Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XVIII. Conformations and Stabilities of Trisubstituted Methanes

William A. Lathan, Leo Radom, Warren J. Hehre, and John A. Pople*

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received June 24, 1972*

Abstract: *Ab initio* molecular orbital theory is used to study the conformations and stabilities of a partial set of 14 of the trisubstituted methanes HCXYZ (X, Y, Z = CH_3, NH_2, OH, or F). Conformational predictions agree with available experimental data. Relative conformational energies are found to be well represented as a superposition of results for corresponding disubstituted methanes. However, calculated bond separation energies are smaller than those predicted on this basis, *i.e.*, they demonstrate a "saturation" effect.

In a previous paper,[1] we presented a systematic theoretical study of the energies and conformations of acyclic molecules containing up to three heavy atoms (C, N, O, or F) for which classical valence structures can be written. The molecules examined included the set of disubstituted methanes H_2CXY where X and Y = CH_3, NH_2, OH, or F. In the present paper, we extend this study to a partial set of saturated trisubstituted methanes HCXYZ where the substituents X, Y, and Z are again CH_3, NH_2, OH, or F.

The aims of the work are the following: (1) to predict the most stable conformation of each of these molecules and to compare with experiment where possible, (2) to examine the interaction among substituents, and (3) to investigate how far the results can be understood as a superposition of effects already present in the disubstituted methanes. Although only a small number of the molecules considered are characterized experimentally, some of them are important as model systems for groupings in larger molecules.

Method and Results

The molecular orbital method used is standard *ab initio* LCAO-SCF theory employing the 4-31G extended Gaussian basis set.[2] Standard geometries[3] are used so that all bond angles are tetrahedral. Dihedral angles are chosen to correspond to staggered conformations of bonds (±60, 180°). For methyl and fluoro substituents, only one such arrangement of bonds is possible. For amino and hydroxy substituents, we refer to Figure 1 which is a projection obtained by looking along the methine bond from H to C. The conformation of hydroxy substituents is specified by the HCOH dihedral angle and for amino by HCN: (where : denotes the fourth tetrahedral direction corresponding to the nitrogen lone pair). The symbols *t*, *g*, and *g′* are used for trans (antiperiplanar, 180°), gauche (+ synclinal, +60°), and gauche′ (− synclinal, −60°).

The total energies for the complete set of structures so defined are listed in Table I. Also given for each molecule are the energies relative to that for the conformation predicted to be most stable. We next examine the possibility that these relative energies may be estimated by adding together relative energies for appropriate conformations of the disubstituted methanes H_2CXY, H_2CXZ, and H_2CYZ. These additivity values are listed in the next column of Table I.[4]

It has been found useful previously to discuss the energies of molecules in terms of bond separation energies.[1,5,6] For the molecules considered in this paper, these are the energies of the bond separation reactions

$$HCXYZ + 2CH_4 \longrightarrow CH_3X + CH_3Y + CH_3Z \qquad (1)$$

in which the C–X, C–Y, and C–Z are separated from each other into the simplest molecules containing such bonds. The energy of the reaction (1) is a measure of the deviation from bond energy additivity in HCXYZ, *i.e.*, it represents the interactions between the bonds. The bond separation energies listed have been calculated using the total energies in Table I and corresponding values[1] for CH_4, CH_3X, CH_3Y, and CH_3Z obtained using the same basis set and geometric model. In addition, we examine whether the bond separation energy of HCXYZ can be obtained in a manner similar to that described above for relative conformational energies, *i.e.*, by adding together the bond separation energies of appropriate conformations of H_2CXY, H_2CYZ, and H_2CZX. The additive bond separation energies are listed in the next column of Table I.[4] Finally, we present for reference, calculated values of the electric dipole moments for each conformation. In Table II, we list corresponding data for the mono- and disubstituted methanes, taken from ref 1.

