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Ab Initio Study and NBO Interpretation of the Anomeric Effect in $CH_2(XH_2)_2$ (X = N, P, As) Compounds

Luis Carballeira* and Ignacio Pérez-Juste

Departamento de Química Física, Facultad de Ciencias, Universidad de Vigo, Vigo, Spain

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The generalized anomeric effects in nitrogen, phosphorus, and arsenic compounds were examined in detail by means of ab initio calculations. The conformational preferences can be considered adequately described at the HF/6-311G**//MP2/6-311G** level, since these results agree with those obtained using larger basis sets and including electron correlation up to the MP4 level. The favored conformers show two or one anti orientations between the X lone pair (Lp-X) and the X−C polar bond. According to the NBO analysis of the Hartree−Fock wave functions, the preferences for the anti Lp-X−C−X orientations and the barriers to internal rotation are due mainly to charge delocalization, which is always stronger than the electrostatic and steric contributions included in the Lewis term. These features are much larger for second-row substituents. From the comparison with the previously reported data for the corresponding oxygen, sulfur, selenium, and tellurium compounds, an increase of the stability of the conformers favored by anomeric orientations and also of the rotational barriers can be observed from group 15 to group 16 of the periodic table. The reason for this fact, more noticeable for second-row compounds, is the predominant role of the Lewis energy, that is, the nonhyperconjugative contributions. The calculated energies for the group separation reactions also increase when moving to the right through the periodic table, but they are not a reasonable measurement of the generalized anomeric effect, since they do not have a direct relationship with the conformational preferences.

Introduction

The anomeric effect, one of the most widely studied conformational phenomena,[1] is the tendency of a R−X−A−Y moiety—in which A is an element of medium electronegativity (e.g., C), Y is more electronegative than A (e.g., O or N), X is an element with lone pairs (n_X), and R is C or H—to assume a gauche orientation rather than the anti one. Two major explanations have been proposed for the origin of the anomeric effect. The electrostatic model of dipole interaction, which was applied for the first time to explain the destabilization of the equatorial conformations in sugars,[2] is based on the notion that the n_X/A−Y dipole−dipole repulsion destabilizes the anti conformation. According to the charge delocalization model, originally applied to explain the geometric distortions of the 2,5-dichloro-1,4-dioxanes,[3a] gauche orientations are favored due to the delocalization of the oxygen p lone pair into the low-lying anti adjacent σ^*_{A-Y} orbital.[3b] This explanation is equivalent to double bond−no-bond resonance or negative hyperconjugation in terms of valence bond theory.[1f]

Many studies on anomeric $RYCH_2XR$ compounds involving second-row atoms (X, Y = NH_2, OH, F) have shown that ab initio MO calculations adequately reproduce the energetic stabilities and the geometric trends in bond lengths and bond angles associated with the anomeric effect. Among these studies, natural bond orbital (NBO) analysis[4] has been used to support the model of charge delocalization.[5] The NBO method allows separation of the energy contributions due to hyperconjugation from those caused by electrostatic and steric interactions, so that hyperconjugative interactions can be studied separately.

For all the combinations of second-row substituents, the group separation reactions

$$RYCH_2XR + CH_4 \rightarrow CH_3XR + CH_3YR \qquad (1)$$

are endothermic. Since $p_Y-\sigma^*_{CX}$ delocalization does not occur on the right-hand side of eq 1, group separation energies were related to this hyperconjugative interaction. Thus, it was stated that the anomeric effect and the group separation energies have the same origin, and these reactions were taken as quantitative measurements of the anomeric effect.[6] Even more, since group separation energies calculated at the Hartree−Fock level are very small or even negative for third-row substituents (X, Y = PH_2, SH, Cl), it was concluded that the anomeric effect for these compounds is negligible.[6a] This fact was explained in terms of the less effective $p_Y-\sigma^*_{CX}$ delocalization for substituents of higher rows of the periodic table, which are poorer σ-acceptors and π-donors than their second-row counterparts. Despite this, however, XCH_2Y compounds containing X, Y = P, S, Cl, and Se display clear preferences for gauche conformations and exhibit bond lengths and bond angles which agree with the presence of $p_Y-\sigma^*_{CX}$ delocalization.[7]

Salzner and Schleyer[8] investigated the origin of the generalized anomeric effects in $CH_2(XH)_2$ compounds (X = O, S, Se, Te) by means of MP2 calculations and NBO analyses of the Hartree−Fock wave functions. Smaller anomeric effects were found for compounds containing S, Se, or Te than for X = O, which were due to nonhyperconjugative (e.g., steric and electrostatic) contributions increasingly favoring the anti conformations in going down the group. They also concluded that, for O, S, Se and Te, the group separation energies of eq 1 are not a measurement of the anomeric effect or $p_X-\sigma^*_{CX}$ hyperconjugation.

Finally, the thermodynamic stabilization energies of a series of XY_2H_n compounds (X = C, N, O, Si, P, S; Y = NH_2, OH, F, SiH_3, PH_2, SH) were calculated from the enthalpies of

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* Corresponding author. E-mail: uviqplco@cesga.es.

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formation obtained using the homodesmic reactions

$$XY_2H_n + CH_3XH_nCH_3 \rightarrow 2CH_3XH_nY \qquad (2)$$

with total energies of all the species computed at the MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p) level.[9] The thermodynamic stabilization energies were used to estimate the magnitude of the interaction between two substituents attached to a common saturated center. It was concluded that the generalized anomeric effect, which is only a part of this so-called geminal interaction, cannot be used for rationalizing the thermochemistry of reactions involving XY_2H_n compounds. However, it was also established that anomeric effects involving third-row atoms are not negligible, although they are smaller than those involving the corresponding second-row atoms. Furthermore, for a given X center, anomeric effects are generally smaller when atom Y belongs to the third period.[9]

To contribute to the study of the anomeric effect involving substituents of higher rows of the periodic table, in this paper we will consider the different conformers of $CH_2(XH_2)_2$ (X = N, P, As). By means of the NBO method,[4] the conformational energies and the rotational barriers around the C−X bonds will be analyzed, and the variation of the anomeric effect in moving down through group 15 of the periodic table will be examined. Moreover, the comparison with the reported results[8] for compounds involving atoms from group 16 will also give a general vision of the influence of moving to the right in the periodic table. Many interesting theoretical studies have been published about the structure and the anomeric effect of methanediamine, $CH_2(NH_2)_2$,[5f] but no experimental information is available. For methylenebis(phosphane), $CH_2(PH_2)_2$, the anomeric effect has been investigated theoretically at the HF/3-21G* level by Schleyer et al.,[6a] and a gas-phase structural study using gas electron diffraction, IR and He(I) photoelectron spectroscopy, and ab initio MO calculations at various HF and MP4 levels has been performed.[10] Finally, no experimental or theoretical study on the structure of methylenediarsine, $CH_2(AsH_2)_2$, has been found.

