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Quantum-chemical Investigation of the Hyprevalent Intramolecular Coordination X←N (X = C, Si, Ge) in Quasimonocyclic Models of IVa Group Atranes

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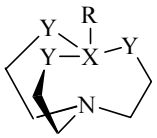
Abstract—The structure and the pentacoordination effect in quasimonocyclic models of IVa group atranes were investigated by *ab initio* [MP2 (full) /6-311+G **] and the density functional [B3LYP/6-311+G **] quantum chemical calculations. The calculations revealed considerable stabilization of the quasimonocyclic conformations relative to their free-of-strain *trans-s-trans* conformations, which is caused by the formation of secondary (R)X←N (X=C, Si, Ge) bonds of the hypervalent type. The strength of the intramolecular (R)X←N coordination increases in the order X=C, Si, Ge. The nature of attractive (R)X←N coordination is determined by donor-acceptor interaction of the nitrogen lone electron pair and antibonding orbital which primary localize at the X-R bond. Energy of X···N (X=Si, Ge) contact is about 3-7 kcal mol^{-1}.

Recently an interest grew to systems with pentacoordination effects in IVa group elements [1]. Well-studied atranes **I** [2–4] belong to these systems. The study of the systems revealed a number of quite unusual physicochemical and biological properties originating from a short contact between the covalently nonbonded centers X and N [3–5].



I, X = Si, Ge, Y = CH_2, O, NR, R = H, F, Cl, Alk, Ar, OR, SR, NR_2.

The key to understanding of these unusual properties is the effect of strong hypervalent interaction X···N [3, 4] of a donor-acceptor character. However the majority of theoretical studies on arranges [6, 7] were aimed mainly at investigation of the general structural features, like the effect of various substituents and medium on the size of the X...N contact, and did not touch on the nature of this interaction. The approximate indirect experimental estimation of the energy of interaction Si···N from the data of photoelectron spectroscopy equals to 13–22 kcal mol^{-1} [3]. The main difficulty for direct evaluation of the attractive interaction between the X and N centers consists in the lack of an isomeric comparable structure for atranes **I** that would possess the complete set of valence bonds characteristic of atrane molecule and did not involve the X···N interaction.

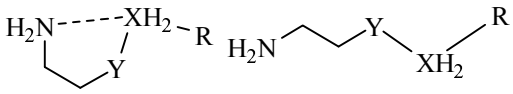
First direct estimation of energy of the Si···N interaction were based on the calculations *ab initio* of complex formation energy (~8–10 kcal mol^{-1}) in bimolecular systems $RY_3Si\cdots NH_3$ [7]. The most complete investigation of systems fit for simulation of the Si···N interaction in atranes was carried out for systems $HOSi(OCH_2CH_2)_n(OH)_{3-n}NH_{3-n}$ (n = 0–3) [8]. The structure characteristics of the system at n = 1 and of the corresponding atrane **I** fragment (X = Si, Y = O, R = OH) are similar, and therefore the system is a convenient model for studying the Si···N interaction in silatranes **I** (X = Si), and with other X centers also for investigation of the total atrane class. An analogous approach to the study of the X···N interactions was already shown to be efficient in estimating energy of hypervalent attractive interaction in systems containing X atoms from the fifth and sixth groups of the periodic table [9].

The goal of the present study was estimation of the energy of X···N interaction that was evaluated as a difference of the calculated by means *ab initio* methods MP2(full)/6-311+G** and theory of density functional

Table 1. Total energy (E_{total}, a.u.), energy of zero harmonic vibrations (*ZPE*, a.u.), and the value of the least harmonic frequency (ω, cm^{-1}) of model compounds **IIa–l** and **IIIa–l** calculated by *ab initio* MP2(full)/6-311+G** (MP2) and density functional B3LYP/6-311+G** (DFT) methods

