Molecular Orbital Theory of the Electronic Structure of Molecules. XXVII. Energies and Conformations of XCH_2Y Systems Involving Li, Be, and B

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Abstract: All possible combinations of Li, BeH, BH_2, CH_3, NH_2, OH, and F substituents interacting through a single methylene group, XCH_2Y, were investigated by ab initio molecular orbital theory employing split valence bases and standard geometrical models. Interaction between the substituents is revealed by the bond separation energy (the energy change during the formal reaction, $XCH_2Y + CH_4 \rightarrow CH_3X + CH_3Y$) and the rotational potentials. Large bond separation energies tend to be found only when X and Y are both electronegative or both electropositive ($X = Y = Li$ is an exception) due to reinforcing π and σ effects. There is a regular trend in the ethyl series, CH_3CH_2X, with the electronegativity of X; the most positive value is obtained when X = F and the most negative when X = Li. Rotational barriers have been analyzed by decomposition into V_1, V_2, and V_3 terms. The threefold potentials (V_3) for any group, X, are nearly independent of the substituent, Y. The onefold potentials (V_1) appear to be dominated by dipolar repulsion effects and are opposite in sign but nearly equal in magnitude for F and Li (or BeH). For compounds with BH_2 substituents, the V_1 terms are smaller and depend to some extent on the BH_2 rotational arrangement. In their coplanar conformation, BH_2 groups can also manifest nonbonded repulsive $H \cdots H$ steric effects. The V_2 terms are more complex, and represent chiefly a composite of σ-π interactions through bonds and direct 1,3 interactions through space. Rotation around XCH_2-BH_2 bonds is dominated by the high π acceptor ability of the BH_2 group, and the barrier responds in a monotonic way to the electronegativity of X; X = Li favors the perpendicular conformation of BH_2 by 20.4 kcal/mol, but X = F produces a planar conformation more stable by 7.1 kcal/mol. The potential curves for FCH_2OH and $LiCH_2OH$ are quite different, and the same is true for FCH_2NH_2 vs. $LiCH_2NH_2$. Coupled rotation is exhibited in the double rotors involving BH_2 and OH or NH_2 groups. $CH_3CH_2BH_2$ slightly favors a conformation in which the vacant orbital hyperconjugates with the C-C rather than the two C-H bonds, and $BH_2CH_2BH_2$ prefers the geometry where both BH_2 groups can B-C hyperconjugate.

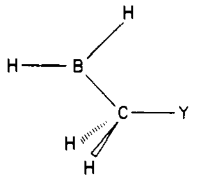
A systematic study of the relative energies, conformations, and bond interactions of a wide range of molecules using a uniform level of approximation is a major objective of this series. We have already investigated the complete set of acyclic molecules with up to three nonhydrogen atoms (C, N, O, F) which may be represented by classical valence structures (single, double, or triple bonds) with no formal charges or unpaired electrons.[2-4] Simple ab initio molecular orbital methods (Hartree-Fock theory with the split valence 4-31G basis)[5] employing standard geometrical models revealed important energetic effects in the three heavy-atom systems, X-Y-Z: (1) bond stabilization energies (stabilities relative to simple two-heavy-atom systems, X-Y and Y-Z), and (2) coupled double rotational potentials for X-Y and Y-Z bonds. Such bond interactions are clearly important in larger molecules so that the three heavy-atom systems are valuable model structures for theoretical study. In the present paper, we begin the extension of this work to the atoms Li, Be, and B in order to complete the full first short period of the periodic table (Li to F).

We investigate here the interaction of Li, BeH, BH_2, CH_3, NH_2, OH, and F groups through a single methylene in the series of compounds XCH_2Y. The previous work, involving only CH_3, NH_2, OH, and F, has shown strong interactions for the polar substituents with accompanying major coupling effects on the rotational potentials.[2,3] In this paper, we aim to compare these interactions with those involving polar bonds to the electropositive substituents Li, BeH, and BH_2. Even though few of these compounds are characterized experimentally, such a study should increase our understanding of substituent interactions and help lay foundations for future work on organometallic compounds.