Methods

Figure 1 shows the TT, TG, GG, and G′G conformers of $CH_2(XH_2)_2$ (X = N, P, As). The letters represent the approximate value (T = 180°, G = 60°, G′ = −60°) of the Lp-X_1−C_2−X_3 and X_1−C_2−X_3-Lp dihedral angles, in this order. According to this notation, the anti Lp-X−C−X orientations correspond to the gauche H−X−C−X structures favored by the anomeric effect indicated in the Introduction. The geometries of all the conformers were fully optimized at several HF and MP2 levels, using different polarized basis sets. Because of the presence of lone pairs, single-point calculations including diffuse functions were also carried out. The influence of electron correlation was examined performing MP2 to MP4(full) calculations. The size of the basis sets employed in the correlated calculations depended on the available computational facilities. Vibrational frequencies and zero point energies (ZPE) were evaluated at the HF/6-311G** level. The computations were performed using Gaussian 94.[11]

The NBO analysis was carried out on the HF/6-311G** wave functions obtained for the MP2/6-311G** geometries. According to the NBO method,[4,5] the total SCF energy, E_{tot}, can be decomposed in two terms. The Lewis energy, E_{Lew}, is associated with the localized HF wave function (corresponding essentially to a Lewis structure, although its interpretation is not direct), and is obtained by zeroing all the orbital interactions, that is deleting the off-diagonal elements of the Fock matrix. The delocalization energy, E_{del}, corresponding to all the possible interactions between orbitals, is calculated as $E_{del} = E_{tot} - E_{Lew}$. To analyze the origin of the rotational barriers, additional HF/6-311G** optimizations and NBO analyses were performed on a series of structures with two simultaneously fixed Lp-X−C−X and X−C−X-Lp dihedral angles.

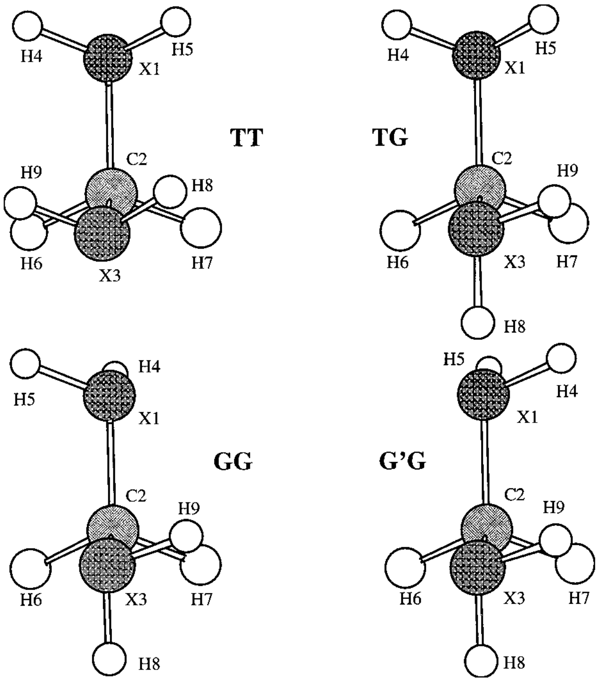

Figure 1. Conformers of $CH_2(XH_2)_2$ compounds (X = N, P, As)

Results

Influence of the Calculation Level on the Relative Energies. Table 1 shows the relative energies of the TT, TG, GG, and G′G conformers of $CH_2(XH_2)_2$ (X = N, P, As) at several computational levels. The influence on the stability of the conformers of the basis set, the electron correlation, and the ZPE can be analyzed from these values. In a previous study[5f] of the anomeric effect in methanediamines, $CR_2(NR_2)_2$ (R = H, CH_3), we compared the results obtained with calculation levels from HF/4-31G//HF/4-31G to MP2/6-31++G**//HF/6-31G** and MP2/6-31G**//MP2/6-31G**. We found that the inclusion of zero point energies and diffuse functions tends to reduce the relative energy of the less stable conformers, while the MP2 correction acts in the opposite way. Hence we concluded that HF/6-31G**//HF/6-31G** calculations were adequate for the analysis of the anomeric effect in methanediamines. The same conclusion was achieved for other anomeric compounds.[5b−e] Since relative energies of the conformers of $CH_2(XH_2)_2$, when X is P or As, are lower than those of X = N, the size of the basis set or the electron correlation treatment could be more important. For this reason, Table 1 incorporates results at higher computational levels than those used for methanediamines, with the purpose of establishing an uniform computational model to be used for X = N, P, and As compounds in the further analysis of the anomeric effect with the NBO method.

Energy data shows again that augmenting the basis set with diffuse functions reduces the relative energy of the less stable conformers of $CH_2(NH_2)_2$, while electron correlation acts in the opposite way, even at the MP4(full) level. The addition of polarization functions does not have an uniform effect since it

TABLE 1: Relative Energies (in kcal mol^{-1}) at Various Computational Levels for the Stable Conformers of the $CH_2(XH_2)_2$ Compounds (X = N, P, As)[a]

