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I.P. Beletskaya on Her Jubilee

Hypervalent Intramolecular X←N (X = C, Si, Ge) Coordination in Atranes: Quantum-Chemical Study

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Abstract—The structure and pentacoordination effect in atranes containig Group IVa element were studied *ab initio* [MP2(full)/6-31G**] and in terms of the density functional theory [B3LYP/6-311+G**]. Stabilization of these compounds is determined mainly by the secondary hypervalent (R)X←N bond (X = C, Si, Ge), whose strength increases in the series X = C, Si, Ge. Attractive (R)X←N interaction originates from donation of unshared electron pair on the nitrogen atom to the antibonding σ^*_{XR} orbital.

Silatranes **I** are characterized by unusual attractive intramolecular Si···N interaction. They were synthesized for the first time in 1961 (Y = O [1]) and were the first representatives of a new large class of compounds, atranes [2].


I
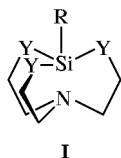
Y = CH$_2$, NR, O; R = Alk, Ar, OR, SR, NR$_2$, SiR$_3$, PR$_2$, H, F, Cl.

The energy of strong attractive Si···N interaction was experimentally estimated at 13–22 kcal/mol [3]; this interaction leads to a sharp shortening of the distance between the corresponding centers (which are not linked through a covalent bond) to 2.05–2.25 Å (X-ray diffraction data [3–5]) or 2.324–2.45 Å (microwave spectroscopy [6–7]). These distances are considerably shorter than the sum of van der Waals radii of the silicon and nitrogen atoms (3.5 A). Replacement of the silicon atom in structure **I** by germanium increases the X···N distance by 0.05 to 0.10 Å [8–11]. The results of experimental studies [3–11] showed that the strength of the X···N (X = Si, Ge) interaction depends on the nature of both equatorial (Y) and axial (R) substituents. The existence of

such interaction leads to appearance of some unusual physical, chemical, and biological properties (see, e.g., [11, 12]).

Early theoretical studies of the electronic structure of silatranes were performed mainly by semiempirical methods or *ab initio* without geometry optimization [13]. The results of *ab initio* calculations with full geometry optimization [13, 14] showed that the Si−N distance strongly depends on the nature of equatorial group Y and that the effect of the R substituent is weaker. Up to now, germatranes **II** (X = Ge, Y = O) with saturated bridging bonds were examined only by the MNDO semiempirical method [15]. These studies revealed that trends in structural variations of germatranes, depending on the substituent nature, are analogous to those observed for the silatrane systems. Until present, no systematic *ab initio* studies were

IIa–IIl
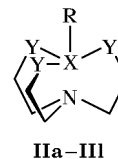
X = C, Y = CH$_2$, R = H (**a**); X = C, Y = CH$_2$, R = F (**b**); X = C, Y = O, R = H (**c**); X = C, Y = O, R = F (**d**); X = Si, Y = CH$_2$, R = H (**e**); X = Si, Y = CH$_2$, R = F (**f**); X = Si, Y = O, R = H (**g**); X = Si, Y = O, R = F (**h**); X = Ge, Y = CH$_2$, R = H (**i**); X = Ge, Y = CH$_2$, R = F (**j**); X = Ge, Y = O, R = H (**k**); X = Ge, Y = O, R = F (**l**).

performed at a sufficiently high level in the frame-work of a single calculation scheme.

In this work, we examined the electronic and steric structure of atranes **II** (X = C, Si, Ge) and the effect of substituents R and Y on the parameters of intra-molecular X···N contact in terms of *ab initio* [MP2(full)/6-31G**] approach and density functional theory [B3LYP/6-311+G**].

Calculation procedure. The calculations in terms of the density functional theory (B3LYP/6-311+G**, DFT) and *ab initio* (MP2(full)/6-31G**, MP2) were performed with the use of Gaussian 98 [16] and GAMESS software packages [17]. Geometric param-eters in stationary points were optimized in the "tight" mode (Gaussian 98) and up to 10^{-5} a.u. for gradients and RMS gradients (GAMESS). The calculated geo-

metric configurations of the systems under study were assigned to stationary points on the potential energy surface (PES) on the basis of calculated harmonic frequencies. According to the recommendations given in [18], basis set superposition error (BSSE) was not taken into account. Analysis of molecular orbitals was performed in terms of the natural bond orbital (NBO) method using B3LYP procedure with the 6-311G** basis set; calculations with the 6-311+G** basis set with account taken of diffuse functions gave unrealistic charge distribution on atoms. The calcu-lated structures were plotted with the aid of PC MODEL software package [20].

