1 and T_{1Q} anisotropies in detail. In particular, the relaxation times can be determined for any orientation, not just for the parallel ($\beta = 0°$) and/or the perpendicular ($\beta = 90°$) orientations, which alone are often insufficient to discriminate between models. The necessity of considering the entire relaxation profile whenever possible is evident in the $T_1(\beta)$ profiles (experiment and theory) and $T_{1Q}(\beta)$ profile (theory) for the C6-position, all of which exhibit a maximum near $\beta = 55°$. Although cholesterol motion is relatively simple on the time scale appropriate to spin–lattice relaxation, allowing a straightforward analysis of the relaxation data, even for systems whose dynamical complexity will require a more sophisticated treatment, the interpretation of anisotropic relaxation time measurements, together with their frequency and temperature dependences, will facilitate the identification of individual motional modes and their correlation times.

The principal aim of this study was to demonstrate that anisotropic spin–lattice relaxation may be used to distinguish between possible descriptions of cholesterol motion in phospholipid bilayers. For cholesterol at 50 mol % in DPPC, a large-angle jump between three equivalent sites with an exchange rate of 3.2×10^7 s^{-1} describes T_1 and T_{1Q} anisotropies for several sites on the steroid molecule, as well as temperature-dependent results. While axial diffusion or axial nearest-neighbor jumps among a larger number of sites may be equally valid descriptions a priori, they are not consistent with all of the relaxation data. Viewed in the broader context of stochastic reorientational motion of a uniaxial rotator, cholesterol reorientation is seen to be an experimental realization of the continuous random walk (CRW) model, first employed by Barnes[25] to describe hindered rotation of alkanes. In this model, the diffusive motions of the alkane methylene protons were described as a random walk on a circle containing N discrete sites. It is not surprising, therefore, that the mathematical problem of determining the rotational scattering law for quasi-elastic scattering from alkanes[25] or liquid crystals[26] performing such a random walk is tantamount to that solved by Torchia and Szabo[16a] in evaluating the NMR azimuthal autocorrelation function (eq 6) for nearest-neighbor jumps among N equivalent sites. Although large-angle hopping motions of the molecular long axis have been detected previously in a smectic liquid crystal,[27] for example, by incoherent neutron quasi-elastic scattering, to our knowledge, this is the first demonstration by NMR that such motions occur in lipid bilayers.

Acknowledgment. We gratefully acknowledge Drs. E. J. Parish and T. Akiyama for the gift of deuteriated cholesterols and Dr. R. G. Griffin for generously providing a copy of the computer program for calculating T_1 anisotropies. We thank Doug Moffatt for his skillful assistance in plotting figures and Michèle Auger for useful discussions.

Registry No. DPPC, 2644-64-6; cholesterol, 57-88-5.

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Ab Initio Calculations on Borylphosphines: Prediction of a Synergistic Substituent Effect in Diborylphosphine

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Abstract: The results of ab initio calculations on the borylphosphines, $H_{3-n}P(BH_2)_n$, $n = 1$–3, are reported. The barrier to rotation of one BH_2 is found to increase on going from $n = 1$ to $n = 2$, so that the two BH_2 groups in diborylphosphine appear to act cooperatively, rather than competitively. The origin of the apparent synergistic substituent effect in diborylphosphine is shown to be the ability of one conjugated BH_2 group to reduce dramatically the energetic cost of planarizing phosphorus. This permits the formation of stronger P–B π-bonds in $HP(BH_2)_2$ than in H_2PBH_2.