Structure	Method	E_{total}	*ZPE*	ω
IIa	MP2	–213.286438	0.151977	43
	DFT	–213.866608	0.149300	66
IIIa	MP2	–213.289072	0.151982	95
	DFT	–213.869912	0.149178	107
IIb	MP2	–312.391651	0.145212	63
	DFT	–313.135166	0.142552	79
IIIb	MP2	–312.391764	0.145124	77
	DFT	–313.136200	0.142383	80
IIc	MP2	–249.149861	0.127941	51
	DFT	–249.767607	0.125563	88
IIIc	MP2	–249.152625	0.128088	92
	DFT	–249.770449	0.125434	99
IId	MP2	–348.268124	0.121343	46
	DFT	–349.047989	0.119084	51
IIId	MP2	–348.262023	0.120991	55
	DFT	–349.041852	0.118319	39
IIe	MP2	–464.400464	0.139159	59
	DFT	–465.262716	0.136614	77
IIIe	MP2	–464.399532	0.138691	84
	DFT	–465.263451	0.135909	86
IIf	MP2	–563.587061	0.135225	65
	DFT	–564.608327	0.132750	82
IIIf	MP2	–563.577058	0.133740	53
	DFT	–564.601360	0.131257	55
IIg	MP2	–500.312749	0.116180	75
	DFT	–501.210324	0.113681	80
IIIg	MP2	–500.310002	0.115767	53
	DFT	–501.209107	0.112991	42
IIh	MP2	–599.500963	0.111935	67
	DFT	–600.557687	0.109565	77
IIIh	MP2	–599.494840	0.111029	49
	DFT	–600.553779	0.108695	38
IIi	MP2	–251.041201	0.137676	62
	DFT	–2252.748163	0.134532	67
IIIi	MP2	–2251.040448	0.137014	82
	DFT	–2252.749463	0.134207	86
IIj	MP2	–2350.199207	0.133270	75
	DFT	–2352.073122	0.130434	80
IIIj	MP2	–2350.186960	0.131789	43
	DFT	–2352.064760	0.129162	42
IIk	MP2	–2286.932874	0.114147	85
	DFT	–2288.678567	0.111141	73
IIIk	MP2	–2286.929712	0.113372	44
	DFT	–2288.677220	0.110603	47
III	MP2	–2386.090448	0.109626	84
	DFT	–2388.002013	0.106832	82
IIIl	MP2	–2386.080318	0.108242	25
	DFT	–2387.995515	0.105772	43

B3LYP/6-311+G** total energies of a quasimonocyclic system **II** and an isomeric open form **III**, and also investigation of dependence of electronic and spatial structure of forms **II** and **III** (X = C, Si, Ge) on the character of the sybstituents R and Y.



IIa–III **IIIa–IIIl**

X = C, Y = CH_2, R = H (**a**); X = C, Y = CH_2, R = F (**b**); X = C, Y = O, R = H (**c**); X = C, Y = O, R = F (**d**); X = Si, Y = CH_2, R = H (**e**); X = Si, Y = CH_2, R = F (**f**); X = Si, Y = O, R = H (**g**); X = Si, Y = O, R = F (**h**); X = Ge, Y = CH_2, R = H (**i**); X = Ge, Y = CH_2, R = F(**j**); X = Ge, Y = O, R = H (**k**); X = Ge, Y = O, R = F (**l**).

Calculation procedure. The calculations by the methods of density functional B3LYP/6-311+G** (DFT) and *ab initio* MP2(full)/6-311+G** (MP2) were carried out using software packages GAUSSIAN 98 [10] and GAMESS [11]. The geometry optimization in the stationary points was performed in the «tight» mode for GAUSSIAN 98 and till the value of 10^{-5} a.u. for gradients and RMS gradients in GAMESS program. The The compliance of the calculated geometrical configuration of the systems under study to the stationary points on the potential energy surface (PES) was controlled by calculation of the frequencies of harmonic vibrations. The superposition error (BSSE) was not taken into account in keeping with recommendations of [12, 13]. The analysis of molecular orbitals was carried out using natural bond orbitals (NBO-analysis) [14] by B3LYP procedure in the basis 6-311+G**. The figures were done with the help of PC MODEL package [15].

1-Aminobutane, 1-amino-3-oxabutane, and their monofluoro derivatives. Structures **IIa–IId** and their isomers **IIIa–IIId** according to calculations conform to the minimum points on the corresponding PES. The calculated total and relative energies and geometrical characteristics of these structures are presented in Tables 1 and 2 and on Fig.1.