	TT	TG	GG	G′G
$NH_2-CH_2-NH_2$				
HF/6-31G**//HF/6-31G**[5f]	0.00	0.47	0.81	5.14
MP2/6-311G**//MP2/6-31G**	0.00	0.89	1.68	5.89
MP2/6-311++G**//MP2/6-31G**	0.00	0.57	0.67	4.92
HF/6-311G**//HF/6-311G**[12]	0.00	0.50	0.94	ns
HF/6-311G**//MP2/6-311G**	0.00	0.47	0.92	5.02
HF/6-311G**//MP2/6-311G** + ZPE	0.00	0.48	0.95	4.79
MP2/6-311G**//MP2/6-311G**	0.00	0.88	1.67	5.89
MP3/6-311G**//MP2/6-311G**	0.00	0.71	1.42	5.46
MP4(full)/6-311G**//MP2/6-311G**	0.00	0.90	1.76	5.81
HF/6-311+G**//MP2/6-311G**	0.00	0.27	0.37	4.48
MP2/6-311+G**//MP2/6-311G**	0.00	0.55	0.69	5.01
MP2/6-311++G**//MP2/6-311G**	0.00	0.55	0.65	4.90
MP3/6-311+G**//MP2/6-311G**	0.00	0.43	0.58	4.69
MP4(full)6-311+G**//MP2/6-311G**	0.00	0.57	0.79	4.92
HF/6-311++G(3df,3pd)//MP2/6-311G**	0.00	0.31	0.43	4.15
MP2/6-311++G(3df,3pd)//MP2/6-311G**	0.00	0.57	0.86	4.64
MP3/6-311++G(3df,3pd)//MP2/6-311G**	0.00	0.52	0.86	4.45
MP4(full)/6-311++G(3df,3pd)//MP2/6-311G**	0.00	0.60	1.02	4.50
$PH_2-CH_2-PH_2$				
HF/3-21G*//HF/3-21G*[6a]	0.36	0.00	0.86	nf
HF/DZP//HF/3-21G*[10]	0.24	0.00	ns	ns
HF/DZP//HF/DZP[10]	0.00	nf	0.53	0.77
HF/DZP //HF/DZP[10] [b]	0.00	nf	0.31	0.43
MP4/DZP//HF/DZP[10]	0.00	nf	0.98	1.00
HF/6-31G**//HF/6-31G**[10]	0.00	nf	0.45	0.60
HF/6-31G**//HF/6-31G**	0.33	0.00	0.78	0.97
HF/6-31G**//HF/6-31G** + ZPE	0.31	0.00	0.76	0.91
HF/6-31++G**//HF/6-31G**[10]	0.00	nf	0.48	0.69
MP4/6-31G**//HF/6-31G**[10]	0.00	nf	0.72	0.67
MP2/6-31G**//MP2/6-31G**	0.20	0.00	0.95	0.97
MP2/6-311G**//MP2/6-31G**	0.06	0.00	0.95	0.98
MP2/6-311++G**//MP2/6-31G**	0.07	0.00	1.02	1.07
HF/6-311G**//MP2/6-311G**	0.29	0.00	0.72	0.93
HF/6-311G**//MP2/6-311G** + ZPE	0.31	0.00	0.69	0.87
MP2/6-311G**//MP2/6-311G**	0.07	0.00	0.97	1.00
MP2/6-311++G**//MP2/6-311G**	0.05	0.00	1.03	1.08
MP3/6-311G**//MP2/6-311G**	0.06	0.00	0.99	1.00
MP4(full)/6-311G**//MP2/6-311G**	0.04	0.00	1.00	1.00
HF/6-311+G**//MP2/6-311G**	0.35	0.00	0.72	0.93
MP2/6-311+G**//MP2/6-311G**	0.09	0.00	0.98	1.07
MP3/6-311+G**//MP2/6-311G**	0.07	0.00	0.98	1.07
MP4(full)/6-311+G**//MP2/6-311G**	0.05	0.00	0.98	1.07
HF/6-311++G(3df,3pd)//MP2/6-311G**	0.59	0.00	0.79	0.93
MP2/6-311++G(3df,3pd)//MP2/6-311G**	0.46	0.00	1.12	1.07
MP3/6-311++G(3df,3pd)//MP2/6-311G**	0.41	0.00	1.09	1.06
MP4(FC)/6-311++G(3df,3pd)//MP2/6-311G**	0.41	0.00	1.10	1.06
$AsH_2-CH_2-AsH_2$				
HF/6-311G**//MP2/6-311G**	0.60	0.00	0.71	0.75
HF/6-311G**//MP2/6-311G** + ZPE	0.63	0.00	0.64	0.68
MP2/6-311G**//MP2/6-311G**	0.48	0.00	0.91	0.84
MP3/6-311G**//MP2/6-311G**	0.44	0.00	0.90	0.84
MP4(full)/6-311G**//MP2/6-311G**	0.45	0.00	0.86	0.80
HF/6-311+G**//MP2/6-311G**	0.59	0.00	0.72	0.77
MP2/6-311+G**//MP2/6-311G**	0.47	0.00	0.85	0.82
MP2/6-311++G**//MP2/6-311G**	0.45	0.00	0.90	0.85
MP3/6-311+G**//MP2/6-311G**	0.41	0.00	0.87	0.84
MP4(full)/6-311+G**//MP2/6-311G**	0.43	0.00	0.83	0.80

[a] nf, structure not characterized as minimum or transition state; ns, structure not studied. [b] Two sets of polarization functions on phosphorus (exponents 1.0 and 0.25).

increases the stability of some conformers, while reducing the stability of others. As the results obtained with the highest computational level (MP4(full)/6-311++G(3df,3pd)//MP2/6-311G**) employed for $CH_2(NH_2)_2$ are quite similar to the HF/6-31G**//HF/6-31G** or HF/6-311G**//MP2/6-311G** ones, we consider that the latter computational methods may be adequate for the study of the anomeric effect.

Previously reported data of $CH_2(PH_2)_2$ were obtained using from HF/3-21G*//HF/3-21G* to MP4/DZP//HF/DZP calculations.[6a,10] In these studies, not all the possible staggered conformers of $CH_2(PH_2)_2$ were characterized or the most stable conformer was not correctly predicted. Table 1 shows that TG is the most stable conformer if basis sets larger than 6-31G** are employed. However, it can also be noted that, for calculations smaller than HF/6-311++G(3df,3pd), the conformational energies (specially for the TT form) depend on the computational level employed. As happened with methanediamine, the HF/6-31G**//HF/6-31G** and HF/6-311G**//MP2/6-311G**

TABLE 2: Selected MP2/6-311G//MP2/6-311G** Geometrical Parameters (Bond Lengths in Angstroms and Bond Angles in Degrees) for the Stable Conformers of the $CH_2(XH_2)_2$ Compounds (X = N, P, As)**

	N				P				As			
	TT	TG	GG	G′G	TT	TG	GG	G′G	TT	TG	GG	G′G
C2−X1	1.4612	1.4506	1.4567	1.4607	1.8597	1.8593	1.8639	1.8630	1.9824	1.9830	1.9863	1.9860
X3−C2	1.4611	1.4684	1.4569	1.4609	1.8592	1.8593	1.8648	1.8630	1.9824	1.9803	1.9863	1.9860
H4−X1	1.0157	1.0161	1.0146	1.0163	1.4114	1.4119	1.4112	1.4117	1.5139	1.5153	1.5142	1.5142
H5−X1	1.0157	1.0154	1.0152	1.0157	1.4114	1.4123	1.4105	1.4114	1.5139	1.5150	1.5139	1.5143
H6−C2	1.0931	1.0939	1.1010	1.0939	1.0954	1.0946	1.0925	1.0946	1.0951	1.0941	1.0917	1.0940
H7−C2	1.0931	1.0993	1.1010	1.1069	1.0954	1.0930	1.0924	1.0906	1.0951	1.0923	1.0917	1.0898
X3−C2−X1	119.06	112.91	106.67	108.89	121.66	115.46	110.93	110.81	120.80	114.28	110.67	110.35
H6−C2−X1	107.46	108.31	114.42	107.67	107.25	106.74	111.41	106.68	107.21	106.84	110.66	106.98
H6−C2−X3	107.48	107.04	107.08	107.67	107.26	107.96	107.54	106.66	107.21	108.17	107.81	106.98
H7−C2−X1	107.47	107.14	107.08	112.49	107.27	107.34	107.67	112.17	107.21	107.53	107.80	111.56
H7−C2−X3	107.48	113.76	114.40	112.50	107.28	112.30	111.36	112.19	107.21	111.76	110.66	111.57
X3−C2−X1−H4	−58.19	−47.22	−179.08	69.75	−47.55	−44.84	−166.28	74.49	−46.69	−42.07	−159.94	73.27
X3−C2−X1−H5	58.06	67.58	−61.99	−175.70	47.55	50.22	−70.82	169.56	46.54	51.07	−66.56	166.52
H8−X3−C2−X1	−58.19	171.68	−179.02	176.80	−47.59	−165.96	−167.02	−168.65	−46.63	−162.79	−159.83	−166.19
H9−X3−C2−X1	58.08	−72.32	−61.97	−68.72	47.51	−70.59	−71.56	−73.61	46.60	−69.36	−66.44	−72.94

conformational energies of $CH_2(PH_2)_2$ agree notably with those computed at the highest level, MP4(fc)/6-311++G(3df,3pd).