Experimental and computational evidence indicates that π-electron-acceptor substituents compete with each other for π-electron density when attached to the same π-electron donor. Consequently, as the number of substituent groups increases, the strength of the π-bond to each substituent decreases. For example, the barrier to rotation of a formyl group has been found to decrease from 17.8 kcal/mol in H_2NCHO[1] to 12.9 kcal/mol in $HN(CHO)_2$[2] to 7.5 kcal/mol in $CH_3CON(CHO)_2$.[2] Calculations on $H_{3-n}N(BH_2)_n$ have shown the barriers to rotation about a B–N bond to decrease monotonically as n goes from 1 to 3.[3] The decrease in barrier heights was correlated with a decrease in the π-overlap populations along each B–N bond.[4]

In this paper we report the results of ab initio calculations on mono-, di-, and triborylphosphine, $H_{3-n}P(BH_2)_n$. Our calculations show that, in contrast to the case with the borylamines, in the borylphosphines the barrier to rotation about a P–B bond actually increases on going from $n = 1$ to $n = 2$. The cause of the apparent synergism between the two boron substituents in $HP(BH_2)_2$ is

Table I. RHF P–B Bond Lengths (Å) and Phosphorus Pyramidalization Angles[a] (deg) and Relative MP4SDTQ Energies (kcal/mol) of Different Geometries of $H_{3-n}P(BH_2)_n$

molecule	geometry	R(P–B)	ϕ[a]	E
H_2PBH_2	equilibrium	1.905[b]	71.0	0[c]
	rotated	1.973	82.4	10.4[d]
	planar	1.808	0.0	4.5
	planar-rotated	1.961	0.0	44.6
$HP(BH_2)_2$	equilibrium	1.869[e]	45.1	0[f]
	rotated	1.900, 1.969	71.9	17.5
	planar	1.849	0.0	0.5
	planar-rotated	1.811, 1.955	0.0	21.1
$P(BH_2)_3$	equilibrium	1.873	0.0	0[g]
	rotated	1.859, 1.951	25.5	12.8
	planar-rotated	1.853, 1.950	0.0	13.0

[a] Angle between the R_2P plane and the extension of the P–R′ bond. [b] At the MP2 level $R = 1.863$ Å and $\phi = 66.4°$. [c] Relative to −367.9199 hartrees. [d] With $\phi = 71.0°$, $E = 12.8$ kcal/mol. [e] At the MP2 level, $R = 1.837$ Å and $\phi = 34.9°$. [f] Relative to −393.2757 hartrees. [g] Relative to −418.6264 hartrees.

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[4] Similar results were obtained for $H_{3-n}BX_n$ for X = NH_2 and X = OH.[3]

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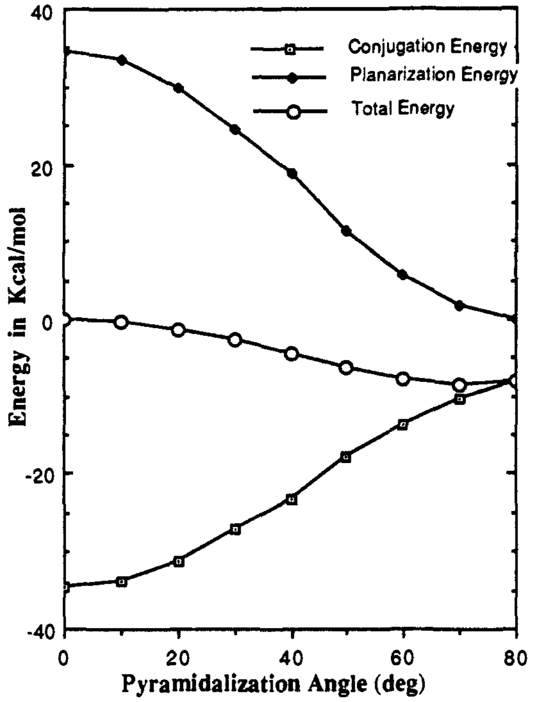

Figure 1. RHF conjugation, planarization, and total energies of H_2PBH_2 as a function of the pyramidalization angle, ϕ, the angle between the HPH plane and the extension of the PB bond.

analyzed.