Discussion

Comparison with Experimental Thermochemical Data. Of the molecules listed in Table I, seven have experimentally measured gaseous heats of formation.[7] These heats can be used together with corresponding data for methane, ethane, methylamine, methanol, and methyl

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[1] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

[2] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

[3] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

[4] They are, of course, obtained directly from the results of ref 1 without further quantum mechanical calculations on the larger molecules.

[5] R. Ditchfield, W. J. Hehre, J. A. Pople, and L. Radom, *Chem. Phys. Lett.*, **5**, 13 (1970).

[6] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

[7] (a) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969; (b) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

Table I. Calculated Total and Relative Energies and Dipole Moments for Monosubstituted Methanes HCXYZ[a]

Substituents X	Substituents Y	Substituents Z	Name	Conformation[b] X	Conformation[b] Y	Conformation[b] Z	Figure	Total energy, hartrees	Relative energy, kcal mol^{-1} Direct	Relative energy, kcal mol^{-1} Additive	Bond separation energy, kcal mol^{-1} Direct	Bond separation energy, kcal mol^{-1} Additive	Dipole moment, Debyes
CH_3	CH_3	CH_3	Isobutane					−157.07065			3.3	3.7	0.10
CH_3	CH_3	NH_2	Isopropylamine			*t*	I	−173.03065	0	0	7.6	8.4	1.67
						g	II	−173.02958	0.67	0.51	6.9	7.9	1.64
CH_3	CH_3	OH	2-Propanol			*g*	III	−192.83683	0	0	9.4	10.7	2.12
						t	IV	−192.83573	0.69	0.66	10.1	11.4	2.20
CH_3	CH_3	F	Isopropyl fluoride					−216.82587			11.8	13.5	2.27
CH_3	NH_2	NH_2	1,1-Diaminoethane		*t*	*g*	V	−188.99385	0	0	13.8	15.4	1.93
					g	*g*	VI	−188.99271	0.71	0.51	13.1	14.9	1.88
					t	*g*′	VII	−188.99264	0.75	0.85	13.1	14.6	1.95
					g′	*g*	VIII	−188.99239	0.91	0.60	12.9	14.8	1.77
					t	*t*		−188.98567	5.13	5.79	8.7	9.7	3.40
					g	*g*′		−188.98299	6.81	6.81	7.0	8.6	3.51
CH_3	NH_2	OH	1-Aminoethanol		*g*′	*g*	IX	−208.80444	0	0	19.1	21.3	1.64
					g′	*g*′	X	−208.80296	0.93	0.83	18.2	20.5	1.60
					g′	*t*		−208.80202	1.52	1.49	17.6	19.8	1.65
					t	*t*		−208.80172	1.71	2.09	17.4	19.2	2.04
					g	*g*′		−208.80157	1.80	1.94	17.3	19.4	1.92
					t	*g*′		−208.79467	6.13	6.87	13.0	14.4	3.43
					t	*g*		−208.79412	6.48	7.27	12.6	14.0	3.43
					g	*g*		−208.79239	7.56	7.78	11.6	13.5	3.58
					g	*t*		−208.79202	7.79	8.04	11.3	13.3	3.61
CH_3	NH_2	F	1-Fluoroethylamine		*g*′		XI	−232.79510	0	0	21.9	24.5	0.58
					t			−232.78560	5.96	6.85	15.9	17.6	3.27
					g			−232.78392	7.02	7.36	14.9	17.1	3.43
CH_3	OH	OH	1,1-Ethanediol		*t*	*g*′	XII	−228.61279	0	0	23.0	25.3	0.28
					g	*g*		−228.60602	4.25	4.71	18.8	20.6	3.03
					g	*g*′		−228.60579	4.39	4.70	18.6	20.6	2.84
					t	*g*		−228.60442	5.25	5.38	17.3	19.9	3.29
					t	*t*		−228.60338	5.91	6.02	17.1	19.3	3.13
					g′	*g*		−228.59478	11.30	11.84	11.7	13.5	4.46
CH_3	OH	F	1-Fluoroethanol		*g*		XIII	−252.59863	0	0	22.7	24.8	1.97
					t		XIV	−252.59709	0.96	0.66	21.8	24.2	2.34
					g′			−252.58892	6.10	6.24	16.6	18.6	4.03
CH_3	F	F	1,1-Difluoroethane					−276.58336			21.8	23.8	2.77
OH	OH	OH	Methanetriol	*t*	*g*	*g*	XV	−264.38225	0	0	31.8	36.0	2.27
				t	*t*	*g*		−264.37958	1.67	0.64	30.2	35.4	2.28
				t	*g*′	*g*		−264.37904	2.01	1.74	29.8	34.3	2.23
				g	*g*	*g*		−264.37636	3.69	4.72	28.2	31.3	3.95
				t	*g*	*g*′		−264.37362	5.41	5.36	26.4	30.7	3.81
				t	*t*	*t*		−264.36916	8.21	6.64	23.6	29.4	3.67
				g	*g*′	*g*		−264.36464	11.05	11.82	20.8	24.2	4.98
OH	OH	F	Fluoromethanediol	*t*	*g*		XVI	−288.36873	0	0	32.0	37.0	1.91
				t	*g*′		XVII	−288.36725	0.93	0.86	31.0	36.1	2.30
				t	*t*			−288.36562	1.95	0.64	30.0	36.4	1.96
				g	*g*			−288.36169	4.42	5.58	27.6	31.4	3.98
				g′	*g*			−288.35985	5.57	6.46	26.4	30.5	3.73
				g	*g*′			−288.35134	10.91	11.80	21.1	25.2	5.21
OH	F	F	Difluoromethanol	*t*			XVIII	−312.35471	0	0	31.8	38.1	3.03
				g				−312.34796	4.25	5.58	27.5	32.5	3.52
F	F	F	Trifluoromethane					−336.33498			28.0	34.6	2.20