Carbatranes II (X = C). According to the calcula-tion results, the structures of carbatranes **IIa–IId** and isomeric structures **IIIa** and **IIIb** correspond to
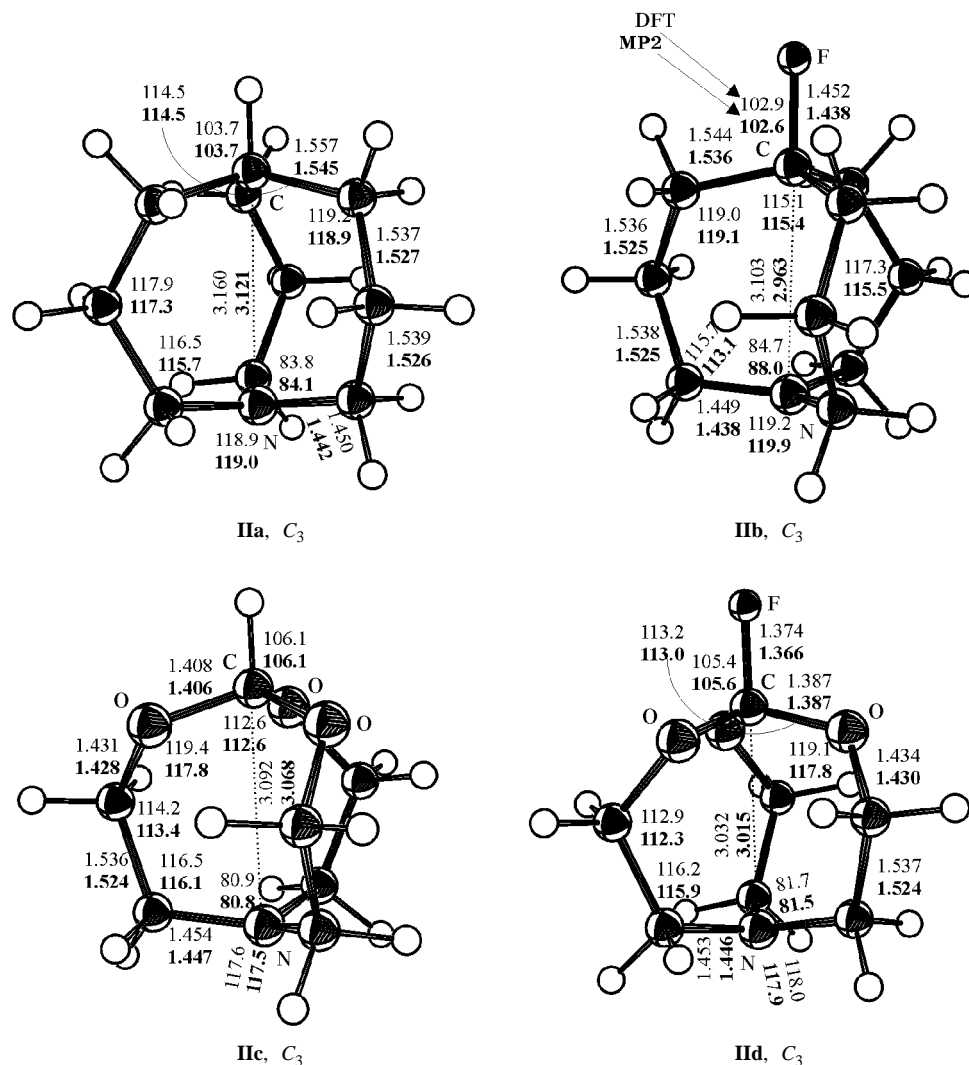