Calculations were performed with the 6-31G* basis set.[5] Geometries were optimized with RHF calculations,[6] and vibrational analyses were performed to identify the nature of each stationary point found. Energies at the stationary points were recalculated with inclusion of electron correlation at the MP4SDTQ level.[7] Reoptimization of selected RHF geometries at the MP2 level was found to have a negligible effect on the MP4 energies, which are reported in Table I along with the P–B bond lengths and phosphorus pyramidalization angles. Calculations were carried out with the GAUSSIAN 86 package of ab initio programs.[8]

As shown in Table I, the barrier to rotation about the P–B bond in H_2PBH_2 is calculated to be 10.4 kcal/mol. This MP4 value is somewhat higher than the rotational barrier of 6.6 kcal/mol, obtained by a previous RHF calculation,[9] but the RHF barriers and optimized geometries[6] from the two sets of calculations are in good accord. Both sets of calculations predict a nonplanar equilibrium geometry at phosphorus, in agreement with the X-ray structure of a sterically shielded derivative.[10]

The barrier to planarity at phosphorus is 4.5 kcal/mol at the MP4 level. Planarization of phosphorus with the boron rotated out of conjugation is calculated to require 34.2 kcal/mol. Thus, as shown in Table I, although π-bonding between phosphorus and boron reduces the equilibrium pyramidalization angle at phosphorus by only 11.4° at the RHF level, the reduction in the MP4 barrier to planarity at phosphorus amounts to 29.7 kcal/mol.

As phosphorus becomes more planar, it can form a stronger π-bond to boron. This is shown graphically in Figure 1, where the RHF conjugation energy in H_2PBH_2 is plotted as a function of the pyramidalization angle, ϕ, at phosphorus. The conjugation energy—the negative of the energy required to rotate the BH_2 out of conjugation with the phosphorus lone pair at a fixed value of ϕ—is more than 3 times larger in magnitude in planar (ϕ = 0°) H_2PBH_2 than at the equilibrium geometry (ϕ = 71.0°).[11]

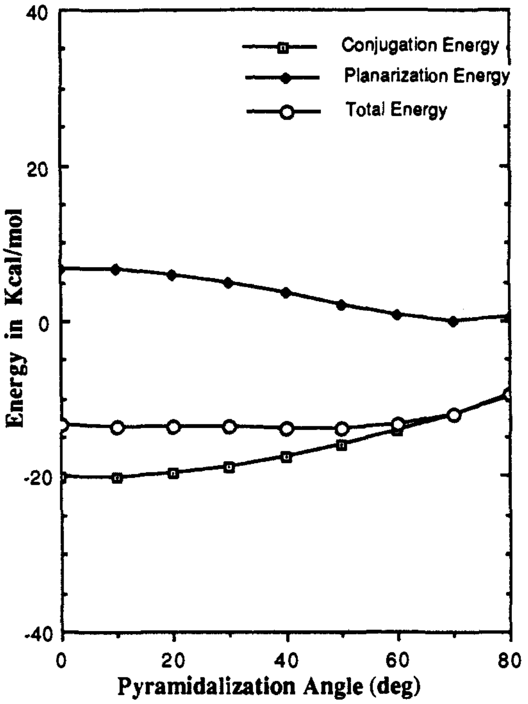

Figure 2. RHF conjugation, planarization, and total energies of $HP(BH_2)_2$ as a function of the pyramidalization angle, ϕ, the angle between the BPB plane and the extension of the PH bond.

Also plotted as a function of ϕ in Figure 1 is the RHF planarization energy. The planarization energy is the energy required to flatten the phosphorus to a value of ϕ with the BH_2 group twisted out of conjugation, starting from the RHF equilibrium value of ϕ = 82.4° for the twisted conformation. Like the magnitude of the conjugation energy, the planarization energy increases as ϕ decreases.