[a] 1 hartree = 627.5 kcal mol^{-1}. [b] Conformations of hydroxy and amino substituents defined respectively by HCOH and HCN: dihedral angles.

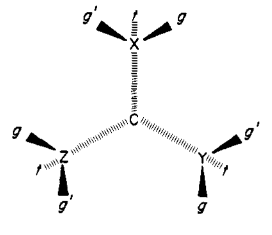

Figure 1. Projection of HCXYZ looking along H–C. The symbols *t*, *g*, and *g*′ describe the dihedral angle which defines the orientation of the substituent with respect to the C–H bond.

fluoride to obtain experimental bond separation energies, *i.e.*, heats of reaction 1. These may then be compared with the corresponding theoretical results for the most stable conformation of each molecule as shown in Table III.[8] Agreement is reasonably good.

Another interesting comparison that can be made is between the stabilities of straight chain and branched isomers, in particular, *n*-C_3H_7X and *i*-C_3H_7X. Theoretical values of this energy difference can be obtained using the total energies we have recently reported[9] for *n*-C_3H_7X, and the total energies for *i*-C_3H_7X from Table I. The calculated and experimental values are given in Table IV and are in quite good agreement. The

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(8) Strictly, the theoretical results should be compared with heats corrected to 0°K and corrected for zero-point vibrational energy. However, in the absence of sufficient data to do this, we simply use $\Delta H°_f$ (298°) values.

(9) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **95**, 693 (1973).

Table II. Calculated Energies and Dipole Moments for Monosubstituted (H_3CX) and Disubstituted (H_2CXY) Methanes[a]