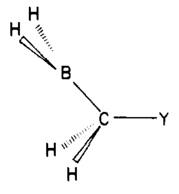
Method and Geometrical Model

The procedure used follows closely that described in ref 2. Hartree-Fock theory is used with the 4-31G basis[5] for H, B,[6] C, N, O, and F and the related 5-21G basis[7,8] for Li and Be. Single runs are carried out at prescribed standard geometries. For some molecules, particularly those involving substituents of opposite polarity, convergence of the self-consistent calculation was not achieved using the standard Gaussian 70 computer program.[9] Recently developed alternative techniques were then used.[10]

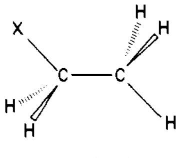
The standard geometrical model has already been specified[2,11] for bonds involving H, C, N, O, and F. To complete the standard model for the remaining groups, we specify linear valence for beryllium and trigonal planar valence for boron (bond angles 120°). Additional standard lengths required are listed in Table I. These were selected as average values from experimental and other theoretical sources. Completion of the specification of the geometrical model requires dihedral angles for the X-C and C-Y bonds if X or Y are BH_2, CH_3, NH_2, or OH. For BH_2 we consider two possibilities, coplanar with the other substituent Y (I) or perpendicular to the other substituent (II). For CH_3, we consider staggered (III) and eclipsed (IV) conformations.



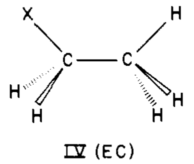
I (COPL)



II (PERP)



III (ST)



IV (EC)

Table I. Additional Standard Bond Lengths

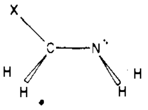
Bond[a]	Length, Å	Bond[a]	Length, Å
Be2–H	1.29	Be–C4	1.69
B3–H	1.16	B–C4	1.57
Li–C4	2.01		

[a] The symbol X*m* denotes atom X with the valence *m*.

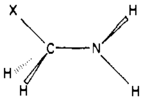
Table II. Calculated Total and Relative Energies

Molecule	Conformation (X, Y)	Total energy, hartrees	Rel energy, kcal mol^{-1}
CH_4		−40.13955	
Li- CH_3		−46.95957	
HBe–CH_3		−54.73290	
H_2B–CH_3	Copl	−65.34630	0
	Perp	−65.34630	0
H_3C–CH_3	Ec	−79.10965	3.26
	St	−79.11484	0
H_3C–NH_2	Sp	−95.06464	2.13
	Ap	−95.06803	0
H_3C–OH	Sp	−114.86842	1.12
	Ap	−114.87020	0
H_3C–F		−138.85648	
Li–CH_2–Li		−53.77464	
Li–CH_2–BeH		−61.56856	
Li–CH_2–BH_2	Copl	−72.16319	20.40
	Perp	−72.19570	0
Li–CH_2–CH_3	Ec	−85.92076	3.29
	St	−85.92601	0
Li–CH_2–NH_2	Ap	−101.87270	6.12
	Ac	−101.87493	4.72
	Sp	−101.87656	3.70
	Sc	−101.88245	0
Li–CH_2–OH	Sp	−121.68067	6.37
	Sc	−121.68227	5.36
	Ac	−121.68432	4.08
	Ap	−121.69082	0
Li–CH_2–F		−145.67635	
HBe–CH_2–BeH		−69.33873	
HBe–CH_2–BH_2	Copl	−79.93831	9.26
	Perp	−79.95306	0
HBe–CH_2–CH_3	Ec	−93.69655	3.12
	St	−93.70152	0
HBe–CH_2–NH_2	Ac	−109.64687	4.69
	Ap	−109.64729	4.43
	Sp	−109.65131	1.91
	Sc	−109.65435	0
HBe–CH_2–OH	Sp	−129.44765	6.90
	Sc	−129.45127	4.63
	Ac	−129.45382	3.03
	Ap	−129.45865	0
HBe–CH_2–F		−153.44035	
H_2B–CH_2–BH_2	Copl, copl	−90.54708	7.87
	Perp, copl	−90.55593	2.32
	Perp, perp	−90.55962	0
H_2B–CH_2–CH_3	Copl, ec	−104.31265	4.10
	Perp, ec	−104.31408	3.21
	Copl, st	−104.31882	0.23
	Perp, st	−104.31919	0
H_2B–CH_2–NH_2	Perp, ac	−120.26368	6.63
	Perp, ap	−120.26817	3.82
	Copl, sp	−120.26852	3.60
	Perp, sp	−120.26925	3.14
	Copl, ac	−120.26962	2.91
	Copl, ap	−120.26967	2.87
	Perp, sc	−120.27005	2.64
	Copl, sc	−120.27425	0
H_2B–CH_2–OH	Perp, sp	−140.06343	10.03
	Perp, sc	−140.06841	6.90
	Perp, ac	−140.06936	6.31
	Perp, ap	−140.07160	4.90
	Copl, ac	−140.07520	2.64
	Copl, sp	−140.07541	2.51
	Copl, sc	−140.07559	2.40
	Copl, ap	−140.07941	0
H_2B–CH_2–F	Perp	−164.05373	7.14
	Copl	−164.06511	0