The calculated energies for $CH_2(AsH_2)_2$ show the same trends associated with ZPE, diffuse functions, and electron correlation already described for methanediamine. However, these variations are smaller than in $CH_2(NH_2)_2$ and the computational level has a minor effect on the relative energies. Even with the lowest HF/6-311G**//MP2/6-311G** computational method, the results are quite similar to those obtained with the highest method, MP4(full)/6-311+G**.

It can be inferred from all the above that HF/6-311G**//MP2/6-311G** calculations seem to be suitable for the study of the anomeric effect in $CH_2(XH_2)_2$ (X = N, P, As) compounds and they will be taken as a reference from now on.[12] It should be also recalled here that the NBO program[11] employed in the following calculations only allows the energetic analysis in terms of interactions between natural bond orbitals for RHF and UHF wave functions.[4f]

The favored structure for $CH_2(XH_2)_2$ (X = N) is TT, while for X = P or As the most stable conformer is TG. For the three compounds the least stable conformer is G′G. According to this, the favored forms agree with those expected for compounds showing anomeric effect. When moving down through group 15 of the periodic table, TG conformers are increasingly favored over TT structures. The energy differences between the least stable G′G conformer and the most stable, TT or TG, drop from 5.0 (X = N) to 0.9 kcal/mol (X = P) and 0.8 kcal/mol (X = As). The energies for the T→G rotation of the first (ΔE(TG−TT)) and the second (ΔE(GG−TG)) XH_2 substituents are also different: the values are 0.5 vs 0.5 kcal/mol (X = N), −0.3 vs 0.7 kcal/mol (X = P), and −0.6 vs 0.7 kcal/mol (X = As). Hence the anomeric effect decreases notably for the higher row substituents, PH_2 and AsH_2, but is not canceled out. These energy data also show that the anomeric stabilizations are not additive.

Geometric Trends. The selection of MP2/6-311G**//MP2/6-311G** geometric parameters in Table 2 illustrates the tendencies associated with the anomeric effect previously described for other compounds.[1,7,13] Thus, for X = N, C−X bonds anti oriented with respect to a X lone pair (X_3−C_2 bonds in TT and TG conformers, and C_2−X_1 bond in TT structures) are up to 1.2% longer than C−X bonds in other conformers. However, this trend is inverted for compounds involving P or As, although the maximum bond length variations do not exceed 0.3% of the shortest C−X bond. The changes in C−H bond lengths show the same behavior.

The changes in X−C−X bond angles are clearly related to anomeric effects, in particular for $CH_2(NH_2)_2$. The X−C−X bond angles in favored anomeric conformers are 11.6% (X = N), 9.8% (X = P), and 9.5% (X = As) wider than in the least favored conformers, in a systematic way with the number of favorable anomeric orientations. Thus, X−C−X bond angles are about 6° larger in TT conformers (with two favored anti orientations of C−X bonds respect to the n_X lone pair) than in TG forms (with only one favored C−X/n_X orientation), and 11°−12° larger than in GG or G′G structures (without favored orientations). Similarly, H−C−X angles also fulfill the expected behavior, opening notably when the H−C bond is in anti orientation with a n_X lone pair. According to all the previous, it can be stated that the observed geometric trends indicate the existence of anomeric effects in the series of compounds studied. However, anomeric effects decrease when moving to higher rows of the periodic table, in such a way that bond length changes practically disappear.

NBO Analysis of the Relative Energies. The energy orderings for NH_2−CH_2−NH_2 (**1**), **1**TT < **1**TG < **1**GG ≪ **1**G′G; PH_2−CH_2−PH_2 (**2**), **2**TG < **2**TT < **2**GG < **2**G′G; and AsH_2−CH_2−AsH_2 (**3**), **3**TG < **3**TT < **3**GG = **3**G′G, can be interpreted using the NBO method. Table 3 shows the relative energy NBO contributions for the conformers of each compound. Several studies on compounds involving atoms with different types of lone pairs (O, S, Se)[5,8] have shown that the effect of the charge delocalization should not be analyzed only on the basis of p_X−σ^*_{CX} hyperconjugations since orbital interactions involving sp lone pairs, that is, sp_X−σ^*_{CX}, are not negligible. Thus, it is convenient to join the contributions involving both types of pairs and call them n_X−σ^*. It was also concluded that the effect of charge delocalization should not be studied comparing only n_X−σ^*_{CX} and n_X−σ^*_{CH} hyperconjugations between conformers, since bond−antibond interactions (e.g., σ_{CH}−σ^*_{XH}, σ_{XH}−σ^*_{CH}, σ_{XH}−σ^*_{CX}) and interactions involving Rydberg orbitals can have a different relative importance. Therefore, the absolute delocalization energies, E_{del}(abs), and the decomposition in contributions due to n_X−σ^* interactions, E_{del}(n_X−σ^*), and due to the remaining orbital interactions, E_{del}(others), are shown in Table 4. On the one hand, although orbital interactions are not strictly additive, it can be seen that the E_{del}(others) values are very similar for the four conformers of each compound, and, as a consequence, E_{del}(abs) and E_{del}(n_X−σ^*) values are parallel. On the other hand, n_X−σ^* interactions represent approximately 33% (**1**), 14% (**2**), and 10% (**3**) of the total delocalization energy. Thus, as previously

TABLE 3: HF/6-311G//MP2/6-311G** Relative Energies (E_{tot}), and Contributions of Hyperconjugation (E_{del}) and Lewis Energies (E_{Lew}) for the Stable Conformers of $CH_2(XH_2)_2$ (X = N, P, As) and $CH_2(YH)_2$ (Y = O, S, Se) Compounds (in kcal mol^{-1})**

$H_2N-CH_2-NH_2$	E_{tot}	E_{del}	E_{Lew}	$HO-CH_2-OH$	E_{tot}	E_{del}	E_{Lew}
TT	0.00	0.00	0.00	C_2	0.00	0.00	0.00
				C_s	3.25	−1.70	4.95
TG	0.47	5.93	−5.46	C_1	3.66	3.77	−0.11
GG	0.93	8.29	−7.37	C_{2v}	8.10	5.61	2.49
G′G	5.03	8.99	−3.96				

$H_2P-CH_2-PH_2$	E_{tot}	E_{del}	E_{Lew}	$HS-CH_2-SH$	E_{tot}	E_{del}	E_{Lew}
TT	0.00	0.00	0.00	C_2	0.00	0.00	0.00
				C_s	1.17	−0.50	1.67
TG	−0.29	3.49	−3.78	C_1	1.13	3.90	−2.77
GG	0.43	7.74	−7.31	C_{2v}	3.38	8.19	−4.81
G′G	0.64	6.67	−6.03				

