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A new approach to the distortion of the tetrahedral geometry at E in the $E(ZXY_2)_4$ compounds

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Density functional theory calculations have been used to study the structural features of a variety of tetrahedral $E(ZXY_2)_4$ compounds. In these compounds, the six Z–E–Z angles deviate from the ideal tetrahedral geometry in such a way that they are either four smaller and two larger (*4s2l*), or four larger and two smaller (*4l2s*). A simple cubic model has been used to explain such structural distortions. Within this cubic model, the stability of the D_{2d} and S_4 conformers of $E(ZXY_2)_4$ compounds can be understood in terms of the homophobic and heterophilic nature of the substituents on the Z atoms. The hyper-conjugation effect has also been emphasized for compounds when the Z atoms have lone pairs of electrons.

Introduction

The importance of the $E(ZR_2)_4$ (E = group 14 atoms, Z = group 15 atoms) compounds, which may be regarded as parent substances of inorganic nonmetal chemistry, has been recently highlighted by Mitzel because of their prospective applications in synthesis and material science.[1] The study of the structural problems of the compounds is, therefore, of both experimental and theoretical significance and has drawn much attention due to their interesting conformational preferences.[1–8]

The most interesting structural chemistry of the $E(ZR_2)_4$ molecules is the distinct deviation from an ideal tetrahedral geometry at the central atom, *i.e.*, two of the six Z–E–Z angles around the central atom are smaller than the ideal tetrahedral angle and the other four are larger (denoted as *4l2s* hereafter), or *vice versa* (*4s2l*).[1,3,5,9] Indeed, many molecules with a general formula of $E(ZXY_2)_4$ have been found to adopt structures with D_{2d} or S_4 symmetry[10–12] and, more importantly, also have the *4l2s* or *4s2l* structural feature.[1–8] Here, X or Y denotes a lone pair if Z is a group 15 or 16 atom. When both X and Y are monovalent, Z should be a group 14 atom. Several studies have been devoted to the understanding of this intriguing structural feature.[3,7] It was noticed that this kind of deviation cannot be attributed to packing effects in crystal lattices since the gas-phase structures of $C(OMe)_4$[13] and $Si(OMe)_4$[14] also show the same phenomena. Furthermore, the same structural feature has been predicted for $C(NMe_2)_4$ and $Si(NH_2)_4$ by theoretical (density functional theory, DFT) calculations.[6] More recently, the D_{2d} or S_4 structural preference has also been observed in the case of 3,3-diethylpentane (CEt_4) and explained as a result of avoiding the unfavoured $g + g$-interaction.[15] Regarding the fact that the distribution of electron density around the Z atom does not have "local C_3 symmetry", it was recently suggested that the deviation may result from the unequal interactions among the Z atoms in different directions.[3] A clear picture has not yet emerged of how the electron density distribution around the Z atoms influences the deviation and a concrete relationship between the Z–E–Z angles and the asymmetric electron density remains indistinct. In other words, these molecular structures are not yet satisfactorily understood.[1]

In this paper, a simple cubic model is proposed to provide a convenient way to understand the interesting structural features. Theoretical calculations were also performed to give further support to the model.

Results and discussion

Cubic model

It is well known that the staggered (and most stable) conformer of the $C(CH_3)_4$ molecule adopts an ideal tetrahedral geometry with T_d symmetry. Substituting one hydrogen atom of each CH_3 group by a Cl atom gives $C(CH_2Cl)_4$. According to the conformational analysis by Stølevik in 1974, $C(CH_2Cl)_4$ may have (3^4=) 81 possible staggered conformers regarding the orientations of the Cl atoms in the molecule, but only six of them are distinguishable.[12] Within these six distinguishable conformers, two of them have C_1 symmetry and the other four adopt D_{2d}, S_4, C_s, and C_2 symmetry, respectively. By placing this $C(CH_2Cl)_4$ molecule into a cube shown in Fig. 1, the structural description of the six distinguishable conformers becomes much clearer.