Fig. 1. Geometric parameters of carbatranes **II** (X = C), calculated *ab initio* MP2(full)/6-31G** (MP2, boldface numbers) and by the B3LYP/6-311+G** method (DFT); bond lengths are given in angstroems, and bond angles, in degrees.
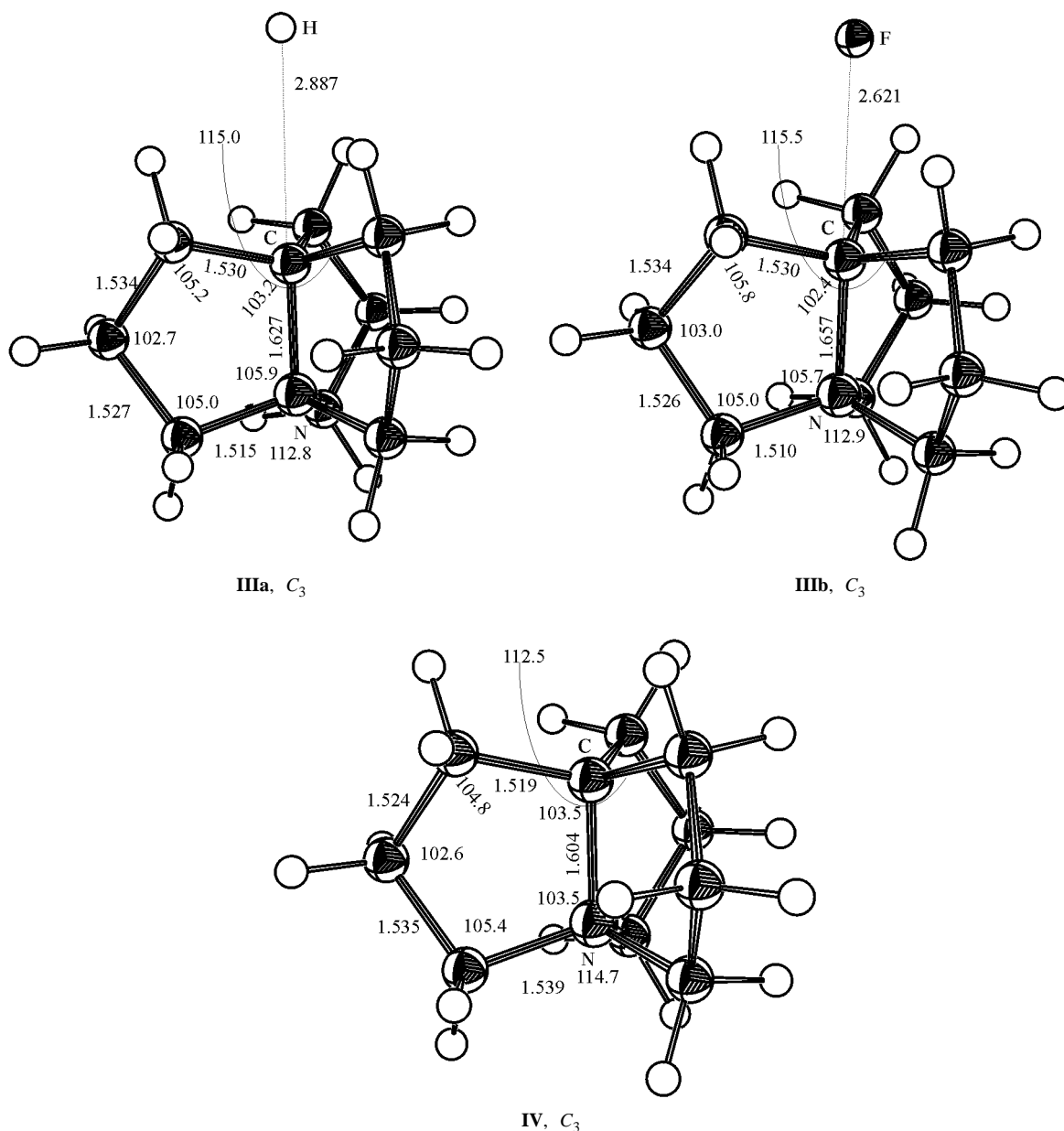
Fig. 2. Geometric parameters of structures **IIIa**, **IIIb**, and **IV** (X = C), calculated by the B3LYP/6-311+G** DFT method; bond lengths are given in angstroems, and bond angles, in degrees.

minima on the respective potential energy surfaces. Their energies and geometric parameters are given in Table 1 and Figs. 1 and 2.

The calculated distance between the nitrogen and carbon atoms in structures **II** ranges from 3.028 to 3.146 Å (DFT) or from 2.963 to 3.121 Å (MP2); these values are smaller by only ~0.2 Å than the sum of the corresponding van der Waals radii (3.39 Å) [21]. Hence there is no attractive interaction between the nitrogen and carbon atoms, while a strong deviation (by about 6–9°) of the bond angles at the carbon

atoms from the tetrahedral value and reduced angle of valence bond pyramidalization at the nitrogen atom in structures **IIa–IId** (relative to the ammonia molecule: 2–7° and ~39°, respectively) indicate even some repulsion between the X and N atoms. The C···N distance slightly shortens in going from **IIa** to **IIb** and from **IIc** to **IId**. This means that the substituents Y and R insignificantly affect the length of the C···N contact. Isomeric structures **IIIa** and **IIIb**, which are in fact tight ion pairs with a long nonvalence distance between the R⁻ ion and carbon center of carbatrane

Table 1. Total energies (E_{tot}), zero-point harmonic vibration energies (ZPE), and least harmonic frequencies (ω) of model structures **IIa–IIl**, **IIIa**, **IIIb**, and **IV**, calculated *ab initio* MP2(full)/6-31G** (MP2) and by the B3LYP/6-311+G** method (DFT)