$H_2As-CH_2-AsH_2$	E_{tot}	E_{del}	E_{Lew}	$HSe-CH_2-SeH$	E_{tot}	E_{del}	E_{Lew}
TT	0.00	0.00	0.00	C_2	0.00	0.00	0.00
				C_s	0.85	−0.27	1.12
TG	−0.60	2.33	−2.93	C_1	0.19	2.23	−2.04
GG	0.11	5.69	−5.58	C_{2v}	2.25	5.53	−3.28
G′G	0.15	5.13	−4.98				

TABLE 4: HF/6-311G//MP2/6-311G** Absolute Delocalization Energies (E_{del}(abs)) and Its Contribution Due to $n_X-\sigma^*$ Orbital Interactions ($E_{\mathrm{del}}(n_X-\sigma^*)$) and to the Rest of the Orbital Interactions (E_{del}(others)) For the Stable Conformers of $CH_2(XH_2)_2$ (X = N, P, As) and $CH_2(YH)_2$ (Y = O, S, Se) Compounds (in kcal mol^{-1})**

$H_2N-CH_2-NH_2$	E_{del}(abs)	$E_{\mathrm{del}}(n_X-\sigma^*)$	E_{del}(others)	$HO-CH_2-OH$	E_{del}(abs)	$E_{\mathrm{del}}(n_X-\sigma^*)$	E_{del}(others)
TT	102.4	36.9	65.5	C_2	106.8	56.3	50.5
				C_s	108.5	58.1	50.4
TG	96.5	31.3	65.2	C_1	103.0	51.3	51.7
GG	94.1	30.1	64.0	C_{2v}	101.2	48.5	52.7
G′G	93.4	27.7	65.7				

$H_2P-CH_2-PH_2$	E_{del}(abs)	$E_{\mathrm{del}}(n_x-\sigma^*)$	E_{del}(others)	$HS-CH_2-SH$	E_{del}(abs)	$E_{\mathrm{del}}(n_x-\sigma^*)$	E_{del}(others)
TT	83.6	16.9	66.7	C_2	81.2	39.6	41.6
				C_s	81.7	39.1	42.6
TG	80.1	11.0	69.1	C_1	77.3	32.7	44.6
GG	75.9	7.1	68.8	C_{2v}	73.0	27.0	46.0
G′G	77.0	8.1	68.9				

$H_2As-CH_2-AsH_2$	E_{del}(abs)	$E_{\mathrm{del}}(n_x-\sigma^*)$	E_{del}(others)	$HSe-CH_2-SeH$	E_{del}(abs)	$E_{\mathrm{del}}(n_x-\sigma^*)$	E_{del}(others)
TT	77.2	11.1	66.1	C_2	70.3	30.7	39.6
				C_s	70.6	30.6	40.0
TG	74.9	6.9	68.0	C_1	68.0	25.8	42.2
GG	71.5	4.8	66.7	C_{2v}	64.8	21.5	43.3
G′G	72.1	5.0	67.1				

suggested,[6a] delocalization energies decrease when moving down through the group, but more notably when passing from the second to the third row. This reduction is due to the smaller size of the Fock matrix elements between the acceptor and donor orbitals for higher row compounds.[8] According to all the previous, the hyperconjugative preference (Table 3) of **1**TT over **1**TG (5.9 kcal/mol), **2**TT over **2**TG (3.5 kcal/mol), and **3**TT over **3**TG (2.3 kcal/mol) is mainly due to the change from an $n_X-\sigma^*_{CX}$ interaction in the TT conformers to a weaker $n_X-\sigma^*_{CH}$ interaction in the TG conformers. In the same way, two $n_X-\sigma^*_{CH}$ interactions in the GG conformers change to two stronger $n_X-\sigma^*_{CX}$ hyperconjugations in the TT forms, which explains why GG conformers are less stable than TT forms (**1**, 8.3 kcal/mol; **2**, 7.7 kcal/mol; and **3**, 5.7 kcal/mol). The same important hyperconjugative interactions are different between G′G and TT forms; therefore the E_{del} values for GG and G′G conformers are similar.

Without considering hyperconjugation, the energy orderings given by E_{Lew} (**1**GG < **1**TG < **1**G′G ≪ **1**TT, **2**GG < **2**G′G ≪ **2**TG ≪ **2**TT, and **3**GG < **3**G′G ≪ **3**TG ≪ **3**TT) are almost opposed to those described above. It is known that the Lewis energies include electrostatic and steric effects which cannot be separated, and previous NBO studies have established that repulsions between bond pairs are greater than those involving lone pairs.[5,8] According to this, the high Lewis energies of the TT conformers could be related to the repulsions between two pairs of aligned X−H/X−H bonds, while in the remaining conformers one or two of these pairs are replaced by other smaller n_X/X−H or n_X/n_X interactions. Figure 1 shows that two pairs of X−H/X−H bonds are aligned in the TT conformers and two n_X lone pairs are aligned with two X−H bonds in the GG structures. In agreement with above, the Lewis energies (Table 3) for GG conformers are clearly smaller than for TT structures (7.4 kcal/mol (X = N), 7.3 kcal/mol (X = P), and 5.6 kcal/mol (X = As)).

The previous considerations indicate that conformers with anomeric orientations (TT and TG) are favored by hyperconjugation, which is more important than the steric and electrostatic effects included in the Lewis term. The smaller anomeric effects found for compounds involving atoms from higher rows of the periodic table (X = P or As) are a consequence of the larger compensation between delocalization and nonhyperconjugative contributions than that observed in X = N.