Substituents					Dipole moment,
X	Y	Name	Conformation	Energy, hartrees	Debyes
CH_3		Ethane		−79.11484	0
NH_2		Methylamine		−95.06803	1.86
OH		Methanol		−114.87020	2.36
F		Fluoromethane		−138.85648	2.41
CH_3	CH_3	Propane		−118.09211	0.05
CH_3	NH_2	Ethylamine	CCN: gauche	−134.04904	1.74
			CCN: trans	−134.04823	1.78
CH_3	OH	Ethanol	CCOH trans	−153.85411	2.18
			CCOH gauche	−153.85306	2.29
CH_3	F	Fluoroethane		−177.84154	2.33
NH_2	NH_2	Methylenediamine	:NCN trans, NCN: gauche	−150.00967	2.04
			:NCN gauche, NCN: gauche	−150.00913	2.06
			:NCN trans, NCN: trans	−150.00872	1.93
			:NCN gauche, NCN: gauche′	−150.00045	3.64
NH_2	OH	Aminomethanol	:NCO trans, NCOH trans	−169.81933	1.72
			:NCO trans, NCOH gauche	−169.81696	1.76
			:NCO gauche′, NCOH gauche′	−169.81600	2.07
			:NCO gauche, NCOH trans	−169.80774	3.65
			:NCO gauche′, NCOH gauche	−169.80734	3.69
NH_2	F	Fluoromethylamine	:NCF trans	−193.80844	0.53
			:NCF gauche	−193.79752	3.46
OH	OH	Methanediol	HOCO gauche, OCOH gauche	−189.62499	0.14
			HOCO gauche, OCOH trans	−189.61747	3.27
			HOCO gauche, OCOH gauche′	−189.61645	3.13
			HOCO trans, OCOH trans	−189.60717	4.59
OH	F	Fluoromethanol	HOCF gauche	−213.60830	2.15
			HOCF trans	−213.59940	4.10
F	F	Difluoromethane		−237.59180	2.68

[a] Taken from ref 1 and associated unpublished data.

Table III. Calculated and Experimental Bond Separation Energies (kcal mol^{-1})

Molecule	Calcd	Exptl[a]
Isobutane	3.3	7.2
Isopropylamine	7.6	9.9
2-Propanol	10.1	12.4
Isopropyl fluoride	11.8	8.4
1,1-Ethanediol	23.0	22.7
1,1-Difluoroethane	21.8	21.7
Trifluoromethane	28.0	34.8

[a] Energies of reaction 1, calculated using $\Delta H°_f$ (298°) values from ref 7.

Table IV. Comparison of Stabilities of n-C_3H_7X and i-C_3H_7X Molecules

	$E(n\text{-}C_3H_7X) - E(i\text{-}C_3H_7X)$, kcal mol^{-1}	
X	Calcd[a]	Exptl[b]
CH_3	1.1	2.0
NH_2	2.9	3.3
OH	3.2	3.9
F	4.0	2.0

[a] Calculated using total energies for i-C_3H_7X from Table I and for n-C_3H_7X from ref 9. [b] Calculated using $\Delta H°_f$ (298°) values from ref 7.

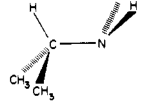
branched isomers are more stable in each case, reflecting the stabilization produced by the additional 1,2-interaction between C–C and C–X bonds.

Evaluation of Additivity Hypothesis. Comparison of the bond separation energies (direct and additive) of Table I shows that these energies for HCXYZ are reasonably well approximated by the sum of the bond separation energies for H_2CXY, H_2CYZ, and H_2CZX. The principal difference is that the directly calculated bond separation energies are all somewhat smaller than those based on additivity. This suggests that the mechanisms leading to the stabilization are the same as those operating in the disubstituted molecules (and discussed in ref 1) but that there is some "saturation" when three such interactions take place in conjunction.

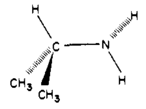
The additivity scheme is even more successful in predicting the relative conformational energies. In all cases, the most stable conformation predicted by the additive hypothesis is the same as that predicted by the direct calculation. In general, the ordering of stabilities of the various conformations is also in agreement. The mean absolute deviation between the directly calculated and additive values of the relative conformational energies is 0.5 kcal mol^{-1}.

We now comment on the results for some of the individual molecules.