The distances between nitrogen and carbon atoms in structures **IIa–IId** according to calculations are within the range 3.128–3.256 (DFT) or 3.033–3.239 Å (MP2). These values are only by ~0.2 Å less than the sum of the van der Waals radii of carbon and nitrogen (3.39 Å) [16] demonstrating that the attractive interaction between the nitrogen and carbon centers is here negligibly small or

lacking. In going from 1-aminobutane (**IIa**) to 1-amino-4-fluorobutane (**IIb**) and from 1-amino-3-oxabutane (**IIc**) to 1-amino-3-oxa-4-fluorobutane (**IId**) the C···N is insignificantly decreased indicating that the effect of Y and R substituents on the length of the contact is unimportant. The stabilizing interaction between the unshared electron pair of nitrogen and XR fragment is hampered both by the large distance X···N and by nonlinearity of the triad N–X–R (bond angle NXR varies in the range 128.0–163.5 deg). The destabilization of structure **II** relative to isomer **III** by ~2 kcal mol^{-1} for all substituents Y and R except for R = F and Y = O (see Table 2) also evidences the lack of interaction between the fragments N and X(R). The unusual stabilization of structure **IId** by ~3 kcal mol^{-1} does not depend on the noncovalent interaction N···X for the contact C···N length in all structures **IIa–IId** has similar values close to the sum of the van der Waals radii of carbon and nitrogen.

4-Amino-1-silabutane, 4-amino-2-oxa-1-silabutane, and their fluoro derivatives. Structures **IIe–IIh** and their isomers **IIIe–IIh** conform to the minima on the corresponding PES. The calculated energy and geometrical characteristics of these structures are presented in Tables 1 and 2 and on Fig.2.

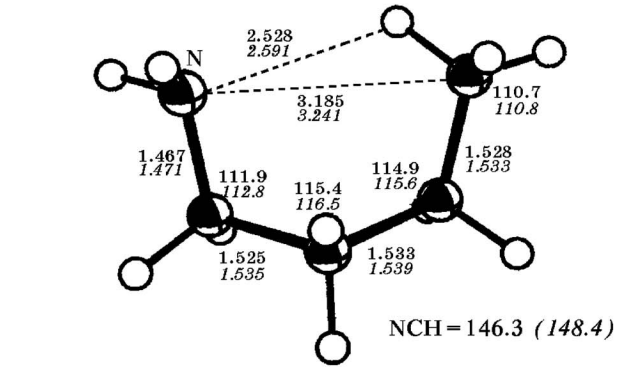
In going from molecules **IIa–IId** to their silicon-containing analogs **IIe–IIh** although the van der Waals radius of silicon is larger than that of carbon the X···N distance significantly decrease to the values of 2.578–3.048 (DFT) or 2.440–2.932 Å (MP2). These distances are considerably less than the sum of van der Waals radii of the silicon and nitrogen (3.50 Å), and their value approaches at the length of an ordinary Si–N bond (~1.8–1.9 Å). The data on Fig. 2 and in Table 2 show that increasing the electronegativity of the R substituents (replacement of hydrogen by fluorine) the distance between centers X···N is considerably shortened (transition **IIe→IIf** and **IIg→IIh**). This fact indicates the high sensitivity of the Si···N to the character of the R substituent. The bond angle NSiR for all systems under consideration varies in the range 172.6–178.8 deg, very close to linear arrangement. In contrast to structures **IIa–IId** silicon-containing structures **IIe–IIf** are more energetically favorable than the isomeric structures **III.** According to results of DFT calculations only structure **IIe** is by ~0.5–1.5 kcal mol^{-1} less stable than isomer **IIIe**. From the MP2 calculations the insignificant destabilization of this structure (by 0.16 kcal mol^{-1}) follows only if the entropy factor is taken into account. From the data of Table 2 the lower boarder of the energy of the noncovalent interaction Si···N in the structures **IIg, IIh** should be estimated at ~3–6 kcal mol^{-1} .

4-Amino-1-germabutane, 4-amino-2-oxa-1-germabutane, and their fluoro derivatives. Like all systems considered before the germanium-containing structures **IIi–IIl** (X = Ge) and **IIIi–IIIl** according to the calculations performed correspond to the energy minima on the PES. Their geometrical and energy characteristics are presented in Tables1 and 2 and on Fig. 3.