The influence on the anomeric effect of the substitution of the element in group 15 of the periodic table by its counterpart in group 16 can be analyzed by comparing the results obtained for $CH_2(XH_2)_2$ (X = N, P, As), and those reported for $CH_2(YH)_2$ (Y = O, S, Se, Te) by Salzner and Schleyer.[8] To have homogeneous data, Tables 3 and 4 include additional HF/6-311G**//MP2/6-311G** calculations carried out here for the compounds containing O, S, Se, and Te, although the original nomenclature[8] has been retained. For every compound the most stable conformer has one or two anti Lp-X−C−X or Lp-Y−C−Y arrangements while none are observed in the less stable one. However, the substitution of X by Y enhances the anomeric effect and the C_2 conformers of $CH_2(YH)_2$ compounds are more favored than the TT conformers of $CH_2(XH_2)_2$. The energy data in Table 3 indicate that the substitution of N by O causes a much greater increase in the anomeric effect than the substitutions of P by S, or As by Se. At the same time, the two latter substitutions produce very similar enhancements of the anomeric effect. It can be seen in Table 4 that substitution of X by Y increases the participation of $n_X-\sigma^*$ interactions, which are 51% (Y = O), 44% (Y = S), and 40% (Y = Se) of the absolute delocalization energy E_{del}(abs). Therefore, the differences between the absolute delocalization energies of $CH_2(XH)_2$ and $CH_2(YH)_2$ compounds are mainly related to the changes in those orbital interactions involving lone pairs, that is, $n_X-\sigma^*_{CX}$ interactions are replaced by $n_Y-\sigma_{CY}^*$, and $n_X-\sigma^*_{CH}$ interactions change to $n_Y-\sigma^*_{CH}$. However, from the TG conformer of $CH_2(XH)_2$ to the C_1 conformer of $CH_2(YH)_2$, the variations on the relative delocalization energies E_{del} are small, that is, −2.2 kcal/mol (X = N → Y = O), 0.4 kcal/mol (X= P → Y = S) and 0.1 kcal/mol (X = As → Y = Se) (see Table 3). Very similar relative variations of E_{del} occur from the GG conformer of $CH_2(XH)_2$ to the C_{2v} conformer of $CH_2(YH)_2$: −2.7 kcal/mol (X = N → Y = O), 0.5 kcal/mol (X = P → Y = S), and −0.2 kcal/mol (X = As → Y = Se). According to this, the anomeric effect increases with substitution due to the larger variations in the Lewis energy values, that is, 5.4 kcal/mol (TG: X = N → C_1: Y = O), 1.0 kcal/mol (TG: X = P → C_1: Y = S), and 0.9 kcal/mol (TG: X = As → C_1: Y = Se). These variations are even greater between GG and C_{2v} conformers: 9.9 kcal/mol (X = N → Y = O), 2.5 kcal/mol (X = P → Y = S), and 2.3 kcal/mol (X = As → Y = Se). The reasons for these trends could be the two aligned XH/XH interactions observed in TT conformers while no YH/YH aligned repulsion can be seen in C_2 structures. In accordance with this idea, the instability due to E_{Lew} shown in the previous data increases in the order $CH_2(XH)_2 < CH_2(YH)_2$, and hence the same happens with E_{tot}.

NBO Analysis of the Rotational Barriers around C−X Bonds. A series of structures with two simultaneously fixed Lp-X−C−X and X−C−X-Lp (X = N, P, As) dihedral angles between 0° and 180°, at intervals of 20°, was optimized at the HF/6-311G** level. Some of these structures, which appear due to the rotation of both Lp-X groups in opposite directions around the X−C bonds, are shown in Figure 2. The relative energies along the rotational path as well as the hyperconjugative and Lewis energies are represented in Figures 2−4 and detailed in Table 5.

Figure 2 shows that the energy for the rotation around the N−C bond is mainly due to the positive hyperconjugative contribution, which is never compensated by the negative electrostatic and steric effects included in the Lewis term. The positions of the minima and the barriers are also determined by the hyperconjugative contribution, and the dihedral angles of these characteristic points are only slightly influenced by the Lewis part. The similarity between the E_{tot} and E_{del} profiles indicates that the main role of the Lewis contribution is to reduce the height of the rotational barriers. In general terms, the same behavior is observed for $PH_2-CH_2-PH_2$ (Figure 3) and $AsH_2-CH_2-AsH_2$ (Figure 4), although now E_{Lew} compensates E_{del} to

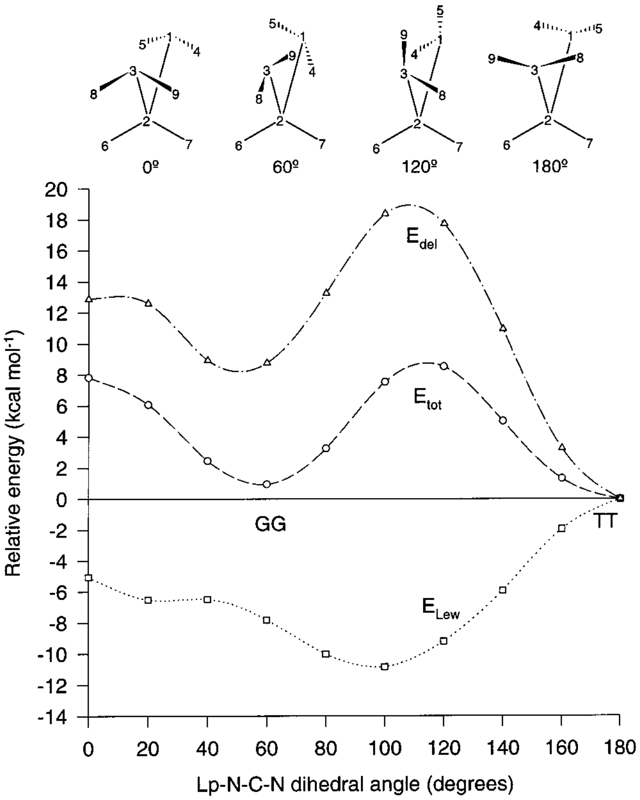

Figure 2. Rotational barrier (E_{tot}) around the N−C bond of methanediamine, $CH_2(NH_2)_2$, obtained with two simultaneously fixed Lp-N−C−N and N−C−N-Lp dihedral angles. Delocalization (E_{del}) and Lewis energies (E_{Lew}) obtained applying the NBO method on HF/6-311G** wave functions. Some selected structures due to the rotation of both NH_2 groups in opposite directions are also represented.

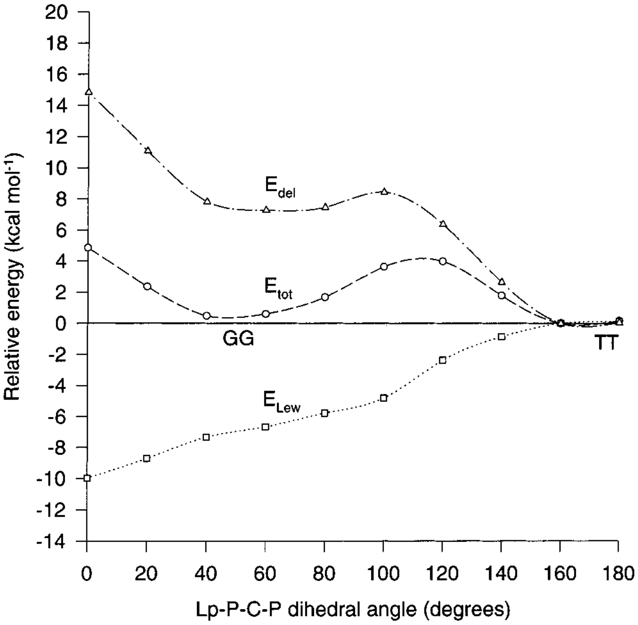

Figure 3. Rotational barrier (E_{tot}) around the P−C bond of methylenebis(phosphane), $CH_2(PH_2)_2$, obtained with two simultaneously fixed Lp-P−C−P and P−C−P-Lp dihedral angles. Delocalization (E_{del}) and Lewis energies (E_{Lew}) obtained applying the NBO method on HF/6-311G** wave functions.