Compound no.	Method	E_{tot}, a.u.	ZPE, a.u.	ω, cm^{-1}
IIa	MP2	–445.849533	0.289657	159
	DFT	–447.354756	0.280397	161
IIb	MP2	–544.875087	0.280700	93
	DFT	–546.635493	0.271862	162
IIc	MP2	–553.388560	0.215786	179
	DFT	–555.103501	0.208740	163
IId	MP2	–652.424140	0.207250	172
	DFT	–654.388103	0.199997	155
IIe	MP2	–696.894999	0.278447	110
	DFT	–698.794710	0.269149	92
IIf	MP2	–796.005986	0.273198	114
	DFT	–798.147523	0.264010	95
IIg	MP2	–804.559460	0.208632	78
	DFT	–806.656106	0.200927	90
IIh	MP2	–903.663544	0.202836	86
	DFT	–906.001744	0.195543	87
IIi	MP2	–2481.358046	0.277045	126
	DFT	–2486.272249	0.267401	102
IIj	MP2	–2580.457768	0.272061	133
	DFT	–2585.606254	0.262464	114
IIk	MP2	–2588.972992	0.205800	77
	DFT	–2594.081985	0.198170	96
IIl	MP2	–2688.063186	0.200441	101
	DFT	–2693.399990	0.192833	100
IIIa	DFT	–447.215080	0.272384	141
IIIb	DFT	–546.594442	0.271367	121
IV	DFT	–446.559886	0.271916	141

cation **IV**, are less stable than the corresponding structures **IIa** and **IIb** by 87.23 and 25.76 kcal/mol, respectively, for R = H and R = F. Molecules **IIIa** and **IIIb** are characterized by a strong charge separation between the R substituent and structure **IV**. The charge on the hydrogen atom (R = H) in **IIIa** is –0.444 a.u., and that on the fluorine atom (R = F) in **IIIb** is –0.728 a.u. It should be noted that the energies of formation of complexes **IIIa** and **IIIb** from cation **IV** and anion R⁻ are very similar, 91.19 (**IIIa**, R = H) and 91.53 kcal/mol (**IIIb**, R = F).

Silatranes II (X = Si). Structures of silatrane molecules **IIe–IIh** (X = Si) correspond to energy minima on the PES; their geometric and energy parameters are presented in Table 1 and Fig. 3. No structures like **III** (tight ion pairs) were found in the silatrane series. As is seen from Fig. 3, the X⋯N center-to-center distance considerably shortens in going from carbatranes to silatranes: to 2.439–2.639 Å

