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Structure and Stability of the Mixed Polymolecular Complexes of Nitrogen and Carbon Nonooxide: A Quantum Chemical Study

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Abstract—The structure and stability of heteromolecular van der Waals clusters $(N_2)_nCO_m$ (n = 1–7; m = 1–3) was studied using ab initio MP2(full)/6-311+G* and CCSD(full)/6-311+G* methods. For clusters with $(n + m) > 3$ the polyhedron structures are the most preferable, whose stability increases with the number of interacting molecules. Incorporation of CO molecules results in weakening of binding in the cluster and lowering the stereochemical rigidity relative to homomolecular systems. Increase of percentage of CO is followed by a decrease of stability of the clusters.

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In recent years, the van der Waals complexes formed by weak long-range intermolecular forces that were on the verge of stable assemblies attracted an enhanced attention of both experimentalists and theoreticians [1–3]. Revealing of the principles of organization of such systems, which are intermediate between the molecular and condensed state of the substance, opens prospects for deeper understanding the structure of condensed state of substance and creation of general theory of nonvalent interactions [1–3]. The formation of homo- and heteromolecular clusters was detected for various inert molecules like N_2, CO, noble gases [1, 4–12]: nowadays they are intensively studied using both experimental and theoretical methods [13–22]. Detailed analysis of such systems is important for understanding of atmospheric processes and the control of environmental pollutions, investigation of characteristics of the gas plasma, dynamic gas streams and molecular lasers [23–25].

As was shown in our previous quantum chemical studies of polymolecular clusters of nitrogen [26], the most stable clusters are those in which the centers of mass of the molecules form regular polyhedron structures. The increase of the number of molecules is followed by enhancement of intermolecular interactions in the complexes and appearing of structural and energetic cooperative effects related to nonadditive enhancement of these interactions.

In the present work, the results of quantum chemical *ab initio* study of the electronic and spatial structure of heteromolecular complexes of nitrogen and carbon monooxide $(N_2)_nCO_m$ (n = 1–7; m = 1–3) are reported modeling the mixtures of gases of different composition. The goal of the study was to investigate the effect of replacement on the structure, stability and cooperative effect in mixed complexes as compared with the homogeneous systems, as well as analysis of the trends of variation of the main characteristics of clusters with the size of the cluster and the degree of replacement.

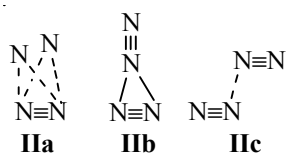
Calculation procedures. The calculations were performed by the nonempirical Hartree–Fock method (RHF) taking into account the correlation of valence and core electrons using the second order Møller−Plesset perturbation theory MP2(full) and the method of coupled clusters CCSD(full) in the valence-split basis set [27] 6-311+G* employing the Gaussian-03 program package [28]. The results obtained for low

molecular systems show that the results of the two methods are well consistent; therefore the calculations of complex systems were performed only at the MP2 level. All stationary points were identified by calculation of the force constant matrix. The superposition error BSSE was neglected in calculations of the formation energy of intermolecular complexes because of its debatable character and since we used rather extended basis set when the superposition error was negligibly small [29]. Graphical images of molecular structures shown in Figures were obtained using the Molden program [30] where as the input parameters the atomic Cartesian coordinates obtained after geometry optimization were used.

Dimeric systems. According to calculations, the mixed complex $N_2\cdots CO$ exists in the form of several close in energy conformers **Ia–If**, corresponding to the energy minima ($\lambda = 0$, hereinafter λ stands for the number of negative eigenvalues of the Hessian matrix) on the potential energy surface (PES). The structural and energy characteristics of systems **Ia–If** are shown in Fig. 1 and Table 1.

In the previously published theoretical [31] and experimental [10, 21, 32–34] works the two principal (T-shape) forms of complex $N_2\cdots CO$ were considered, in one of which the molecule of CO was oriented to the N≡N bond by the oxygen atom, and in the other, by the carbon atom. One more version of the T-shape structure is the orientation of the N_2 molecule to the CO bond [35]. Our calculations revealed six types of stable conformations of complex $N_2\cdots CO$: three forms **Ia–Ic** are characterized by the T-shape geometry, forms **Id** and **Ie** correspond to a skewed parallel configuration, and form **If** is characterized by linear structure.