In this cubic representation (see Fig. 1), the four CH_2Cl groups occupy four corners of the cube while the other four corners remain empty. The dotted and bold arrows in Fig. 1 are used to distinguish the H and Cl atoms, respectively. The six distinguishable conformers can therefore be described depending on the orientation of the four Cl atoms toward the four empty corners. Conformers **1** (D_{2d}) and **2** (S_4) represent the situations when only one Cl atom orients itself towards each empty corner. Conformer **3** (C_s) is the case when three Cl atoms share one common empty corner and the fourth Cl atom points to one of the three remaining empty corners. In conformer **4** (C_2), the four Cl atoms are divided into two groups. Each group has two Cl atoms sharing one common empty corner. Conformers **5** and **6** (both with C_1 symmetry) are the cases in which one empty corner is shared by two Cl atoms. The third and fourth Cl atoms orient themselves toward two of the three remaining empty corners. It is obvious that this cubic representation can be extended to describe the structural features of molecules with the general formula of $E(ZXY_2)_4$.

$C(CH_2X)_4$, $C(CHX_2)_4$ and $Si(CH_2X)_4$ (X = halide). Theoretical calculations for various $C(CXY_2)_4$ (X, Y = H or halide) molecules indeed give six distinguishable conformers for each molecule. The results show that the two high symmetry conformers (D_{2d} and S_4) are generally most stable (see Table 1). For $C(CHI_2)_4$, the S_4 conformer is found to be slightly higher energy than the C_1' conformer.[16] Based on the cubic model described

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Table 1 The calculated relative energies (kcal mol^{-1}) for different conformers of $E(ZXY_2)_4$

	Calculated relative energy/kcal mol^{-1}					
	1 D_{2d}	**2** S_4	**3** C_s	**4** C_2	**5** C_1	**6** C_1'
$C(CH_2F)_4$	1.1 (1.1)	0.0 (0.0)	12.4 (11.9)	8.7 (8.2)	4.8 (4.5)	4.4 (4.1)
$C(CH_2Cl)_4$	0.0 (0.0)	0.1 (0.0)	13.7 (13.4)	10.5 (10.1)	5.5 (5.3)	5.3 (5.0)
$C(CH_2Br)_4$	0.0 (0.0)	0.7 (0.5)	18.0 (14.3)	11.8 (11.3)	6.1 (5.8)	6.2 (5.8)
$C(CH_2I)_4$	0.0 (0.0)	1.1 (1.0)	15.0 (14.7)	12.4 (11.8)	6.7 (6.1)	6.4 (6.4)
$C(CHF_2)_4$	3.5 (3.6)	0.0 (0.0)	11.4 (11.2)	9.4 (9.4)	4.8 (4.7)	4.7 (4.7)
$C(CHCl_2)_4$	1.8 (2.1)	0.0 (0.0)	—[a]	9.4 (9.4)	4.9 (4.9)	4.2 (4.3)
$C(CHBr_2)_4$	0.0 (0.0)	0.0 (0.2)	—	8.1 (8.1)	3.6 (3.6)	2.6 (2.7)
$C(CHI_2)_4$	0.0 (0.0)	3.8 (3.8)	—	8.4 (8.3)	4.3 (4.0)	2.7 (2.5)
$Si(CH_2F)_4$	0.9 (0.9)	0.0 (0.0)	—	—	2.5 (2.6)	—
$Si(CH_2Cl)_4$	0.4 (0.5)	0.0 (0.0)	—	—	2.8 (2.7)	—
$Si(CH_2Br)_4$	0.0 (0.1)	0.0 (0.0)	—	—	2.7 (2.6)	—
$Si(CH_2I)_4$	0.0 (0.1)	0.2 (0.0)	—	—	2.7 (2.6)	—
$C(NH_2)_4$	0.0 (0.0)	2.3 (2.1)	—	—	—	—
$Si(NH_2)_4$	0.0 (0.0)	2.6 (1.7)	—	—	—	—
$C(PH_2)_4$	1.4 (1.5)	0.0 (0.0)	—	—	—	—
$Si(PH_2)_4$	0.0 (0.0)	0.0 (0.0)	—	—	—	—
$C(OH)_4$	5.1 (5.1)	0.0 (0.0)	—	—	—	—
$Si(OH)_4$	—	0.0 (0.0)	—	—	—	—

[a] The '—' symbols are used when the corresponding conformers are not local minima. The values in parentheses are the relative energies including the zero-point energy correction.