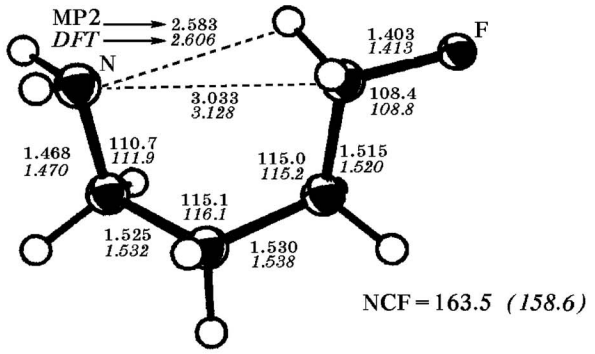
The replacement of the silicon center X by germanium atom results in further shortening of the distance between centers X···N to the values of 2.652–3.139 (DFT) or 2.547–3.006 Å (MP2) that are sufficiently close to the

Table 2. Calculated by *ab initio* MP2(full)/6-311+G** (MP2) and density functional B3LYP/6-311+G** (DFT) methods relative energies ΔE, relative stabilization energies taking into account the energy of zero harmonic vibrations (*ZPE*) ΔE_{ZPE}, relative change in enthalpy ΔH and Gibbs free energy ΔG_{25} for structures **II** with respect to isomers **III**. All values are given in kcal mol^{-1}. The positive sign of energy corresponds to preference of structure **II**.

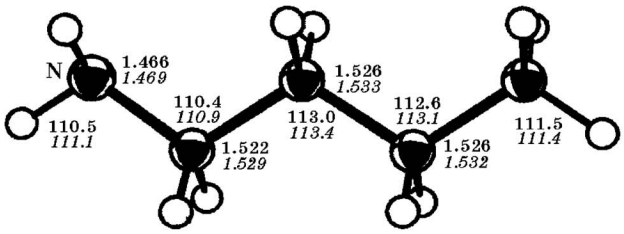
Structure	Method	ΔE	ΔE_{ZPE}	ΔH	ΔG_{25}
IIa	MP2	–1.65	–1.65	–1.58	–1.52
	DFT	–2.07	–2.15	–2.06	–2.16
IIb	MP2	–0.07	–0.13	0.02	–0.35
	DFT	–0.65	–0.75	–0.65	–0.90
IIc	MP2	–1.73	–1.64	1.59	–1.50
	DFT	–1.78	–1.86	–1.76	–1.97
IId	MP2	3.83	3.61	3.81	3.27
	DFT	3.85	3.37	3.66	2.75
IIe	MP2	0.58	0.29	0.60	–0.16
	DFT	–0.46	–0.90	–0.58	–1.46
IIf	MP2	6.28	5.35	5.94	4.04
	DFT	4.37	3.44	3.97	2.22
IIg	MP2	1.72	1.46	1.80	0.76
	DFT	0.76	0.33	0.72	–0.59
IIh	MP2	3.84	3.27	3.72	2.06
	DFT	2.45	1.91	2.33	0.61
IIi	MP2	0.47	0.06	0.40	–0.56
	DFT	–0.82	–1.02	–0.78	–1.42
IIj	MP2	7.68	6.76	7.31	5.28
	DFT	5.25	4.45	4.93	3.12
IIk	MP2	0.85	0.51	0.86	–0.31
	DFT	0.85	0.51	0.86	–0.31
IIl	MP2	6.36	5.49	6.08	3.67