The total energy of conjugated H_2PBH_2—the energy of the conjugated geometry, relative to that of the equilibrium geometry of the rotated conformation—is the sum of the conjugation and planarization energies. The total energy at the RHF level is also plotted as a function of ϕ in Figure 1. Because, as shown in Figure 1, the magnitudes of the conjugation and pyramidalization energies have a similar functional dependence on ϕ, the RHF curve for the total energy is rather flat.[12] This is why, although the RHF total energy minimum occurs at ϕ = 71.0° (66.4° at the MP2 level), the energetic cost of completely planarizing phosphorus in the conjugated molecule is fairly small, amounting to 8.6 kcal/mol at the RHF level and 4.5 kcal/mol when electron correlation is included at the MP4 level.[13]

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(11) Although, for the sake of economy, Figure 1 was constructed with RHF energies, qualitatively similar plots would have been obtained with the MP4 energies. For example, the MP4 conjugation energy of -40.1 kcal/mol at ϕ = 0° is slightly more than 3 times larger in magnitude than the MP4 conjugation energy of -12.8 kcal/mol at ϕ = 71.0°.

(12) This may explain why the X-ray structure of a sterically shielded derivative[10] has a significantly smaller pyramidalization angle at phosphorus than the one that we calculate for H_2PBH_2. Minimization of steric interactions between substituents attached to phosphorus would tend to favor a more planar geometry.

(13) This reduction in the calculated barrier to phosphorus planarity on inclusion of electron correlation is consistent with our previous experience in computing the barriers to planarity at pyramidal radical centers.[14]

(14) Feller, D.; Davidson, E. R. Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 2596. Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. Hrovat, D. A.; Sun, H.; Borden, W. T. *J. Mol. Struct.* (*Theochem.*) **1988**, *163*, 51. Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

In $HP(BH_2)_2$ the barrier to rotation of one BH_2 group is 17.5 kcal/mol, which is *greater* by 7.1 kcal/mol than the calculated barrier to rotation in H_2PBH_2. Thus, the two boron substituents in $HP(BH_2)_2$ appear to behave cooperatively, rather than competitively. Clues to the origin of the calculated synergism are contained in Table I.

At the monorotated geometry of $HP(BH_2)_2$, the presence of one BH_2 substituent, properly oriented for π-bonding to phosphorus, causes some flattening at phosphorus and makes the MP4 barrier to planarity at phosphorus only 3.6 kcal/mol. As might have been expected, the optimized pyramidalization angle and the size of the barrier to planarity in monorotated $HP(BH_2)_2$ are close to those in conjugated H_2PBH_2 and substantially less than the values of these quantities at the rotated geometry of H_2PBH_2. Thus, the potential function for planarizing phosphorus in the monorotated conformation of $HP(BH_2)_2$, which is shown in Figure 2, is much more similar to that in Figure 1 for the total energy of conjugated H_2PBH_2 than to that for the planarization energy of the rotated conformation of H_2PBH_2.

The relative softness of the potential function for planarizing phosphorus in the monorotated conformation of $HP(BH_2)_2$ allows the fully conjugated molecule to have a considerably more planar equilibrium geometry ($\phi = 45.1°$ at the RHF level and $\phi = 34.9°$ at MP2) than that of conjugated H_2PBH_2. As shown in Figure 2, the curve for the total energy of fully conjugated $HP(BH_2)_2$ is quite flat—so flat, in fact, that only 0.6 kcal/mol is computed at the RHF level (0.5 kcal/mol at MP4) to be required to planarize the fully conjugated molecule completely. With such a small calculated barrier to planarity, it is not all surprising that the X-ray crystal structure of a sterically shielded derivative shows the phosphorus to be planar.[15]

Because the potential function for planarizing phosphorus in the monorotated conformation of $HP(BH_2)_2$ is substantially softer than that in the rotated conformation of H_2PBH_2, the curve for the total energy parallels that for the conjugation energy much more closely in $HP(BH_2)_2$ (Figure 2) than in H_2PBH_2 (Figure 1). Consequently, the energy difference between the equilibrium geometry of the conjugated conformation and the equilibrium geometry of the monorotated species (which is the energy 0 in both Figures 1 and 2) is larger in $HP(BH_2)_2$ than in H_2PBH_2. Thus, the comparative softness of the potential function for planarizing phosphorus in the monorotated geometry of $HP(BH_2)_2$ is responsible for making the increase in total energy on rotating a BH_2 group out of conjugation larger in diborylphosphine than in H_2PBH_2.