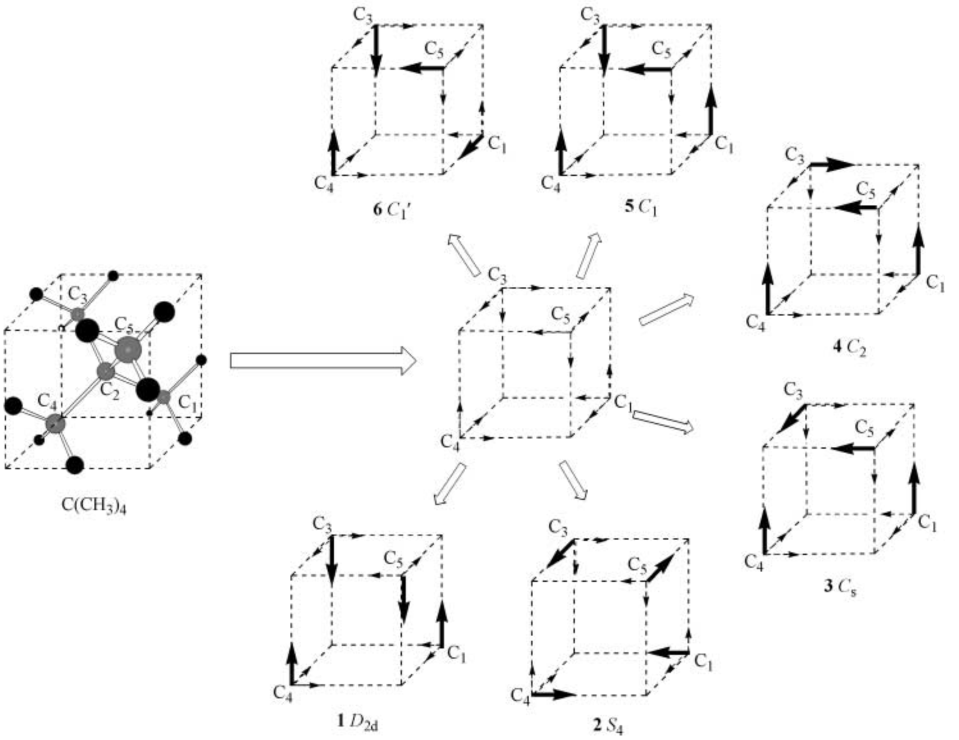

Fig. 1 Cubic model of the six distinguishable conformers of $E(ZXY_2)_4$.

above, for the two high symmetry (D_{2d} and S_4) conformers, the unique substituents X (the bold arrows) tend to be away from each other, *i.e.*, each orients itself toward an empty corner. The high stability of these two conformers suggests the homophobic nature among the substituents. The homophobic nature can be conveniently related to the commonly accepted repulsive interactions (electrostatic and steric repulsions). On the other hand, such a high symmetry arrangement could also enhance the heterophilic interaction, if there is any, among substituents with different electronic properties. The heterophilic interaction should be mainly due to the electrostatic attraction between electropositive and electronegative substituents.

The homophobic nature is also demonstrated by the highly unstable conformer (**3**) of $C(CXY_2)_4$ compounds in which three bold arrows point to a common empty corner in the cubic model. For $C(CHX_2)_4$ (X = Cl, Br and I), conformer **3** is no longer a local minimum because of highly repulsive interactions among the halide ligands. The second unstable conformer (**4**) of these compounds has two pairs of bold arrows, each sharing a common empty corner. For the two C_1 conformers (**5** and **6**),

Table 2 The calculated Z–E–Z angles (°) of the two high symmetry conformers of E(ZXY$_2$)$_4$