Isopropylamine. The conformation with lowest calculated energy is t (I) with the nitrogen lone pair gauche to both methyl groups. This parallels predicted[1] and observed[10,11] structures (CCN: gauche) for ethylamine. Experimental studies[10,11] on isopropylamine have suggested that the energy difference between the t (I) and g (II) conformations is quite small; it has been estimated[10] at 0.12 kcal mol^{-1} in CCl_4 solution, I being the more stable. The theory gives 0.67 kcal mol^{-1}.



I



II

2-Propanol. Here the predicted structure g (III) has the hydroxyl hydrogen trans to one of the methyl

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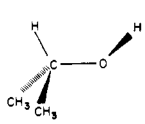
(10) P. J. Krueger and J. Jan, *Can. J. Chem.*, **48**, 3229 (1970).

(11) D. W. Scott, *J. Chem. Thermodyn.*, **3**, 843 (1971).

groups. This form is found to be 0.69 kcal mol^{-1} more stable than *t* (IV) in which both CCOH angles are gauche. Again we may note that the most stable conformation for ethanol (both calculated[1] and observed[12]) has CCOH trans. The microwave spectrum of 2-propanol has recently been measured and both *g* (III) and *t* (IV) conformations have been detected.[13] Relative intensity measurements[14] have indicated that III is 0.28 kcal mol^{-1} more stable than IV.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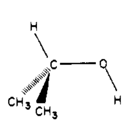
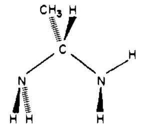
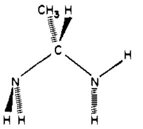

IV

1,1-Diaminoethane. We find four conformations of relatively low energy for this molecule. These are *tg* (V), *gg* (VI), *tg'* (VII), and *g'g* (VIII). The most stable form (V) has the :NCN trans, NCN: gauche arrangement predicted[1] for diaminomethane, CH$_2$(NH$_2$)$_2$. No experimental information is currently available.


V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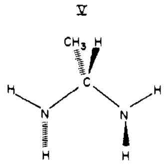
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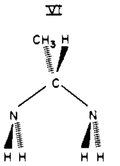
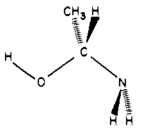
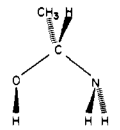
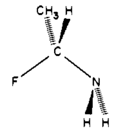

VIII

1-Aminoethanol. The two conformations of lowest energy are *g'g* (IX) and *g'g'* (X). X is the most stable structure and contains the :NCO trans, NCOH trans arrangement predicted to occur in aminoethanol.[1]

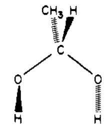

IX


X

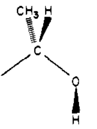
1-Fluoroethylamine. Only one low-energy conformation *g'* (XI) is predicted for this molecule. This structure has FCN: trans as in fluoromethylamine.[1]

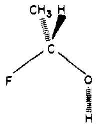

XI

1,1-Ethanediol. Again, only one confirmation is predicted to have low energy. This is *tg'* (XII) which has a gauche–gauche structure analogous to that predicted for methanediol[1,15] and observed for related molecules such as dimethoxymethane.[16-18]

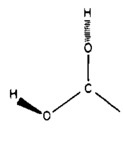

XII

1-Fluoroethanol. Here, two conformations, *g* (XIII) and *t* (XIV), are found to have relatively low energies and both have the FCOH gauche arrangement predicted[1,19-21] for fluoromethanol. The most stable calculated structure is XIII.

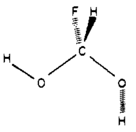

XIII

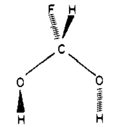

XIV

Methanetriol (Orthoformic Acid). We find that the most stable conformation is *tgg* (shown looking along the H–C bond in XV). Symmetrical structures such as *ggg* (C_3 symmetry) and *ttt* (C_{3v} symmetry) have relatively high energies. Although the experimental structure of methanetriol is not known, the trimethyl ester CH(OCH$_3$)$_3$ has been studied.[22,23] Dipole moment and Kerr constant results[22] may be interpreted in terms of a large proportion of the *tgg* isomer. Infrared studies[23] suggest a mixture of *tgg* and *tg'g* in the vapor and in solution. In the liquid, the *tg'g* structure is found to be more stable by 0.61 kcal mol^{-1}. The *ttg* form which we predict to be the second lowest energy structure of methanetriol is sterically hindered in CH(OCH$_3$)$_3$. Calculated bond separation energies for methanetriol are large and positive reflecting the stabilizing interaction of the three C–O bonds.