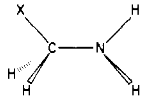
For NH_2, which has tetrahedral angles in the standard model, we consider four possibilities based on the orientation of the fourth tetrahedral direction denoted by :N. Starting with XCN: synperiplanar (V, dihedral angle 0°), we proceed in 60° steps through synclinal (VI), anticlinal (VII), and antiperiplanar (VIII). For OH groups, the same classification is used, based on the XCOH angle (IX-XII).



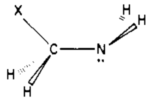
V (SP)



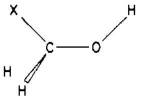
VI (SC)



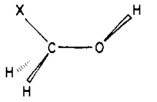
VII (AC)



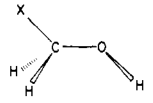
VIII (AP)



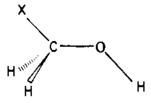
IX (SP)



X (SC)



XI (AC)



XII (AP)

The complete results for energies are listed in Table II. This gives total energies and energies relative to the most stable conformation for each species.

Discussion

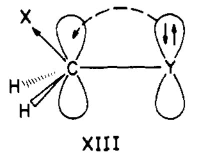
Most of the results shown in Table II can be understood in terms of a combination of σ and π bonding changes. The substituents formed from electropositive elements are σ-type electron donors in order of effectiveness, $BH_2 < BeH < Li$. At the same time they are π-type electron acceptors in the opposite order $Li < BeH < BH_2$. Conversely, the groups involving electronegative elements are σ acceptors in the order $NH_2 < OH < F$ and π donors in the order $F < OH < NH_2$. (NH_2 with a nonplanar geometry is not strictly a pure π donor, but the lone-pair orbital has a large amount of p character.) The reasons for these orderings are quite clear. The σ-donor or σ-acceptor character of the substituent is directly related to the electronegativity of the orbital forming the bond, which increases steadily across the periodic table from lithium to fluorine. The π-donor ordering is related to the ionization potential of the lone pair of electrons in NH_2, OH, and F. This increases from NH_2 to F causing the lone pair to be less available for donation. On the other hand, the substituents Li, BeH, and BH_2 all have vacant p orbitals and will be π acceptors. The electron affinity of the vacant p orbital will be greatest for BH_2, primarily because of access to greater nuclear charge than for BeH or Li.

If two substituents X and Y are attached to the same carbon atom, these electronic characteristics will interact in several ways.

A. If X and Y are both σ donors or both σ acceptors, a destabilizing interaction is expected. This is primarily for electrostatic reasons. If X is a σ donor, it will make the central carbon more negative and consequently less attractive for a second σ donor Y. σ acceptors behave similarly.

B. If X is a σ donor and Y a σ acceptor, there should be stabilizing interactions since the electron deficiency induced by one atom is reduced by electron donation from the other, $X \rightarrow CH_2 \rightarrow Y$.

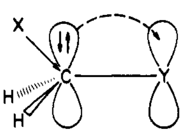
C. If X is a σ acceptor and Y a π donor, there should be stabilization by back-donation from the π electrons of Y into the partially vacated carbon orbital of the C–X bond (XIII). Alternatively,[4] this can be considered as back-dona-



XIII

tion into the antibonding σ^* orbital of C–X which is lowered in energy by the electronegative character of X.

D. If X is a σ donor and Y a π acceptor, there should also be stabilization because of π donation from the highly populated carbon orbital of the C–X bond into the acceptor orbital on Y (XIV). Or, in other terms, the σ bonding C–X orbital, which is destabilized by the electropositive character of X, can more effectively donate electrons to Y. This is the converse of effect C.

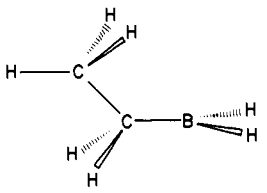


XIV

E. In a similar way, if X is a σ donor and Y a π donor, or if X is a σ acceptor and Y a π acceptor, the corresponding interaction will be destabilizing.