	D_{2d} Symmetry			S_4 Symmetry		
	Z–E–Z **4** × $\mathbf{P}_{//}$	Z–E–Z **2** × $\mathbf{P}_0$	Feature	Z–E–Z **4** × $\mathbf{P}_1$	Z–E–Z **2** × $\mathbf{P}_{//}$	Feature
C(CH$_2$F)$_4$	**110.2**	108.1	4*l*2*s*	109.0	**110.9**	4*s*2*l*
C(CH$_2$Cl)$_4$	**111.8**	104.9	4*l*2*s*	108.4	**111.6**	4*s*2*l*
C(CH$_2$Br)$_4$	**112.1**	104.3	4*l*2*s*	108.3	**111.8**	4*s*2*l*
C(CH$_2$I)$_4$	**112.5**	103.6	4*l*2*s*	108.1	**112.2**	4*s*2*l*
C(CHF$_2$)$_4$	106.6	**115.3**	4*s*2*l*	**110.2**	108.0	4*l*2*s*
C(CHCl$_2$)$_4$	105.2	**118.3**	4*s*2*l*	**110.4**	107.6	4*l*2*s*
C(CHBr$_2$)$_4$	105.1	**118.6**	4*s*2*l*	**110.4**	107.6	4*l*2*s*
C(CHI$_2$)$_4$	105.2	**118.4**	4*s*2*l*	**110.4**	107.6	4*l*2*s*
Si(CH$_2$F)$_4$	109.4	109.6	~[a]	109.6	109.2	~
Si(CH$_2$Cl)$_4$	**110.5**	107.4	4*l*2*s*	109.1	110.1	~
Si(CH$_2$Br)$_4$	109.8	108.8	~	109.5	109.3	~
Si(CH$_2$I)$_4$	**110.5**	107.4	4*l*2*s*	109.3	109.8	~
C(NH$_2$)$_4$	104.9	**119.0**	4*s*2*l*	**112.1**	104.4	4*l*2*s*
Si(NH$_2$)$_4$	102.5	**124.5**	4*s*2*l*	**112.5**	103.5	4*l*2*s*
C(PH$_2$)$_4$	105.9	**116.8**	4*s*2*l*	**111.0**	106.4	4*l*2*s*
Si(PH$_2$)$_4$	105.2	**118.5**	4*s*2*l*	**111.6**	105.3	4*l*2*s*
C(OH)$_4$	**112.4**	103.7	4*l*2*s*	106.9	**114.8**	4*s*2*l*
Si(OH)$_4$	—[b]	—	—	105.7	**117.4**	4*s*2*l*

[a] The '~' symbol is used when the two distinct angles differ less than 1°. [b] The '—' symbols are used when the corresponding conformers are not local minima.

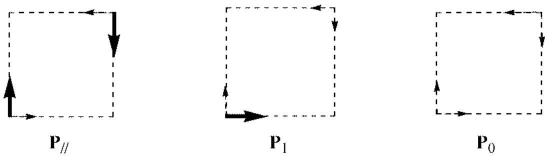

Fig. 2 The three square-face patterns of conformers with D_{2d} and S_4 symmetry of E(ZXY$_2$)$_4$.

only one empty corner is shared by two bold arrows. These two conformers have similar stability and are only less stable than the two high symmetry conformers.

Now, we come to the 4*l*2*s* or 4*s*2*l* structural features observed for these compounds. Clearly, the deviation of the six Z–E–Z angles from the tetrahedral angle is closely related to the anisotropic arrangement of the X and Y substituents. This anisotropic feature can be easily described by examining the detailed arrangement of X and Y on the six square faces of the cubic model. On each square face, the interaction among X and Y should determine how the corresponding Z–E–Z angle deviates.

Fig. 2 shows the three square-face patterns, $\mathbf{P}_{//}$, $\mathbf{P}_1$ and $\mathbf{P}_0$, recognized from the two most stable conformers (**1** and **2**) regarding the number and orientation of arrows. Conformer **1** (D_{2d}) has four $\mathbf{P}_{//}$, with two bold (and two dotted as well) arrows antiparallel to each other, and two $\mathbf{P}_0$, with all dotted arrows on the face. The aforementioned homophobic nature gives us hints in comparing the relative preference for the three patterns shown in Fig. 2. If the homophobic interactions among the bold arrows dominate, the Z–E–Z angle corresponding to the $\mathbf{P}_{//}$ pattern should be greater than the tetrahedral angle while the angle corresponding to the $\mathbf{P}_0$ pattern should be smaller. Table 2 shows that all the C(CH$_2$X)$_4$ (X = F, Cl, Br or I) molecules fit the notion that halide–halide repulsive interaction dominates. For the D_{2d} conformer **1**, we have four $\mathbf{P}_{//}$ and two $\mathbf{P}_0$ square faces. Consequently, the D_{2d} conformer for each molecule has the 4*l*2*s* structural feature. For the S_4 conformer **2**, we have two $\mathbf{P}_{//}$ and four $\mathbf{P}_1$ square faces. It is expected that the S_4 conformer of C(CH$_2$X)$_4$ has the 4*s*2*l* structural feature. From Table 2, one can also see that the repulsive interaction between the two halides on a $\mathbf{P}_{//}$ square face increases down the group. The difference between the two distinct Z–E–Z angles becomes greater for heavier halides. The trend observed for C(CHX$_2$)$_4$ is opposite to the one for C(CH$_2$X)$_4$. It is understandable that the bold arrows in the cubic model in these cases represent the H atoms that have less repulsive interactions. The results here again support the conclusion that the halide–halide repulsive interaction plays the most important role in determining the structural feature of these compounds.