(DFT) or 2.275–2.276 Å (MP2). These values are much smaller than the sum of van der Waals radii of the silicon and nitrogen atoms (3.50 Å), and they approach the length of ordinary Si–N bond, ~1.8–1.9 Å. The calculated geometric parameters of structures **IIe–IIh** (X = Si) are well consistent with the data of gase-phase microwave measurement. For example, the experimental Si–N distance is 2.45 Å in methylsilatrane (Y = O) [6] and 2.324 Å in fluorosilatrane (Y = O) [7]. The calculated length of the Si⋯N contact is fairly similar to those found by the X-ray diffraction method: 2.146 Å for H-silatrane, 2.042 Å for fluorosilatrane, and 2.175 Å for methylsilatrane [4]. The data given in Fig. 3 and Table 2 indicate that the X⋯N distance shortens in going from **IIe** to **IIf** and from **IIg** to **IIh**. Simultaneously, the angle of valence bond pyramidalization at the nitrogen atom (8–17°) decreases, as compared to ammonia molecule (~39°).
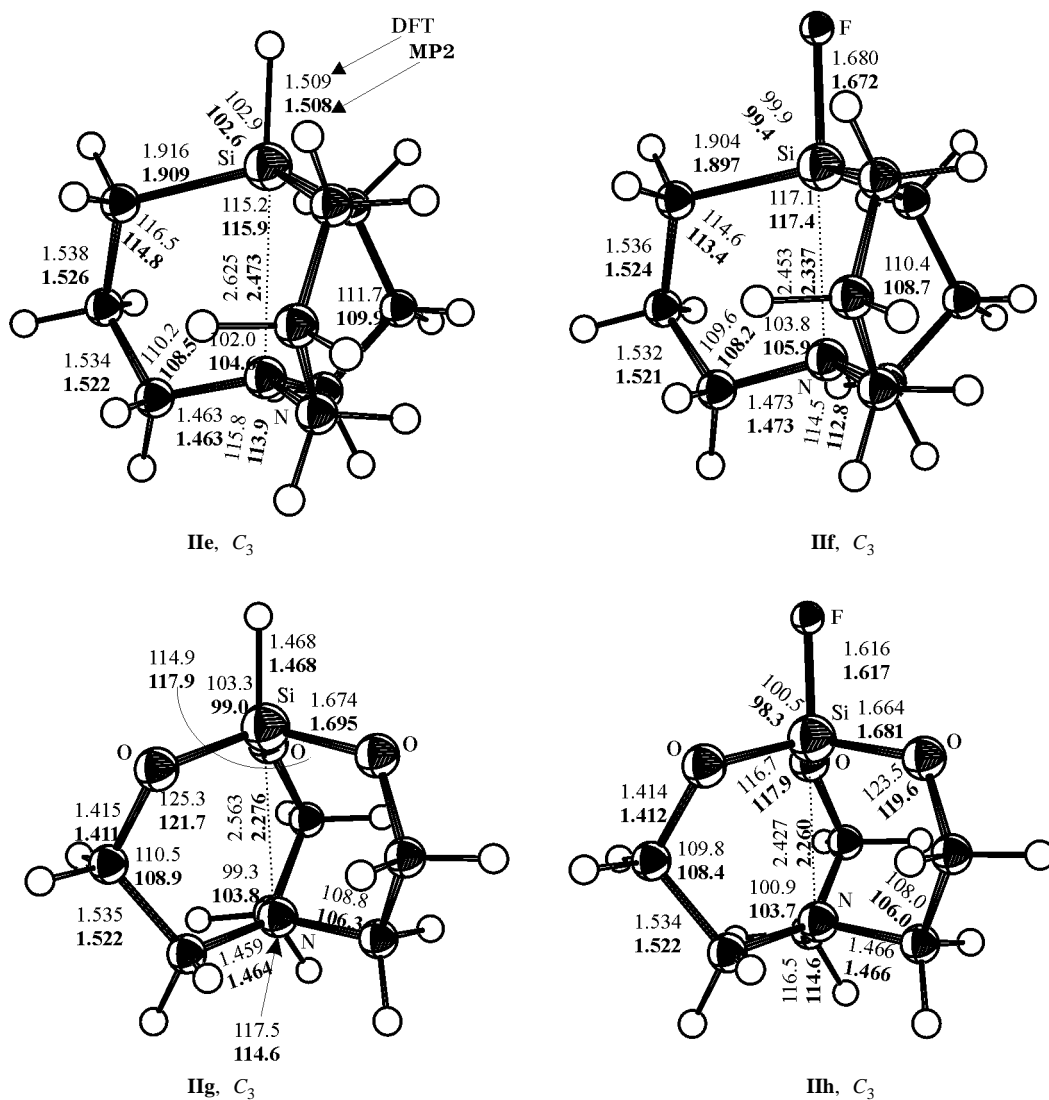
Fig. 3. Geometric parameters of silatranes **II** (X = Si), calculated *ab initio* MP2(full)/6-31G** (MP2, boldface numbers) and by the B3LYP/6-311+G** method (DFT); bond lengths are given in angstroems, and bond angles, in degrees.

Germatranes II (X = Ge). Like carba- and sila-trane molecules, the calculated germatrane structures **IIi–IIl** (X = Ge) correspond to energy minima on the PES. Their geometric and energy parameters are given in Table 1 and Fig. 4.

Replacement of the silicon atom by germanium is accompanied by further shortening of the X···N dist-ance: to 2.328–2.711 Å (DFT) and 2.239–2.540 Å (MP2). These distances are close to the length of an ordinary Ge–N bond (~1.9 Å). Unlike silatranes, the X···N distance in germatranes is more sensitive to the nature of substituents R and Y. Depending on the substituent, the X···N distance in germatranes changes by ~0.2 Å against ~0.1 Å in silatranes. In addition, germatrane systems **II** (X = Ge) are charac-