The π-type effects C, D, and E can, to some extent, be turned on or off by rotation about the C–X or C–Y bonds if the substituents are BH_2, NH_2, or OH. In addition to these bond interaction effects, we should also consider possible direct interactions between X and Y. These include direct coulomb attractive or repulsive energies, steric overlap forces, or possible attraction by direct interaction of lone-pair orbitals on one with the vacant orbital of the other.

Before considering the interaction of two polar substituents, we shall first comment on the barriers for the substituted ethanes C_2H_5X. Here changes are not very large for either electropositive or electronegative substituents. In all cases, the favored conformation for the C–C bond remains staggered and the corresponding theoretical barrier is close to that in ethane (C_2H_6 3.3, C_2H_5Li 3.3, C_2H_5BeH 3.1, and $C_2H_5BH_2$ 3.2). For ethylborane, the favored structure of the BH_2 group is the perpendicular form XV, but the barrier to rotation about the C–B bond (0.2 kcal mol^{-1}) is much less than in the isoelectronic *n*-propyl cation.[12]



XV

Now we turn to the effects of substitution on the rotational potentials for polar bonds. Consider first the substituted methanols XCH_2OH. If X is a σ acceptor such as fluorine, the C–O rotational potential is modified in favor of the synclinal structure as discussed previously.[3,13] This is partly due to the π-donor and σ-acceptor interaction XIII and partly to the dipole effect involving the CX and OH bonds. If X is a σ donor, on the other hand, opposite effects are expected and are indeed found in the theoretical results. The rotational potential curves for the CO bond in $LiCH_2OH$ and FCH_2OH[3] are contrasted in Figure 1. These curves are obtained by taking the calculated energies for the XCOH dihedral angles 0, 60, 120, 180° and fitting to a potential function

$$V(\phi) = \tfrac{1}{2}V_1(1 - \cos\phi) + \tfrac{1}{2}V_2(1 - \cos 2\phi) + \tfrac{1}{2}V_3(1 - \cos 3\phi) \quad (1)$$

The resulting constants are listed in Table III along with constants from similar analyses of other compounds. This procedure is identical with that followed in ref 3. The V_3 potentials in $LiCH_2OH$ and FCH_2OH are similar (same sign favoring staggered conformations) and the magnitude of V_3 is close to that in methanol. Both the V_1 and V_2 potentials are reversed in sign as expected. As a result $LiCH_2OH$ should have a single minimum energy rotamer with LiCOH antiperiplanar.

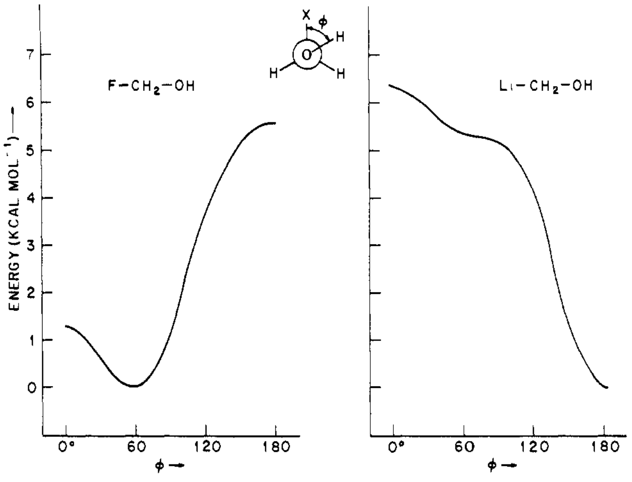


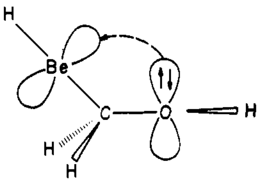
Figure 1.

Table III. Potential Constants V_i (kcal mol^{-1}) for Internal Rotation[a]