TABLE 5: HF/6-311G//HF/6-311G** Relative Contributions (in kcal mol^{-1}) of the Lewis Energies (E_{Lew}) and the Hyperconjugation Energies (E_{del}) to the Rotational Barriers (E_{tot}) around the X−C Bonds in $CH_2(XH_2)_2$ (X = N, P, As) Compounds**

	E_{tot}			E_{Lew}			E_{del}		
Lp-X−C−X[a]	N	P	As	N	P	As	N	P	As
0	7.82	4.86	3.85	−5.05	−9.97	−8.42	12.88	14.83	12.27
20	6.08	2.36	1.85	−6.52	−8.71	−7.43	12.60	11.07	9.29
40	2.45	0.47	0.44	−6.48	−7.34	−6.38	8.93	7.81	6.82
60	0.95	0.60	0.55	−7.82	−6.67	−5.61	8.77	7.27	6.16
80	3.25	1.67	1.20	−10.01	−5.78	−4.47	13.26	7.45	5.67
100	7.54	3.63	2.64	−10.84	−4.81	−3.25	18.38	8.45	5.89
120	8.54	3.99	2.99	−9.19	−2.38	−1.05	17.73	6.37	4.03
140	5.02	1.79	1.33	−5.92	−0.86	−0.59	10.95	2.64	1.92
160	1.33	0.00	0.00	−1.94	0.00	0.00	3.26	0.00	0.00
180	0.00	0.15	0.15	0.00	0.12	−0.03	0.00	0.04	0.18

[a] Angles are given in degrees.

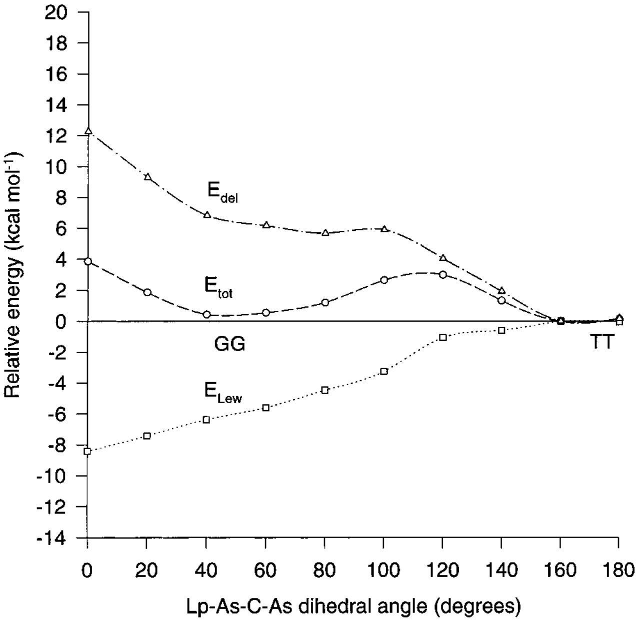

Figure 4. Rotational barrier (E_{tot}) around the As−C bond of methylenediarsine, $CH_2(AsH_2)_2$, obtained with two simultaneously fixed Lp-As−C−As and As−C−As-Lp dihedral angles. Delocalization (E_{del}) and Lewis energies (E_{Lew}) obtained applying the NBO method on HF/6-311G** wave functions.

TABLE 6: MP2/6-311G//MP2/6-311G** Group Separation Energies $CH_2(XH_2)_2 + CH_4 = 2CH_3XH_2$, X = N, P, As (in kcal mol^{-1})**

conformer	$CH_2(NH_2)_2$	$CH_2(PH_2)_2$	$CH_2(AsH_2)_2$
TT	10.46	1.94	1.83
TG	9.57	2.01	2.31
GG	8.79	1.04	1.39
G′G	4.56	1.01	1.46

a greater extent and the rotational barriers for X = P or As are much smaller than for X = N (Table 5). It should be noted that the profiles of the rotational energy, E_{tot}, and its components, E_{del} and E_{Lew}, are very similar for X = P and X = As, while they differ from those of X = N. It should be noted that although rotation around the C−X bonds is easier when moving down through the group, the change is much more noticeable when passing from the second to the third row of the periodic table, and the changes in the E_{del} and E_{Lew} values are more drastic.

From the comparison of Figures 2−4 with the previously reported rotational barriers around the C−Y bonds in $CH_2(YH)_2$ (Y = O, S, Se) (see Figures 8−10 in ref 8), it can be concluded that the rotational behaviors for both sets of compounds are identical. On the other hand, if the energy values in Table 5 are compared to those in Table 4 of ref 8, it can be seen that when passing from group 15 to group 16 the delocalization energies as well as the Lewis energies increase and the rotational barriers for $CH_2(YH)_2$ (Y = O, S, Se) compounds are higher. The reason for the increase of the rotational barriers is the more significant changes in the Lewis energies. Thus, when passing from X = N, P, and As to Y = O, S, and Se, the Lewis term along the rotational path becomes much less negative or even slightly positive.

Group Separation Energies. The stabilization energies for $CH_2(XH_2)_2$ (X = N, P, As) compounds can be calculated according to the reaction

$$CH_2(XH_2)_2 + CH_4 \rightarrow 2CH_3{-}XH_2 \qquad (3)$$

It has been shown that group separation energies computed for higher row compounds at the HF level can become negative because of the neglect of electron correlation.[8] For this reason, the stabilization energies shown in Table 6 are computed at the MP2/6-311G**//MP2/6-311G** level. For X = N, the TT form is stabilized by 10.5 kcal/mol, while for X = P and As, TT conformers are stabilized by 1.9 and 1.8 kcal/mol, respectively. Therefore, stabilization energies decrease from X = N to X = P by 8.6 kcal/mol, and the values for X = P and As are very similar. The same trends are observed for $CH_2(YH)_2$ (Y = O, S, Se) compounds (see Table 6 in ref 8); that is, the stabilization energies change in the same way when moving down through the group. Thus, they decrease from Y = O to Y = S in 14.5 kcal/mol, and the values for Y = S and Se are very similar, 2.6 and 2.3 kcal/mol, respectively. It should be noted, however, that the stabilization of the most stable conformers increases with the substitution of X = N, P, and As by its counterpart Y = O, S, and Se.

It is also remarkable the fact that for X = N, P, and As, GG and G′G conformers have positive stabilization energies, with high values for X = N. According to the previous NBO intepretation, the GG and G′G structures do not show the anomeric effect; therefore the group separation energies cannot be taken as a measurement of the anomeric effect. In addition, group separation energies and relative energies do not show the same trends. For instance, the relative (Table 1) and stabilization energies (Table 6) for the GG conformer along the series X = N, P, and As are not parallel. These observations reinforce the conclusion obtained for the series of Y = O, S, Se, and Te compounds.[8]

Conclusions

The conformational stability of $CH_2(XH_2)_2$ (X = N, P, As) compounds can be considered adequately described at the HF/

6-311G**//MP2/6-311G** or MP2/6-311G**//MP2/6-311G** computational levels. These results are not significantly different from those obtained including more polarization or diffuse functions in the basis set and electron correlation up to the MP4-(full) level. For all the compounds, the relative energy orderings can be related to the existence of anomeric effects because the favored conformers show one or two anti orientations between a lone pair and a polar X−C bond. Anomeric effects decrease noticeably for the higher row substituents, PH_2 and AsH_2, although they do not vanish completely. The same conclusion can be reached from the analysis of the known geometric trends related to anomeric interactions. It should be also noted that bond angle changes indicate the presence of anomeric effects more clearly than bond length variations.