Therefore, transition from the homomolecular system $N_2\cdots N_2$, where we have earlier found only three types of conformations **IIa–IIc** [26], to the isoelectronic heteromolecular system $N_2\cdots CO$ is followed by the increase in the number of possible structures. Unlike the dimer of nitrogen, for which the most stable conformation corresponds to the cross form **IIa**, for the mixed complex such a structure does not exist on the PES: its optimization results in relaxation of the system to form **Ia**.



IIa **IIb** **IIc**

The most stable forms of the mixed dimer $N_2\cdots CO$ correspond to structures **Ia** and **Id** stabilized by the N···O interactions between the most electronegative centers. Systems **Ib** and **Ie** characterized by the N···C interaction, as well as system **Ic** characterized by the three-centered interaction N···CO, are slightly (within 0.15 kcal mol^{-1}, Table 1) destabilized with respect to **Ia** and **Id**.

Unlike the dimer of nitrogen, which does not show any stabilizing interaction in the case of linear orientation of the molecules, we observed the linear form **If** for the mixed complex stabilized by the interaction of the nitrogen atom with the oxygen atom of the CO molecule. However, this form corresponds to the least stable isomer and is destabilized relative to **Ia** by 0.41 (MP2) or 0.35 (CCSD) kcal mol^{-1} (hereinafter all values of energy are given taking into account the ZPE correction).

N≡N----C=O
Ig, $C_{\infty v}$

Another linear form, **Ig**, characterized by the interaction of the nitrogen atom with the carbon atom of the CO molecule does not correspond a minimum on the PES.

According to the results of calculations, the stabilizing intermolecular contacts N···O(C) in all complexes **I** are substantially elongated with respect to the corresponding sums of the van der Waals radii. Complexes **Ia** and **Ib** formed due to the three-centered interactions are somewhat more stable than complexes **Id** and **Ie**, respectively, which are stabilized by the two-centered interactions. At the same time, in complexes **Id** and **Ie** the monomers are closer to each other than in the more stable systems **Ia** and **Ib**.

The energy of formation of the most stable complex **Ia** calculated as the difference between the total energy of the complex and the sum of the energies of the isolated monomers is 0.49 (MP2) or 0.37 (CCSD) kcal mol^{-1}; for other complexes the energy of formation is slightly lower (Table 1). The conclusion made on the maximal stability of the T–shape structure **Ia** is proved by the experimental data obtained from the microwave measurements [21]. According to our calculations, the distance between the centers of mass in the energetically most preferable isomer **Ia** is 3.847 Å at the MP2 level and 3.938 Å at the CCSD level, which is in good agreement with the IR spectroscopy data (4.025 Å).