Molecule	V_1	V_2	V_3
$CH_3–CH_3$[b]	0	0	−3.26
$LiCH_2–CH_3$	0	0	−3.29
$HBeCH_2–CH_3$	0	0	−3.12
$H_2BCH_2–CH_3$ (perp)	0	0	−3.21
$H_2BCH_2–CH_3$ (copl)	0	0	−3.86
$F–CH_2–CH_3$[b]	0	0	−3.63
$CH_3–OH$[b]	0	0	−1.12
$LiCH_2–OH$	−5.10	+2.05	−1.27
$HBeCH_2–OH$	−5.67	+0.51	−1.23
$H_2BCH_2–OH$ (perp)	−3.81	−1.15	−1.32
$H_2BCH_2–OH$ (copl)	−1.50	+1.69	−1.00
$FCH_2–OH$[b]	+5.25	−2.20	−0.96
$CH_3–NH_2$[b]	0	0	−2.13
$LiCH_2–NH_2$	+4.76	−3.40	−2.34
$HBeCH_2–NH_2$	+4.81	−1.10	−2.29
$H_2BCH_2–NH_2$ (perp)	+3.11	+1.54	−2.43
$H_2BCH_2–NH_2$ (copl)	+1.45	−2.37	−2.18
$FCH_2–NH_2$[b]	−4.86	+4.28	−2.01
$CH_3–BH_2$	0	0	0
$LiCH_2–BH_2$	0	−20.40	0
$HBeCH_2–BH_2$	0	−9.25	0
$H_2BCH_2–BH_2$ (perp)	0	−2.32	0
$H_3CCH_2–BH_2$ (st)	0	−0.24	0
$H_2NCH_2–BH_2$ (sp)	0	+0.46	0
$HOCH_2–BH_2$ (ap)	0	+4.90	0
$FCH_2–BH_2$	0	+7.14	0

[a] Conformations with dihedral angle $\phi = 0$ are defined as XCCH (ec), XCOH (sp), XCN: (sp), XCBH (copl). [b] Reference 3.

The XC–OH rotational potential can be handled in the same way if X is HBe. The results (Table III) show V_1 and V_3 values close to those of lithium, but the value of V_2 is markedly reduced (from +2.05 to +0.51). To understand this, we note that a favorable direct bonding 1,3 interaction (XVI) is most effective with ϕ = 90° and consequently



XVI

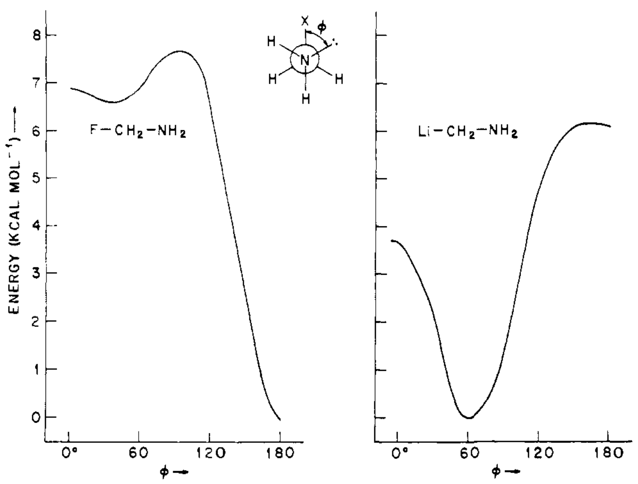
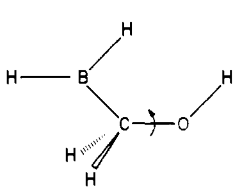
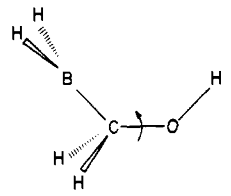


Figure 2.

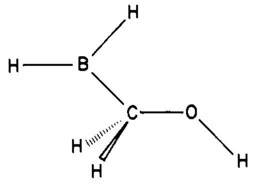
leads to a negative contribution to V_2. This direct bonding effect should be larger for beryllium than for lithium (Be being a better π acceptor than Li) leading to the less positive value for V_2. Further evidence in favor of this interpretation comes from a similar analysis of the C–N rotational potentials for $H_2BCH_2NH_2$ with BH_2 held fixed in either coplanar or perpendicular conformations. If BH_2 is coplanar (XVII), the 1,3 interaction between the lone-pair p orbital on oxygen and the vacant p orbital on carbon cannot occur. Consequently, the value of V_2 returns to a more positive value of +1.69 kcal mol^{-1}. In the perpendicular conformation XVIII, on the other hand, the 1,3 interaction will become larger and a negative value of V_2 (−1.15 kcal mol^{-1}) is obtained. For the whole range of conformations of BH_2CH_2OH, the most stable conformation is the (copl, ap) structure XIX in which the unfavorable σ–π interaction is avoided and the dipolar interaction between bonds is greatest.