terized by a stronger dependence of the X···N distance on the nature of the R substituent. According to the calculations, the angle of bond pyramidalization at the nitrogen atom almost does not change in going from silatranes to germatranes: it ranges from ~11 to 16 deg. The calculated Ge···N contact is about 0.10–0.15 Å longer than those found experimentally by the X-ray diffraction method for *tert*-butylgermatrane (Y = O, 2.238 Å [8]) and fluorogermatrane (2.104 Å [9]). By analogy with the silatrane systems, for which the X···N distance is overestimated by DFT calcula-tions and underestimated by MP2 calculations (rela-tive to the data obtained by microwave spectroscopy), a similar pattern could be expected for germatranes. Thus the results of DFT and MP2 calculations can be
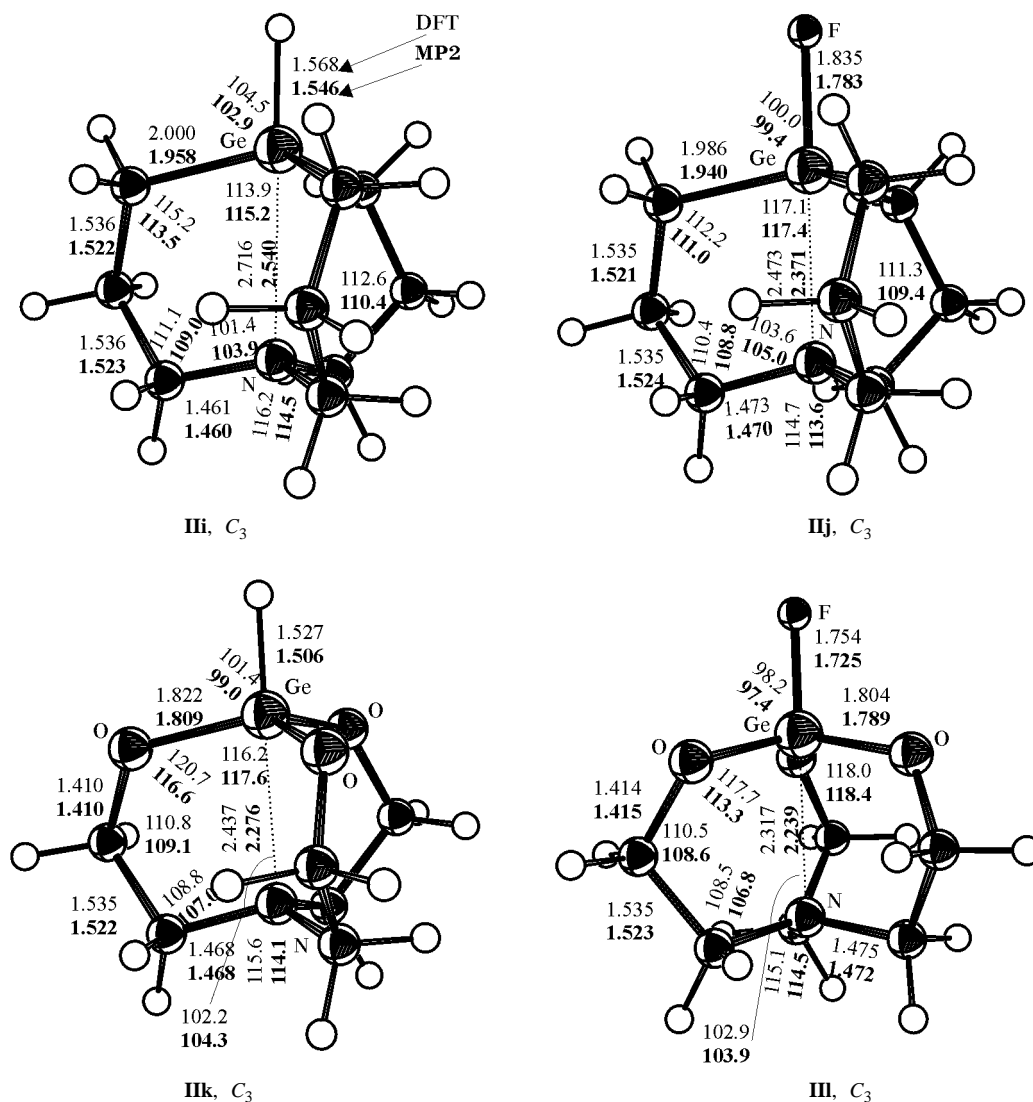
Fig. 4. Geometric parameters of germatranes **II** (X = Ge), calculated *ab initio* MP2(full)/6-31G** (MP2, boldface numbers) and by the B3LYP/6-311+G** method (DFT); bond lengths are given in angstroems, and bond angles, in degrees.

Covalence factor and Mulliken population of the X···N contact. In order to compare the nonvalence X···N distance with the corresponding standard covalent bond lengths, we used covalence factor χ [19] (Table 2) which is calculated by the following formula:

$$\chi = \frac{\Sigma R_i - d_{XN}}{\Sigma R_i - \Sigma r_i}.$$

Here, ΣR_i is the sum of van der Waals radii of the X and N atoms, Σr_i is the sum of their covalent radii, and d_{XN} is the calculated or experimental distance between the X and N atoms. Depending on the substituent (R or Y), the covalence factor χ in carbatranes changes weakly, within the range 0.12–0.19. Likewise, the Mulliken polulation of the X···N contact varies from 0.021 to 0.031. In going from carbatranes to their silicon-containing analogs **IIe–IIh**, the covalence factor sharply increases and attains the range 0.54–0.66; correspondingly, the Mulliken population of the Si···N contact changes from 0.087 to 0.118. Germatrane systems **IIi–Ill** are characterized by a wider range of variation of the covalence factor, from 0.51 to 0.75, while the Mulliken population of the Ge···N contact varies from 0.076 to 0.148.