XV

Fluoromethanediol. Two relatively low-energy forms of this molecule are *tg* (XVI) and *tg'* (XVII), the latter being 0.93 kcal mol^{-1} higher in energy.


XVI


XVII

Difluoromethanol. The only conformation of this molecule with low calculated energy is *t* (XVIII). This

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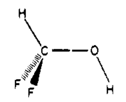

XVIII

structure has two FCOH gauche arrangements which are found to be strongly favored in fluoromethanol itself.[1,19–21]

Conclusions

Several conclusions may be drawn from this work. (1) The predicted stable conformations for the trisubstituted methanes are in agreement with the small amount of experimental information available. (2) The conformational preferences in the trisubstituted methanes are well represented as a superposition of results for disubstituted methanes. (3) Calculated bond separation energies are in reasonable agreement with experimental values. (4) The bond separation energies estimated by adding appropriate values for disubstituted methanes are found to be less than those given by the full calculation, *i.e.*, there is a "saturation" of the stabilizing interactions. (5) Isopropyl derivatives (i-C_3H_7X) are predicted to be more stable than corresponding n-propyl isomers (n-C_3H_7X) and the calculated and experimental energy differences are in quite good agreement.

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Ab Initio Gaussian Lobe Self-Consistent Field Computations on the Interconversion of Ammonium Oxide with Hydroxylamine, and Implications for the Rearrangements of Substituted Hydroxylamines

Carl Trindle*[1a] and Donald D. Shillady[1b]

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and the Chemistry Department, Virginia Commonwealth University, Richmond, Virginia 23220.

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Abstract: *Ab initio* restricted SCF calculations in a minimal basis of Slater-type orbitals mimicked by two or four Gaussian lobe functions on the system H_3NO interconverting with H_2NOH (Figure 1) elucidate a non-least-motion rearrangement path, bearing some resemblance to the allowed motion for 1,3-sigmatropic shifts. We discuss the observed stability of F_3NO relative to F_2NOF, and the course of a rearrangement of a tris(trialkylsilyl)hydroxylamine with reference to these model calculations.

The chemistry of substituted hydroxylamines includes O to N migration[2] and insertion of O substituents into the O–N bond.[3] In an effort to rationalize the stereochemical course of these rearrangements, and with the hope of tracing the cause of stability of F_3NO (known[4]) relative to F_2NOF (unknown), we have undertaken an exploration of portions of the potential surface of the H_3NO–H_2NOH system. Our method is conventional restricted Hartree–Fock computation in the LCAO–MO–SCF formalism of Roothaan,[5] with a very small basis of Gaussian lobe mimics of Slater-type basis functions. After establishing the degree of reliability of this mode of calculation, we show by numerical result and qualitative argument that the rearrangement is of the "non-least-motion" type. The effect of p and d orbitals of the migrating fragment on the path of reaction is considered, with reference to the experimentally established rearrangement of tris(trialkylsilyl)hydroxylamine.[6]

Computational Details

The program which performs the SCF computation is a collection of familiar methods and has been described elsewhere.[7] A minimal basis of Slater-type orbitals mimicked by Gaussian lobe functions was employed. In surface explorations only two Gaussian lobes were used to represent each STO; for a few significant geometries, a four-Gaussian mimic was employed. Neither of these computational modes yields highly accurate results; we are led to emphasize qualitative features of the results.

To ease the geometry variation in the surface exploration, the programs PROXYZ and STEPIT,[8] which compute geometries and vary chosen parameters, respectively, were adapted to drive the SCF program.

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