XVII

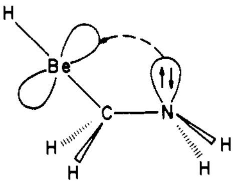


XVIII

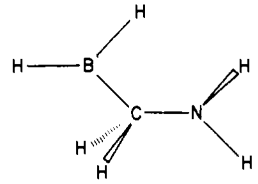


XIX

The results for substituted methylamines XCH_2NH_2 show similar patterns. Again, the substituent lithium gives results opposite to F. Potential curves for $LiCH_2NH_2$ and FCH_2NH_2 are shown in Figure 2. For these molecules, the V_2 potential (measuring the σ–π type of interaction) is larger than in the substituted methanols. NH_2 is a stronger π donor and corresponding energy contributions are increased. The V_2 potential for electropositive X favors conformations in which the lone-pair direction is rotated by 90° from the XCN plane, leading to two minima in synclinal conformations. If X is HBe, the values of V_1 and V_3 are found to be close to those for Li, but the magnitude of V_2 is again reduced. This can also be interpreted in terms of increased direct 1,3 bonding which is most effective in the synperiplanar form XX. Strictly this effect also contributes to V_1 for the amino group. As for the C–O bonds, this interpretation receives further support from the BH_2CH_2–NH_2 potentials, also listed in Table III. If BH_2 is coplanar, the 1,3 interaction is eliminated and V_2 becomes more negative than for HBe. If BH_2 is perpendicular, the total value becomes positive, indicating that the through-space effect is dominant in the V_2 potential. However, if the whole potential, including V_1, is considered, the most stable structure is the (copl, sc) form XXI.

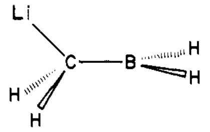


XX

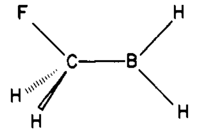


XXI

The effect of substituents X on the C–B rotational potential in molecules XCH_2–BH_2 is simple to analyze. Taking the coplanar form I as ϕ = 0, only the V_2 terms in eq 1 survive (Table III). Here the π-type effects are large, particularly for lithium substitution. Lithium is the strongest σ donor of the whole series and BH_2 is the strongest π acceptor. Consequently the perpendicular conformation XXII is favored over the coplanar form by the remarkably large value of 20.4 kcal/mol^{-1}. The electronic effect is equivalent to extensive resonances with a structure $Li^+CH_2{=}BH_2^-$ which can only occur in conformation XXII. For HBe substitution, the effect is still strong but reduced in magnitude. For fluorine, on the other hand, the sign of V_2 is reversed and the perpendicular conformation XXIII is preferred. This is expected, since σ acceptance of electrons by fluorine would inhibit π-bond formation in the coplanar form. These results all parallel effects already found for β substitution of classical structures for the ethyl cation.[4,12]

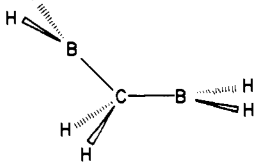


XXII



XXIII

Finally, the symmetrically substituted molecule $H_2BCH_2BH_2$ is found to be most stable in the double-perpendicular form XXIV, as expected, since boron is a σ



XXIV

Table IV. Bond Separation Energies of XCH_2Y (kcal mol^{-1})

	Y						
X	Li	BeH	BH_2	CH_3	NH_2	OH	F
Li	−3.1	+9.8	+18.4	−5.6	−3.5	+0.4	−0.1
HBe	+9.8	+7.8	+8.4	−4.2	−4.4	−3.1	−5.9
H_2B	+18.4	+8.4	+4.1	−1.5	−0.3	+1.5	+1.2
H_3C	−5.6	−4.2	−1.5	+1.2	+3.6	+5.4	+6.1
H_2N	−3.5	−4.4	−0.3	+3.6	+8.3	+13.0	+14.7
HO	+0.4	−3.1	+1.5	+5.4	+13.0	+15.2	+13.3
F	−0.1	−5.9	+1.2	+6.1	+14.7	+13.3	+11.5

donor and π acceptor. The twofold barrier to rotation for a single BH_2 group is 2.3 kcal mol^{-1}.

Steric repulsion effects for coplanar BH_2 groups are illustrated by the 0.65-kcal/mol increase in the methyl rotational barrier in going from perpendicular to coplanar $BH_2CH_2CH_3$, and more dramatically in coplanar-coplanar $BH_2CH_2BH_2$, which is 5.55 kcal/mol less stable than the conformation with one BH_2 coplanar and the other BH_2 perpendicular.