Thus the results of calculations predict enhancement of the interaction between the nitrogen atom and

Table 2. Calculated covalence factors χ (B3LYP/6-311+G**) and Mulliken populations of the X···N contact and results of NBO analysis (B3LYP/6-311G**): charges q on the molecular centers X and N (Mulliken charges are given in parentheses), X–N center-to-center distances l_{XN} (Å), differences ΔE between the n_N and σ^*_{XR} energy levels, and energies of donor–acceptor interactions $n_N \rightarrow \sigma^*_{XR}$

Compound no.	χ	Pop$_{XN}$	q_X	q_N	l_{XN}, Å	ΔE, a.u.	$n_N \rightarrow \sigma^*_{XR}$, kcal/mol
IIa	0.12	0.021	–0.197 (–0.050)	–0.542 (–0.402)	3.146	0.64432	–
IIb	0.15	0.031	0.436 (0.404)	–0.544 (–0.408)	3.085	0.42071	0.68
IIc	0.16	0.023	0.746 (0.524)	–0.535 (–0.392)	3.082	0.65862	–
IId	0.19	0.026	1.218 (0.652)	–0.535 (–0.402)	3.028	0.48658	–
IIe	0.54	0.087	1.394 (0.794)	–0.570 (–0.476)	2.629	0.55399	4.68
IIf	0.65	0.133	1.883 (1.246)	–0.578 (–0.505)	2.469	0.55891	8.90
IIg	0.59	0.095	1.998 (1.075)	–0.574 (–0.523)	2.550	0.59168	3.29
IIh	0.66	0.118	2.366 (1.416)	–0.583 (–0.542)	2.439	0.62475	6.66
IIi	0.51	0.076	1.206 (0.690)	–0.561 (–0.465)	2.711	0.49063	4.72
IIj	0.66	0.131	1.687 (1.106)	–0.570 (–0.501)	2.487	0.46310	12.65
IIk	0.68	0.126	1.808 (1.084)	–0.562 (–0.510)	2.435	–[a]	–[b]
IIl	0.75	0.148	2.205 (1.433)	–0.586 (–0.525)	2.328	–[a]	10.34[c]

[a] There is no unshared electron pair on the nitrogen atom.

[b] Five-coordinate germanium atom; UEP on the nitrogen atom is lacking.

[c] Energy of the $n_F \rightarrow \sigma^*_{XR}$ interaction.

X–R moiety as the electronegativity of X decreases and the electronegativity of R and Y increases.

NBO analysis. The stabilizing effect of X···N interaction is determined by both electrostatic interaction between the X and N centers and strong orbital interaction between unshared electron pair on the nitrogen and vacant σ^*_{XR} orbital.

As follows from the Mulliken and NBO charge distributions given in Table 2, the X···N bond is essentially polarized: the X and N atoms possess opposite charges. The charge of X = C in carbatrane molecules **IIa–IId** changes from –0.197 to 0.436–1.218 a.u., and the charge on the nitrogen atom ranges from –0.544 to –0.535 a.u. In silatrane molecules **IIe–IIh**, the charges on the X = Si and N atoms vary within the ranges 1.394–2.366 and –0.583 to –0.570 a.u., respectively. The corresponding ranges of charge variation in germatrane molecules **IIi–IIl** are 1.206–2.205 and –0.586 to –0.561 a.u.

It is known that the energy of orbital interaction is determined by both their overlap and energy difference. The overlap depends in turn on the distance between the fragments where the orbitals are localized. Table 2 contains the lengths of the X···N contacts, energy differences between the nitrogen UEP (n_N) and nonbonding orbital of the X–R fragment (σ^*_{XR}), and energies of their interaction. It is seen that the energy of intramolecular interaction between n_N and

σ^*_{XR} increases in going from X = C to X = Si and then to X = Ge. The energy of the $n_N \rightarrow \sigma^*_{XR}$ interaction in carbatranes is insignificant (~1 kcal/mol), which is consistent with long N···C distances in carbatranes. In going to silatranes and germatranes, the energy of attractive $n_N \rightarrow \sigma^*_{XR}$ interaction sharply increases: from 3–4 (X = Si, R = H) to 6–9 kcal/mol (R = F) and from 4.72 (X = Ge, Y = CH$_2$, R = H) to 12.65 kcal/mol (R = F). Replacement of Y = CH$_2$ by Y = O in germatranes enhances the X–N interaction so strongly that NBO analysis shows the existence of X–N bond while donor–acceptor interaction occurs between the R fragment and X–N bond. Insofar as hydrogen atom has no unshared electron pair, the $n_R \rightarrow \sigma^*_{XN}$ interaction is possible only for R = F. The energy of this interaction is estimated at 10.34 kcal/mol.