The effect of the homophobic/heterophilic nature of the substituents can also be tested by examining the trend of the structural distortion for compounds with larger central atoms in which the interactions among the substituents are weakened. The Si(CH$_2$X)$_4$ compounds provide good examples for this purpose because the C–Si distance is longer than C–C, giving weaker interactions among the substituents. One expects smaller deviations from the ideal tetrahedral angle around Si atoms. Indeed, only three conformers are obtained from the geometry optimisations. In addition, relative energies among the different conformers are smaller. Geometrically, the deviations from the ideal tetrahedral angle around Si atoms are also very small (see Table 2).

So far, the simple cubic model has been successfully used to discuss the structural features of the C(CH$_2$X)$_4$, C(CHX$_2$)$_4$ and Si(CH$_2$X)$_4$ (X = halide) compounds. Can this model be applied to compounds where Z = group 15 or 16 atoms, *i.e.*, with lone pair(s) on Z atoms?

E(ZH$_n$)$_4$ (E = C or Si; Z = O, N or P; n = 1 when Z = O and n = 2 when Z = N or P). Geometry optimisations of the E(ZH$_2$)$_4$ compounds only give two stable conformers. These two stable conformers belong to the D_{2d} and S_4 symmetry (see Table 1). This result can be easily related to the homophobic nature of the substituents described above. The homophobic/heterophilic interactions here are mainly electrostatic since the H atoms could not have large steric effects. However, the absence of the other four conformers suggests that the homophobic/heterophilic interactions are not large enough to allow the four higher energy conformers to be local minima. On the other hand, the very small atomic charges calculated[17] for the H atoms of the E(PH$_2$)$_4$ compounds (see Table 3) indicate that the electrostatic interactions could not be the dominant

Table 3 The calculated natural atomic charges by NBO analysis

	D_{2d} Symmetry			S_4 Symmetry		
Compound	qE	qZ	qH	qE	qZ	qH
$C(NH_2)_4$	0.59	−0.94	0.39	0.60	−0.93	0.39
$Si(NH_2)_4$	2.12	−1.36	0.41	2.14	−1.36	0.41
$C(PH_2)_4$	−1.14	0.26	0.01	−1.14	0.26	0.01
$Si(PH_2)_4$	0.46	−0.18	0.03	0.47	−0.19	0.03
$C(OH)_4$	1.04	−0.76	0.50	1.05	−0.77	0.50
$Si(OH)_4$	—[a]	—	—	2.29	−1.10	0.52

[a] The '—' symbols are used when the corresponding conformers are not local minima.

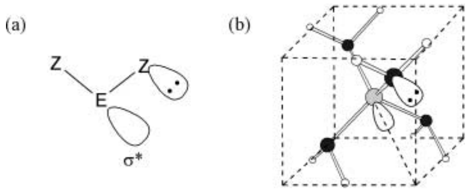

Fig. 3 A schematic illustration of the hyper-conjugation interaction between a lone pair of electrons on Z and a E–Z σ* anti-bonding orbital in an $E(ZH_2)_4$ molecule. The σ* orbital is only partially depicted for the purpose of clarity.

effect in determining the structural features of these compounds. Examining the calculated geometry of D_{2d} and S_4 conformers, we find that the structural distortions away from the ideal tetrahedral one are also very significant in these compounds (see Table 2). Clearly, other important factor(s) are responsible for the structural features in these tetrahedral compounds which contain lone pairs of electrons on the Z atoms.

Previously, conformational studies of $EH_2(OH)_2$ (E = C or Si) indicated that hyper-conjugation derived from the donation of lone pairs on oxygens to the E–H σ* anti-bonding orbitals (Fig. 3a) determines the orientations of the OH groups.[7] The application of this hyper-conjugation concept to the $E(ZH_2)_4$ tetrahedral compounds is quite promising. Within our cubic presentation, the maximum amplitude available for the lone pair donation of a given E–Z σ* anti-bonding orbital points to one of the empty corners (see Fig. 3b). Therefore, the D_{2d} and S_4 conformers provide a situation where each lone pair finds a σ* anti-bonding orbital for interaction, maximizing the hyper-conjugation. In such a way, the hydrogen–hydrogen repulsions and hydrogen–lone pair attractions are also optimal.