In order to make an overall comparison between the various interactions that take place between the C-X and C-Y bonds, it is useful to list the bond separation energies for all the compounds XCH_2Y. These are defined as the energies of isodesmic processes[14]

$$X\text{-}CH_2\text{-}Y + CH_4 \rightarrow X\text{-}CH_3 + CH_3\text{-}Y \qquad (2)$$

and measure the stabilizing interactive effect of the two groups X and Y. All the effects listed earlier in this section should be reflected in positive (stabilizing) or negative (destabilizing) contributions to the bond separation energies.

The complete set of bond separation energies is listed in Table IV, including those involving two electronegative groups previously discussed in ref 2. The values in Table IV are based on the total energies for each species in its calculated lowest energy conformation. A number of significant comments can be made about this table.

(1) Entries in the lower right-hand part of Table IV (X = NH_2, OH, and F and Y = NH_2, OH, and F) are quite large and positive corresponding to stabilizing interactions. Previous studies of the rotational potentials have indicated that this is primarily due to π-donor and σ-acceptor coupling.[2,3]

(2) Entries in the upper left part (X = Li, BeH, and BH_2 and Y = Li, BeH, and BH_2) are also mostly positive and quite large. Our studies of the rotational potentials again indicate this to be a σ-π effect, this time involving π acceptor and σ donor. Dilithiomethane is an apparent exception to this rule, because of direct steric repulsion between the lithium atoms as indicated by a large negative overlap population. A widened LiCLi angle results when the $LiCH_2Li$ geometry is optimized.[15]

(3) Entries in the upper right section of the table (X = Li, Be, and BH_2 and Y = NH_2, OH, and F) are mostly small and of either sign. Since the σ-π interaction is unfavorable under these circumstances, the lowest energy conformations tend to minimize such interactions. Where this is not possible, as in $LiCH_2F$, the remaining σ-π destabilization is probably compensated by the favorable σ-σ interaction.

(4) It is noteworthy that the largest entry in the table is +18.4 kcal mol^{-1} for $LiCH_2BH_2$, corresponding to the strongest σ donor (Li) and the strongest π acceptor (BH_2). In a similar way, the compound FCH_2NH_2 with the strongest σ acceptor and the strongest π donor also gives a large positive value (+14.7 kcal mol^{-1}).

(5) If we follow the entries down the column with Y = BH_2, the bond separation energy falls rapidly from +18.4 kcal mol^{-1}, but levels off for electronegative elements. This leveling off (near zero values) is due to the fact that BH_2 takes up the coplanar conformation I if X is electronegative, thus eliminating the unfavorable σ-π interaction. If we construct a similar column of bond separation energies with BH_2 *held fixed* in the perpendicular conformation II, and the X group arranged most favorably, the corresponding numbers are +18.4, +8.4, +4.1, −1.5, −2.9, −3.4, and −5.9 kcal/mol. This shows a steady trend from large positive to large negative values.

(6) The results for the ethyl compounds C_2H_5X also show a steady change from negative values for electropositive X to positive values for electronegative X. This is probably because a methyl group is more effective as a π donor than as a π acceptor and effect C (XIII with Y = methyl) is dominant. Such an effect is implied by the known preference for metals to be attached to primary carbons of alkanes rather than secondary or tertiary positions.[16] We intend to present a more detailed analysis of lithium through fluorine substituent effects on various hydrocarbons subsequently.

Conclusions

This paper has been concerned with the interaction between C-X and C-Y bonds in disubstituted methanes and also with related effects concerning rotational barriers. The conclusions may be summarized as follows.

(1) The σ-donating or σ-accepting character of one group X clearly influences the π-electron structure of the other bond C-Y. The stabilizing interaction between a σ-acceptor X and a π-donor Y discussed previously is paralleled by the complimentary stabilizing interaction between a σ donor X and a π acceptor Y.

(2) For those polar groups Y which involve internal rotation about the C-Y bond, the nature of the rotational potential as a function of a substituent X (in XCH_2-Y) is easily understood in terms of the way in which the σ effect of X can be switched on or off by the rotational motion. For all such rotational systems, electronegative and electropositive substituents always lead to opposite trends in the shapes of the potential curves.

(3) The largest effects are found with strong σ donors X and strong π acceptors Y. This leads to a rotational barrier of more than 20 kcal mol^{-1} for $LiCH_2$-BH_2.

(4) If X and Y are both groups leading to an internal rotation degree of freedom, the double-rotor potentials, as far as they have been explored, can be understood in terms of a superposition of these σ-π interaction effects in both directions $X(\sigma)$-$Y(\pi)$ and $X(\pi)$-$Y(\sigma)$.