The NBO method indicates that the preference for the anti Lp-X−C−X orientations is mainly due to charge delocalization. This hyperconjugative stabilization is always stronger than the energy of the conformers considered as hypothetical Lewis structures. According to this, the electrostatic and steric contributions included in the Lewis term are less important than delocalization. The smaller anomeric effects observed in higher row compounds (X = P or As) are due to the larger compensation between delocalization and nonhyperconjugative contributions. The comparison between $CH_2(XH_2)_2$ (X = N, P, As) and $CH_2(YH)_2$ (Y = O, S, Se) compounds indicates that the replacement of X by Y increases the preference for the favored conformers. This increase in the anomeric effect when moving to the right in the periodic table is more intense for second-row substituents. The larger anomeric effects for $CH_2(YH)_2$ (Y = O, S, Se) compounds are mainly due to the reduction of repulsions between aligned bonds in those conformers with favored anomeric orientations.

The rotational barriers around the X−C bond were interpreted by means of the NBO method. They are due mainly to the positive hyperconjugative contribution, which is not compensated by the always negative steric and electrostatic interactions. When moving down through the group of the periodic table, the rotation around the C−X bonds is easier, but much more noticeably from the second to the third row, when the changes in the hyperconjugative and Lewis terms are larger. From group 15 to group 16 of the periodic table, the rotational barriers increase because both E_{del} and E_{Lew} increase, but now the variation in the Lewis energy is more important.

The group separation energies at the MP2 level indicate the stabilization of the conformers with anomeric orientations, although this stabilization is noticeably reduced when passing from X = N to X = P or As. The GG and G′G conformers have positive stabilization energies, although these structures do not have anomeric interactions. In addition, the tendencies in the group separation energies and in the relative energies are not parallel. According to this, group separation energies cannot be taken as a reasonable measurement of the anomeric effect. The comparison with the group separation reactions involving $CH_2(YH)_2$ compounds (Y = O, S, Se, Te) shows that the group separation energies increase when moving to the right in the periodic table, especially for the second-row compounds, but the same conclusions with regard to the anomeric effect are obtained.

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References and Notes

(1) (a) Thatcher, G. R. J.; Ed., *The Anomeric Effect and Associated Stereoelectronic Effects*; ACS Symposium Series 539; American Chemical Society: Washington, DC, 1993. (b) Jeffrey, G. A.; Pople, J. A.; Binkley, J. S.; Vishveshwara, S. *J. Am. Chem. Soc.* **1978**, *100*, 373. (c) Smits, G. F.; Krol, M. C.; Altona, C. *Mol. Phys.* **1988**, *65*, 513. (d) Lemieux, R. U. *Molecular Rearrangements*; De Mayo, P., Ed.; Interscience Publishers: New York, 1964; p 709. (e) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983. (f) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, *39*, 1141. (g) Praly, J. P.; Lemieux, R. U. *Can. J. Chem.* **1987**, *65*, 213. (h) Juaristi, E., ed. *The Anomeric Effect*: CRC Press: Boca Raton, 1995.

(2) Edward, J. T. *Chem. Ind.* **1955**, 1102.

(3) (a) Altona, C. Ph.D. Thesis, University of Leiden, 1964. (b) Romers, C.; Altona, C.; Buys, H. R.; Havings, E. *Top. Stereochem.* **1969**, *4*, 39.

(4) (a) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1978**, *102*, 1700. (b) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (d) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (e) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (f) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, Version 3.1; Gaussian Inc.: Pittsburgh, PA, 1992. (g) Weinhold, F. A. In *Encyclopedia of Computational Chemistry*; Schleyer, P. V. R., Ed.; John Wiley & Sons, Ltd. Publishers: New York. 1998; Vol. 3; pp 1792−1810.

(5) (a) Reed, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (b) Salzner, U.; Schleyer, P. v. R. *J. Org. Chem.* **1994**, *59*, 2138−2155. (c) Salzner, U. *J. Org. Chem.* **1995**, *60*, 986−995. (d) Carballeira, L.; Pérez-Juste, I. *J. Org. Chem.* **1997**, *62*, 6144−6151. (e) Carballeira, L.; Pérez-Juste, I. *J. Comput. Chem.* **2000**, 21, 462. (f) Carballeira, L.; Pérez-Juste, I. *J. Comput. Chem.* In press.

(6) (a) Schleyer, P. v. R.; Jemmis, J. E.; Spitznagel, G. W.; *J. Am. Chem. Soc.* **1985**, *107*, 6393. (b) Apeloig, Y.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 5901.

(7) (a) Juaristi, E. *Heteroat. Chem.* **1990**, *1*, 267. (b) Bachelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Johnston, B. D.; Pinto, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6582. (c) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6752. (d) Salzner, U.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 190.

(8) Salzner, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 10231−10236.

(9) Leroy, G.; Dewispelaere, J.-P.; Benkadour, H.; Riffi Temsamani, D.; Wilante, C. *J. Mol. Struct. (THEOCHEM)* **1995**, *334*, 137−143.

(10) Knuppel, P. C.; Pawelke, G.; Sommer, H.; Stelzer, O.; Oberhammer, H.; Lappert, M. F.; Suffolk, R. J.; Watts, J. D. *J. Organom. Chem.* **1988**, *355*, 55−70.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.;. Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian; Inc.; Pittsburgh, PA, 1995.

(12) The 6-31G** basis set was not considered for As, because it is not recommended.[11] The denomination 6-311G** corresponds really with the "negative ion" basis set by MacLean and Chandler (12s,9p) → (621 111, 52 111) for P,[11] and the (14s,12p,6d) → (8s,7p,3d) basis set for As defined by: Curtiss, L. A.; McGrath, M. P.; Blandeau, J.-P.; Davis, N. E.; Binning Jr., R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(13) (a) Schafer, L.; Van Alsenoy, C.; Williams, J. O.; Scarsdale, J. N.; Geise, H. J. *J. Mol. Struct*. **1981**, *76*, 349−361. (b) Carballeira, L.; Mosquera, R. A.; Ríos, M. A. *J. Mol. Struct.* **1988**, *176*, 89−105. (c) Krol, M. C.; Huige, C. J. M.; Altona, C. *J. Comput. Chem.* **1990**, *11*, 765. (d) Senderowitz, H.; Fuchs, B. *J. Mol. Struct. (THEOCHEM)* **1997**, *395−396*, 123−155.