For the D_{2d} conformer, maximizing the hyper-conjugation interaction gives a compressed tetrahedron in which the 4*s*2*l* structural feature is obtained. Here, the bold arrows in Fig. 1 (**1** D_{2d}) are taken as the lone pairs of electrons. The smaller Z–E–Z angles correspond to the square faces with the $\mathbf{P}_{//}$ patterns. For the S_4 conformers, an elongated tetrahedron with 4*l*2*s* structural features is observed and the smaller Z–E–Z angles also correspond to the $\mathbf{P}_{//}$ square-faces.

The $C(OH)_4$ compound gives two stable conformers with D_{2d} and S_4 symmetry while $Si(OH)_4$ gives only the S_4 one (see Table 1). In the cubic model (see Fig. 1), the bold arrows are now representing the hydrogens. Therefore, the distortion pattern at the central atom (C or Si) should be opposite to the one observed for $E(ZH_2)_4$ (E = C or Si; Z = N or P). For the D_{2d} conformer, the 4*l*2*s* structural feature is expected. The S_4 conformer should have the 4*s*2*l* structural feature (see Table 2).

We also notice from Table 1 that the D_{2d} symmetry conformer is markedly less stable for $C(OH)_4$ and is not a local minimum for $Si(OH)_4$. These results can be related to the stronger H···O interactions in the S_4 conformer. The calculations give much shorter H···O distances in the S_4 conformer than those in the D_{2d} conformer (Fig. 4).

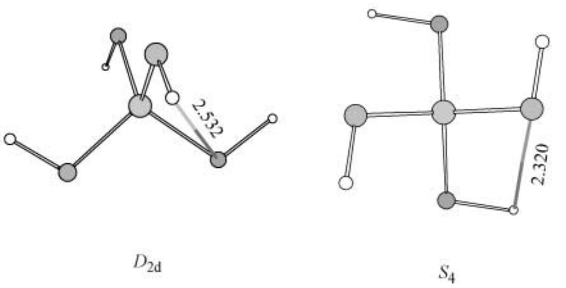

Fig. 4 Comparison of the two stable conformers of the $C(OH)_4$ compound.

Conclusions

The cubic model proposed in this paper provides the simplest way to understand the interesting structural features of the class of $E(ZXY_2)_4$ compounds. Within this cubic model, the stability of the D_{2d} and S_4 conformers (**1** and **2**) can be understood in terms of the homophobic nature of the substituents on the Z atoms. The hyper-conjugation effects should be considered when the Z atoms have lone pairs of electrons. The homophobic interactions and the hyper-conjugation effects determine the structural features of the compounds. The 4*l*2*s* and 4*s*2*l* structural features are closely related to the square-face patterns of the cube.

The cubic model described in this paper is expected to be extremely useful in studying conformational problems of other large organic or biological systems and will give us deeper insight regarding the nature of various long-range interactions.

Experimental

Calculation details

Full geometry optimisations for all the six distinguishable conformers of compounds with formula of $E(ZXY_2)_4$ (E = C and Si; Z = C, O, N and P; X or Y = H, halides or lone pairs) were carried out at the B3LYP level using the Gaussian 98 program package[18] on Silicon Graphics workstations and Pentium III computers. The Lanl2DZ effective core potentials and basis sets[19] were used for both Br and I and the standard 6-31G basis sets are used for all other atoms in the calculations. Frequency calculations have also been performed. The results show that all the optimised structures listed in Table 1 do not have any imaginary frequencies. To test the effect of polarisation functions, geometry optimisations have been done for the six conformers of $C(CH_2F)_4$ using a larger basis set 6-31G(d). No significant change was found in the re-optimised structures. The relative energies are 0.7, 0.0, 8.7, 6.0, 3.3 and 3.1 kcal mol^{-1} for conformers **1**, **2**, **3**, **4**, **5** and **6**, respectively. Comparing these data with the first entry of Table 1, we found that the order of the relative energies does not change with the larger base set. These results indicate that the qualitative picture given in the paper should be reliable.

Acknowledgements

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18 *Gaussian 98* (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
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