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Conformational Study of Cyclic and Acyclic Phosphate Esters. CNDO/2 Calculations of Angle Strain and Torsional Strain

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Abstract: Angle strain and torsional strain energies were calculated using the CNDO/2 LCAO-MO method for various geometries of dimethyl phosphate monoanion and compared with energies for 2′,3′-cyclic ribose phosphate and 3′,5′-cyclic ribose phosphate. While the calculations fail to identify the source of the strain energy in the 3′,5′-cyclic six-membered ring nucleotides, they do indicate that a significant portion of the high heat of hydrolysis of the five-membered ring, 2′,3′-cyclic nucleotides is associated with relief of torsional strain and that preferred torsional conformations of acyclic esters are strongly coupled to the RO-P-OR bond angles. This coupling of ester, O-P-O bond angles, and torsional angles is also demonstrated by CNDO calculations on various geometries of trimethyl phosphate. Eclipsing of one of the phosphate ester bonds reduces the bond angle between the esterified oxygen atoms by ca. 5° and eclipsing of both ester bonds further reduces the bond angle by another 5°. These predictions of the CNDO calculations are shown to be supported by x-ray crystallographic structures of cyclic and acyclic, monoanionic, and neutral phosphate esters.

One of the major unresolved questions regarding the manner in which 3′,5′-cyclic-adenosine monophosphate (cAMP) stimulates the activity of many different enzyme systems (glycogenolysis, lipolysis, protein synthesis, active transport, etc.)[2a] is its mode of binding to the enzyme cAMP protein kinase.[2b,3] The very large heat of hydrolysis of cAMP (−14 kcal/mol)[4,5] has prompted suggestions that cAMP covalently binds to the enzyme.[5,6] As pointed out by Westheimer and co-workers[7] this heat of hydrolysis quite inexplicably is not coupled with any demonstrable ring strain such as found in cyclic five-membered ring phosphate diesters; the O-P-O bond angle is similar to that of acyclic phosphates.[8,9]

A potential explanation for the anomalous behavior of the 3′,5′-cyclic nucleotides is that the strain energy is not associated with a decreased O-P-O bond angle but rather with a combination of factors such as ribose ring strain and phosphate diester torsional strain. In this paper we wish to present some semiempirical quantum mechanical calculations directed toward the elucidation of the importance of torsional strain and bond angle strain in both cyclic and acyclic phosphate esters. The acyclic phosphate diesters have aroused considerable theoretical interest because of the primary role the phosphate moiety plays in the structural definition of the polynucleic acids.[10,11]

Method of Calculation

Dimethyl phosphate monoanion and trimethyl phosphate, modeled on the basis of x-ray crystallographic structures of acyclic alkyl phosphates (see references in Tables II and III), were chosen for the quantum mechanical calculations on the acyclic esters (Figures 1 and 2). For the cyclic monoanions, molecular parameters from the crystal structures of 2′,3′-cyclic-cytidine monophosphate (cCMP)[12], 3′,5′-cyclic-uridine monophosphate (cUMP),[8] and 3′,5′-cyclic-guanosine monophosphate (cGMP)[13] have been used. However, we have retained only the ribose and phosphate ester portion of the structure, substituting a hydroxyl group for the nucleotide base.

The semiempirical SCF LCAO-MO calculations employed the CNDO option in the CNINDO/2 program of Pople and Segal.[14] Only the valence basis orbitals were considered and for phosphorus, 3d orbitals were included. The major structural parameters that we have varied in the dimethyl phosphate model are the RO-P-OR bond angle, θ, and the two dihedral angles ω and ω' defined in Figure 1. The angle θ' in Figure 1 is determined by the assumed C_{2v} symmetry of the phosphate tetrahedron, the fixed O-P-O bond angle, and the variable bond angle θ. Dihedral angles are defined by clockwise rotation about the phosphate ester bond, RO-POR (see ref 11 for convention). For the trimethyl phosphate molecule only bond angle, θ, and dihedral angle, ω, were varied (Figure 2). A torsional potential for a phosphate diester with a fixed 105° O-P-O bond angle was obtained by computing the energy of the dimethyl phosphate molecule using different torsional angles taken at 30° intervals (Table I and Figure 3). The symmetry of the problem has limited greatly the number of separate structures required to define this map (note the reflection planes along the diagonals).