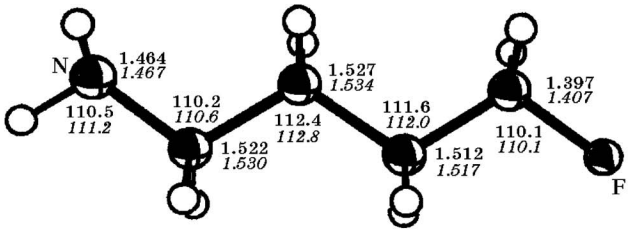
IIa, C_1



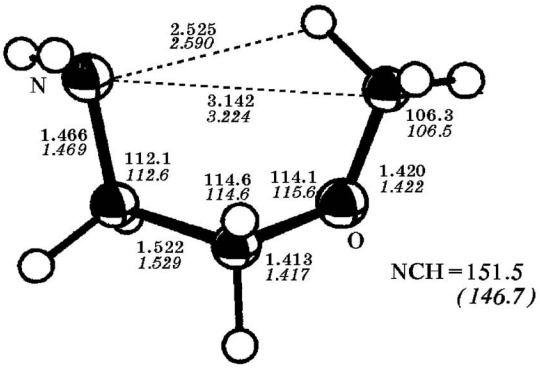
IIb, C_1



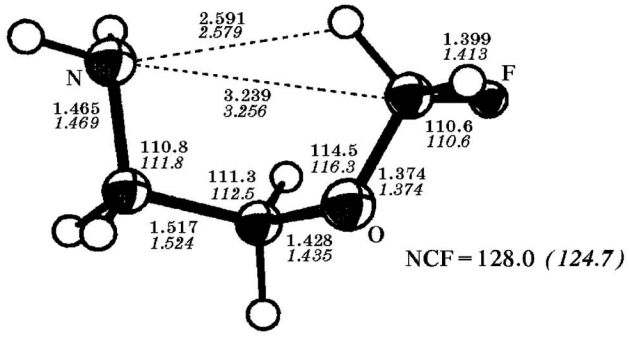
IIIa, C_1



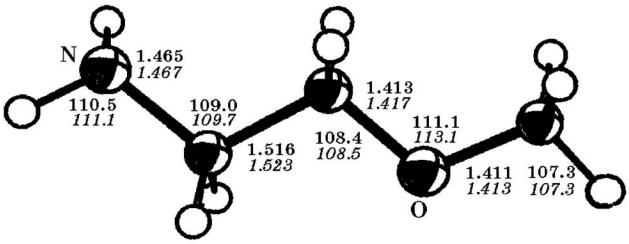
IIIb, C_1



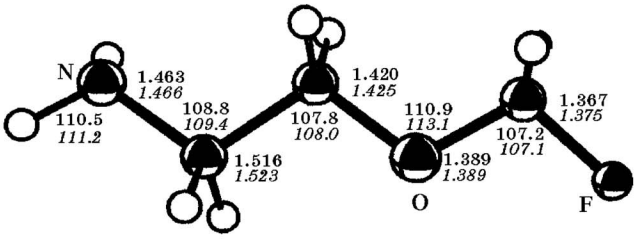
IIc, C_1



IId, C_1



IIIc, C_1



IIId, C_1

Fig. 1. Structures **II** and **III** (X = C) optimized by *ab initio* MP2(full)/6-311+G** (MP2) and density functional B3LYP/6-311+G** (DFT) methods. Bond lengths are given in Å, bond angles in degrees.