Nevertheless, comparison of the curves for the conjugation energies in Figures 1 and 2 reveals the expected competition between the two BH_2 groups. At values of ϕ below 60°, the magnitude of the conjugation energy is larger in H_2PBH_2 than in $HP(BH_2)_2$.[16] For example, as shown in Table I, the MP4 energy required to rotate one BH_2 group out of conjugation in planar $H_{3-n}P(BH_2)_n$ decreases from 40.1 kcal/mol for $n = 1$ to 20.6 kcal/mol for $n = 2$ and to 13.0 kcal/mol for $n = 3$. Moreover, correlated with the decrease in the strength of the individual π-bonds in planar $H_{3-n}P(BH_2)_n$, as n increases, a monotonic increase in the optimized P–B bond length from 1.808 Å for $n = 1$ to 1.849 Å for $n = 2$ to 1.873 Å for $n = 3$ is observed.

Actually, even at the optimized geometries for $n = 2$ and 3, a competitive effect is seen, since the energy required to rotate one BH_2 group decreases from 17.5 kcal/mol for $n = 2$ to 12.8 kcal/mol for $n = 3$. For these two molecules the phosphorus planarization energies at the equilibrium geometries are both sufficiently small that the difference between the total energies of the conjugated molecules is dominated by the difference in their conjugation energies. Consequently, H_2PBH_2 should be viewed as the anomalous member of this series. Despite the fact that its conjugation energies are largest in magnitude, the high energetic cost of planarizing phosphorus at rotated geometries makes the *net* energy lowering that accompanies P–B π-bonding anomalously small in this molecule.

Provided that substituents with sufficiently modest steric requirements were used, our quantitative predictions of the sizes of the rotational barriers in $H_{3-n}P(BH_2)_n$ should be testable experimentally. Of more general significance is the qualitative description, given by the results of this theoretical study, of the conditions under which cooperative, rather than competitive, effects are likely to be observed for electronically similar, conjugating substituents.

Acknowledgment. We thank the National Science Foundation for support of this research and for partial funding of the purchase of the Convex C-2 computer on which some of these calculations were performed. We also thank the San Diego Supercomputer Center for a generous allocation of computer time.

Supplementary Material Available: Listing of RHF-optimized geometries and energies for $H_{3-n}P(BH_2)_n$ (6 pages). Ordering information is given on any current masthead page.

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(15) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *Inorg. Chem.* **1988**, *27*, 3919.

(16) At pyramidalization angles above 60°, where the conjugation energies in both H_2PBH_2 and $HP(BH_2)_2$ are small, that in $HP(BH_2)_2$ is slightly greater. This result is predicted by simple second-order perturbation theory. The numerator in the second-order expression for the P–B interaction energy in $HP(BH_2)_2$ is exactly twice that in H_2PBH_2 [i.e., $\{\int \phi_P \mathcal{H} (\phi_{B1} + \phi_{B2})/\sqrt{2}\}^2 = 2(\int \phi_P \mathcal{H} (\phi_B))^2$]. However, because of the stabilizing interaction between empty boron p orbitals in the $\phi_{B1} + \phi_{B2}$ combination in $HP(BH_2)_2$, the energy difference between the filled phosphorus orbital and the empty boron orbital with which it mixes is smaller in $HP(BH_2)_2$ than in $HPBH_2$. Since these energy differences appear in the denominators of the second-order expressions for the P–B interaction energies, the interaction energy in $HP(BH_2)_2$ is expected to be somewhat larger than twice that in H_2PBH_2. Consequently, at values of ϕ that are large enough to make the P–B interactions sufficiently weak, so that second-order perturbation theory is applicable, the energy required to twist a BH_2 group out of conjugation in $HP(BH_2)_2$ is expected to be slightly larger than in H_2PBH_2. This explains the small cooperative effect of the two BH_2 groups on the conjugation theory in $HP(BH_2)_2$ that is found at values of $\phi > 60°$.