Thus the results of our calculations show a strong dependence of the X···N distance in atranes on the nature of the X atom and a relatively weak dependence of the same parameter on the nature of substituents R and Y. The X···N interaction is contributed mainly by donor–acceptor interaction between unshared electron pair on the nitrogen atom and nonbonding σ^*_{XR} orbital of the X–R fragment.

REFERENCES

1. Frye, C.L., Vogel, G.E., and Hall, J.A., *J. Am. Chem. Soc.,* 1961, vol. 83, p. 996; Voronkov, M.G., *Pure Appl. Chem.,* 1966, vol. 13, p. 35.

2. Verkade, J.G., *Coord. Chem. Rev.,* 1994, vol. 137, p. 233; Alder, R.W. and Read, D., *Coord. Chem Rev.,* 1998, vol. 176, p. 113.

3. Voronkov, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1991, p. 2664.

4. Greenberg, A. and Wu, G., *Struct. Chem.,* 1990, vol. 1, p. 79; Hencsei, P., *Struct. Chem.,* 1991, vol. 2, p. 21.

5. Voronkov, M.G., Barishok, V.P., Petukhov, L.P., Rahklin, R.G., and Pestunovich, V.A., *J. Organomet. Chem.,* 1988, vol. 358, p. 39; Lukevics, E., Dimens, V., Pokrovska, N., Zicmane, I., Popelis, J., and Kemme, A., *J. Organomet. Chem.,* 1999, vol. 586, p. 200; Corriu, R.J.P., *J. Organomet. Chem.,* 1990, vol. 400, p. 81.

6. Shen, Q. and Hilderbrandt, R.L., *J. Mol. Struct.,* 1980, vol. 64, p. 257.

7. Forgacs, G., Kolonits, M., and Hargittai, I., *Struct. Chem.,* 1990, vol. 1, p. 245.

8. Gurkova, S.N., Gusev, A.I., Alekseev, N.V., Segel'-man, I.R., Gar, T.K., and Khromova, N.Yu., *Zh. Strukt. Khim.,* 1983, vol. 24, p. 162.

9. Eujen, R., Petrauskas, E., Roth, A., and Brauer, D.J., *J. Organomet. Chem.,* 2000, vol. 613, p. 86.

10. Lukevics, E., Ignatovich, L., and Beliakov, S., *J. Organomet. Chem.,* 1999, vol. 588, p. 222; Livant, P., Northcott, J., and Webb, T.R., *J. Organomet. Chem.,* 2001, vol. 620, p. 133; Karlov, S.S., Shutov, P.L., Churakov, A.V., Lorberth, J., and Zaitseva, G.S., *J. Organomet. Chem.,* 2001, vol. 627, p. 1.

11. Lukevits, E. and Ignatovich, L.M., *Khim. Geterotsikl. Soedin.,* 1992, p. 725.

12. Satge, J., Rima, G., Fatome, M., Sentenae-Roumanor, H., and Lion, C., *Eur. J. Med. Chem. Chim. Ther.,* 1989, vol. 24, p. 48.

13. Schmidt, M.W., Wundus, T.L., and Gordon, M.S., *J. Am. Chem. Soc.,* 1995, vol. 117, p. 7480 (see also references therein to semiempirical calculations and earlier *ab initio* calculations).

14. Csonka, G.I. and Hencsei, P., *J. Comput. Chem.,* 1994, vol. 15, p. 385; Csonka, G.I. and Hencsei, P., *J. Mol. Struct. (THEOCHEM),* 1996, vol. 362, p. 199.

15. Beliakov, S., Ignatovich, L., and Lukevics, E., *J. Organomet. Chem.,* 1999, vol. 577, p. 205.

16. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Jr., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98, Revision A.9,* Pittsburgh, PA: Gaussian, 1998.

17. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem.,* 1993, vol. 14, p. 1347.

18. Cammi, R., Bonaccorsi, R., and Tomasi, J., *Theor. Chim. Acta.,* 1985, vol. 68, p. 271; Cook, D.B., Sordo, T.L., and Sordo, J.A., *J. Chem. Soc., Chem. Commun.,* 1990, p. 185.

19. Reed, A.E., Curtiss, L.A., and Weinhold, F., *Chem. Rev.,* 1988, vol. 88, p. 899.

20. *PC MODEL,* Bloomington, IN: Selena Software, 1987.

21. Emsley, J., *The Elements,* Oxford: Clarendon, 1989, Translated under the title *Elementy,* Moscow: Mir, 1993, p. 256.