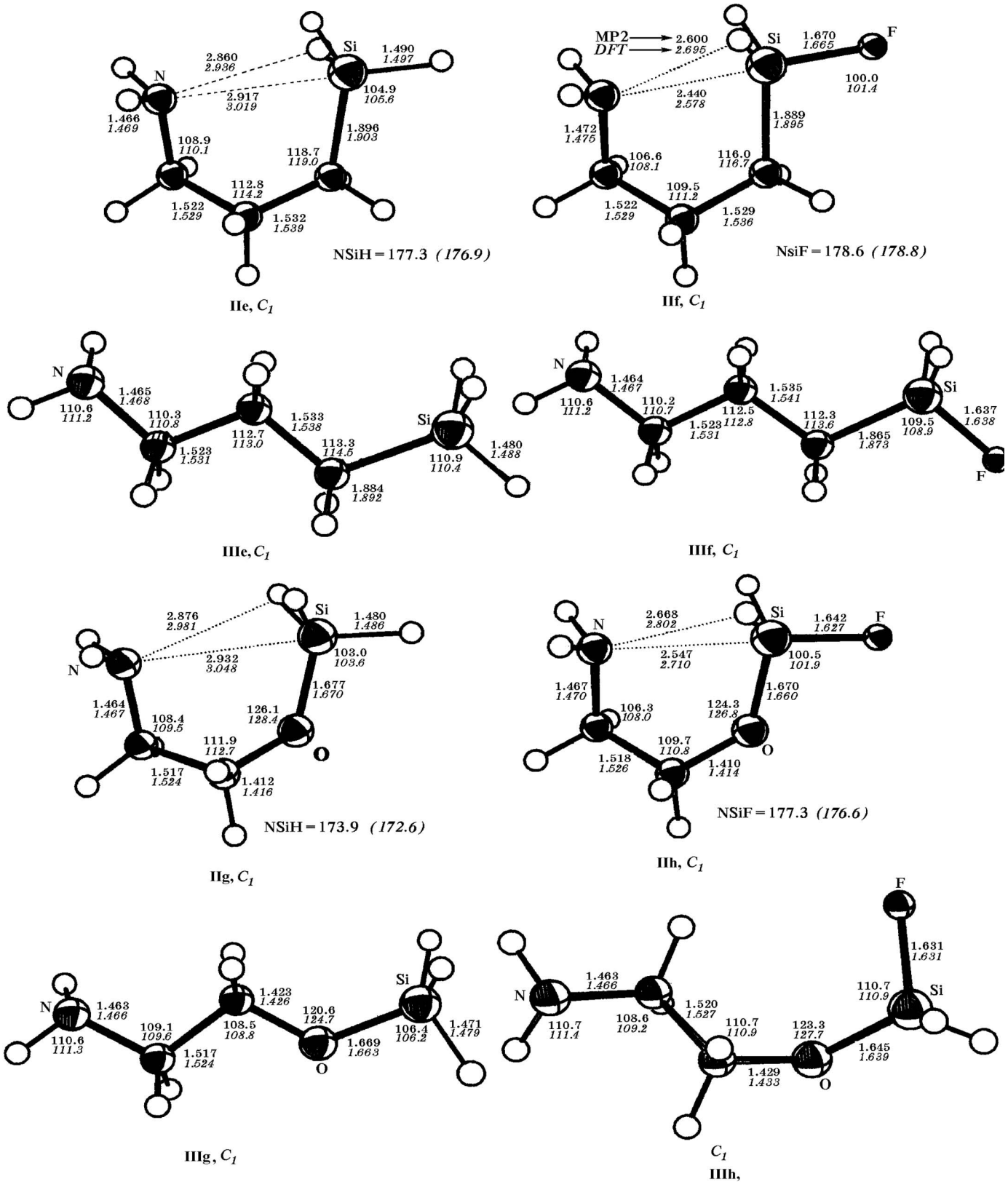


Fig. 2. Structures **II** and **III** (X = Si) optimized by *ab initio* MP2(full)/6-311+G** (MP2) and density functional B3LYP/6-311+G** (DFT) methods. Bond lengths are given in Å, bond angles in degrees.

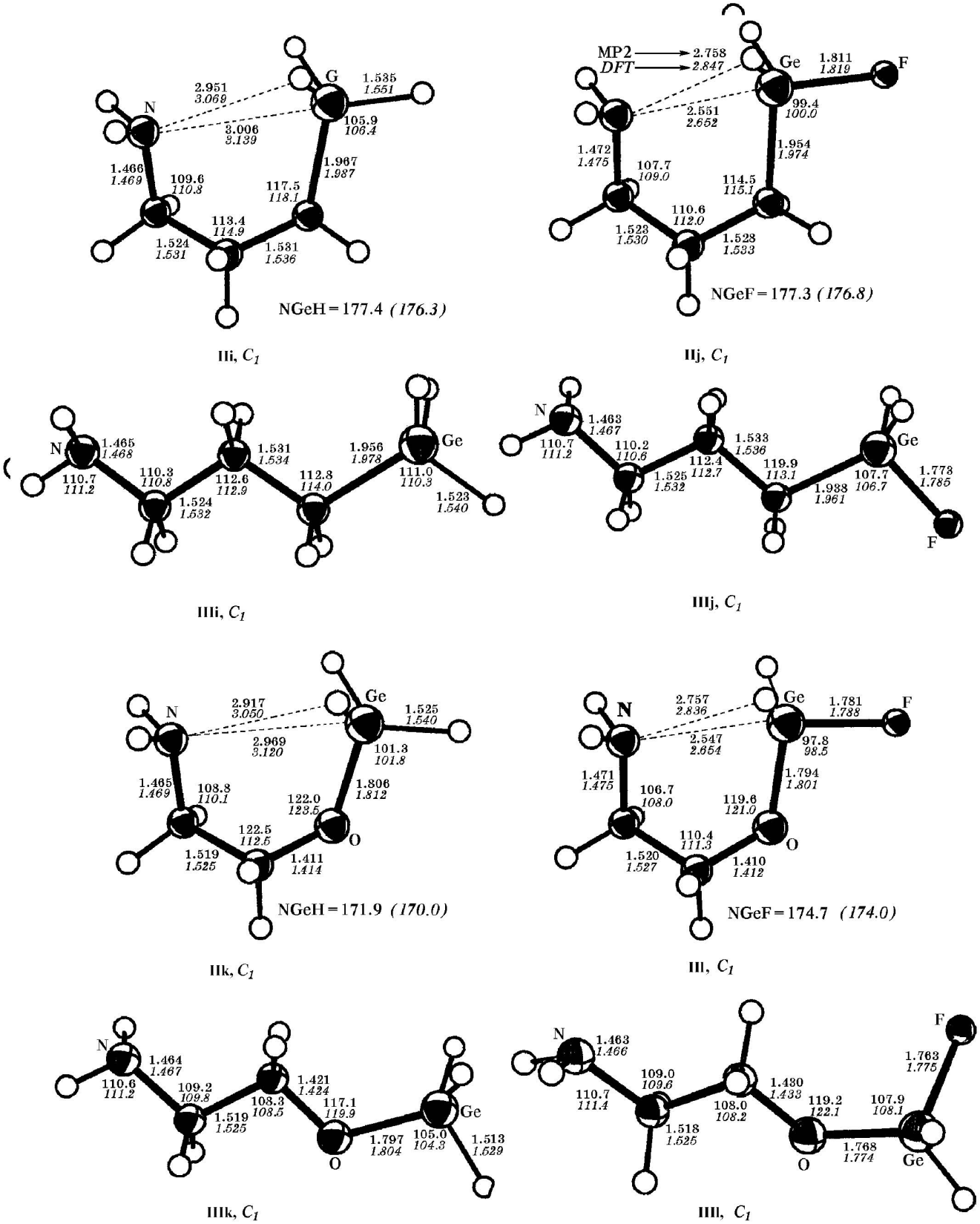


Fig. 3. Structures **II** and **III** (X = Ge) optimized by *ab initio* MP2(full)/6-311+G** (MP2) and density functional B3LYP/6-311+G** (DFT) methods. Bond lengths are given in Å, bond angles in degrees.

length of an ordinary Ge–N bond (~1.9 Å). Like in the case of silicon-containing structures **IIe**–**IIh** the length of the X···N contact is strongly affected by the character of the R substituent, and it decreases by ~0.4° at transition H→F. The bond angle NGeR for all systems **IIi–III** is close to linear and changes within the limits 170.0–177.3 deg. The data of Table 2 evidence that the monoquasicyclic molecules **IIj**–**III** are more stable than their open-chain isomers **IIIj**–**IIII.** At the same time according to the DFT calculations the **IIi** form is by ~0.8–1.4 kcal mol^{-1} energetically less stable than its isomer **IIIi.** However fom the MP2 calculations the destabilization of this structure by 0.56 kcal mol^{-1} follows only if the entropy factor is taken into account.Thus the energy of Ge···N interaction amounts to ~4–8 kcal mol^{-1}.

Covalency factor and Mulliken occupancy of the X–N contact. For comparison of nonvalent distance X–N with the corresponding standard covalent values we used a covalency factor χ [14] (Table 3)calculated by the formula

$$\chi = \frac{\sum R_i - d_{XN}}{\sum R_i - \sum r_i},$$

where ΣR_i is the sum of van der Waals radii of atoms X and N, Σr_i is the sum of their covalent radii, and d_{XN} is the calculated or experimentally determined distance between X and N.

Covalency factor χ in structures **IIa–d** (X = C) with various substituents R and Y lies in the range 0.07–0.14. In going to the silicon-containing structured **IIe–IIh** the covalency factor sharply grows to the value 0.29–0.58. The values of the covalency factor for germanium-containing systems **IIi**–**III** vary virtually within the same limits as those of the silicon-containing systems (from 0.27 to 0.55).

Hence basing on the calculated data it is possible to conclude that the interaction between the nitrogen center and the structural fragment X–R gets stronger at decreasing electronegativity of X and growing electronegativity of substituents R and Y.

Estimation of N···X(R) interaction by NBO analysis. The nature of the stabilizing interaction X···N originates from both the electrostatic interaction between X and N centers and by a strong orbital interaction: donation of the unshared electron pair of the nitrogen atom (n_N) to the unoccupied orbital σ^*_{NR} as seen from Table 3. The charge distribution shows a signigicant polarization of the X···N bond. In going from X = C to X = Si and further to X = Ge in compounds **II** a strong increase is observed in the energy of orbital interaction of the unshared electron pair of the nitrogen with the nonbonding orbital of the X–R fragment (Table 3). In the carbon-containing systems **IIa–IId** (X = C) no interaction was found between the orbitals n_N and σ^*_{NR}, and the energy of a hydrogen bond N···H–C [$E(n_N \rightarrow \sigma^*_{CH})$] is also insignificant (<1 kcal mol^{-1}).

Energy of X···N interaction for X = Si varies from 2–3 (R = H) to 5–9 kcal mol^{-1} at R = F, and with X = this

Table 3. Covalency factor χ and data of NBO analysis: charges q on molecular centers X and N (Malliken charges given in parentheses), ΔE as the difference between the energy levels of the orbitals n_N and σ^*_{XR} (a.u.) of molecule **II**, energy of the donor-acceptor interaction $E(n_N \rightarrow \sigma^*_{XR})$ (kcal mol^{-1}), and distance between centers X···N in structures **II** (l_{XN}, Å) and in the correspondinf atranes I (l^*_{XN}, Å) [17], method B3LYP/6-311+G**

Structure	χ	q_X	q_N	ΔE	l_{XN}	l^*_{XN}	$E(n_N \rightarrow \sigma^*_{XR})$
IIa	0.08	–0.56 (–0.551)	–0.851 (–0.433)	0.73198	3.241	3.160	-
IIb	0.14	0.09 (–0.281)	–0.852 (–0.461)	0.55070	3.128	3.103	0.69
IIc	0.09	–0.190 (–0.279)	–0.851 (–0.447)	0.73193	3.224	3.092	-
IId	0.07	0.381 (–0.032)	–0.855 (–0.477)	0.53423	3.256	3.032	-
IIe	0.31	0.891 (0.691)	–0.855 (–0.461)	0.55307	3.019	2.716	3.04
IIf	0.58	1.448 (0.871)	–0.846 (–0.509)	0.55710	2.578	2.473	9.16
IIg	0.29	1.198 (0.772)	–0.854 (–0.489)	0.55337	3.048	2.437	2.08
IIh	0.50	1.700 (0.938)	–0.862 (–0.538)	0.56649	2.710	2.317	5.19
IIi	0.26	0.716 (0.590)	–0.862 (–0.467)	0.50435	3.139	2.625	2.82
IIj	0.55	1.283 (0.894)	–0.845 (–0.518)	0.46063	2.652	2.453	10.79
IIk	0.27	1.018 (0.763)	–0.845 (–0.490)	0.50014	3.120	2.563	2.30
III	0.55	1.519 (1.071)	–0.864 (–0.556)	0.47280	2.654	2.427	8.92

energy grows from 2.3 (R = H) to 10.8 kcal mol^{-1} at R = F. The energy of the orbital interaction $n_N \rightarrow \sigma^*_{XR}$ changes in parallel with the relative stabilization of structure **II**.

Thus the results of the above calculations show the strong dependence of the distance X···N in the saturated quasimonocyclic systems **II** on the electropositivity of the atomic center X and on the electronegativity of the substituent R with relatively weak sensitivity to substituents Y. The nature of the interaction is governed mainly by the donor-acceptor interaction of the unshared electron pair of nitrogen with the nonbonding orbital of the X–R fragment. The lower limit of the energy of the X···N contact for systems II with X = Si, Ge is in the range ~3–8 kcal mol^{-1}, and with X = C this energy does not exceed 1 kcal mol^{-1}.

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