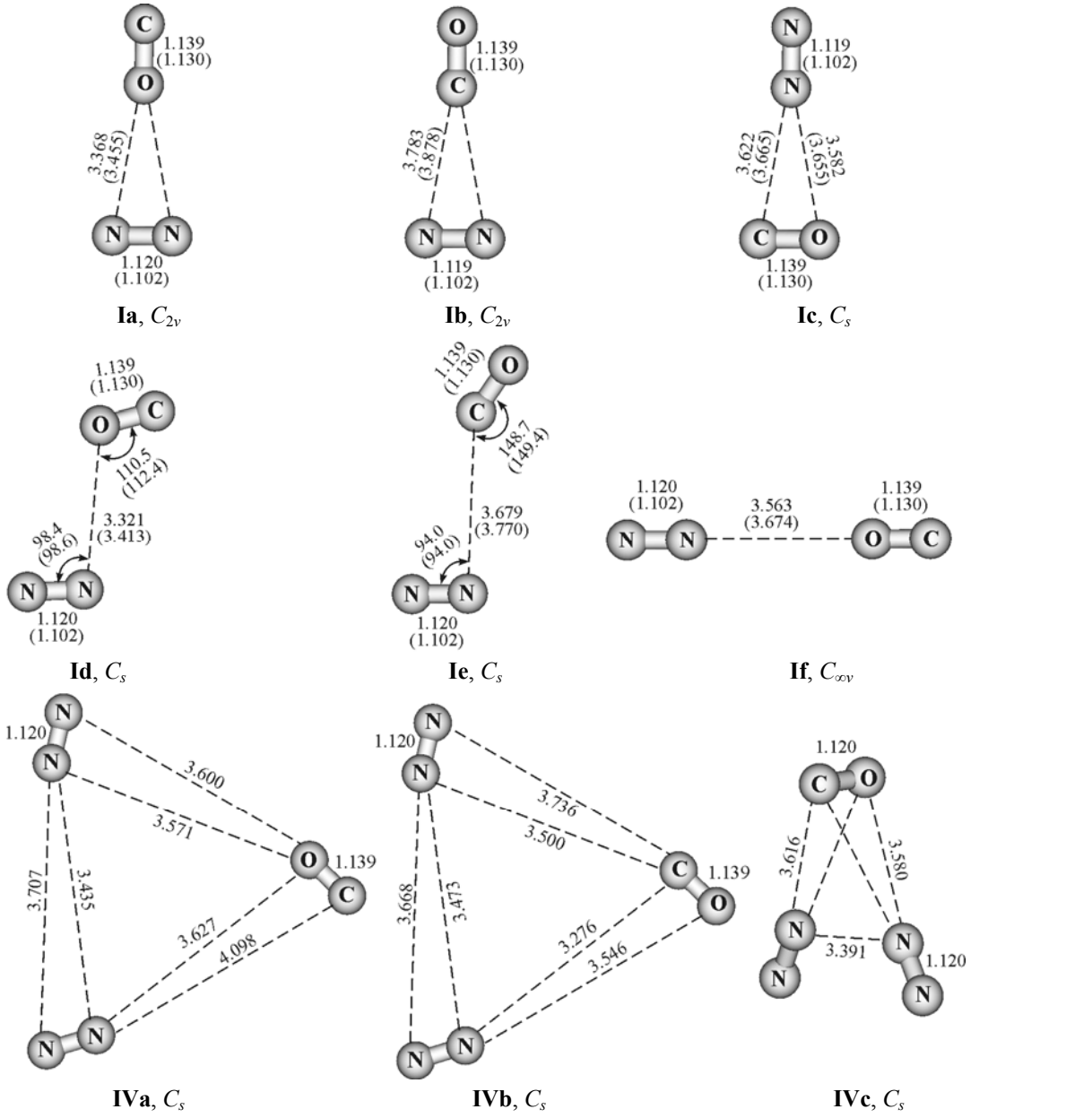
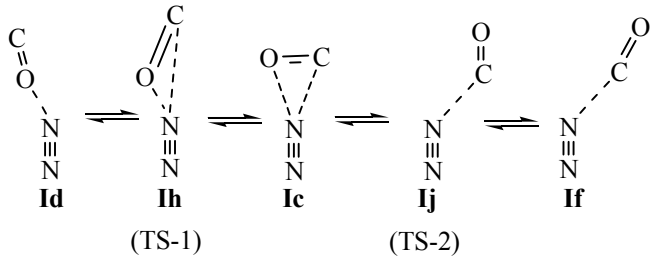


Fig. 1. MP2(full)/6-311+G* and CCSD(full)/6-311+G* (in paremtheses) geometrical characteristics of systems **I** and **IV**. Hereinafter the bond distances are given in Å, angles in deg.

The energies of stabilization of the mixed complexes **I** are comparable with those of the previously studied dimers of nitrogen **II** (0.44–0.51 kcal mol^{-1} [26]). Therefore, as dimer $(N_2)_2$, complex $N_2\cdots CO$ exists in the form of a series of the structurally different but energetically almost equivalent isomers. The transition from the homomolecular system $N_2\cdots N_2$ to the heteromolecular $N_2\cdots CO$ somewhat decreases the energy of binding in the complexes and substantially increases the number of possible isomers.



The results of calculations are indicative of a high stereochemical nonrigidity of the heteromolecular com-

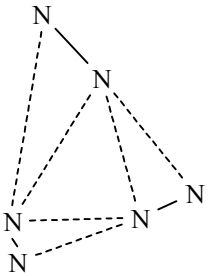
Table 1. Energy characteristics[a] of compounds **I, IV, VI** calculated by the MP2(full)/6-311+G* and CCSD(full)/6-311+G* methods

Structure	Method	E_{tot}	E_{tot} + ZPE	ΔE	ΔE_{ZPE}	E_f	$E_{f\,ZPE}$	λ	ω_1
Ia, C_{2v}	MP2	222.455084	222.444917	0	0	0.71	0.49	0	28.9
	CCSD	222.459521	222.448620	0	0	0.58	0.37	0	26.6
Ib, C_{2v}	MP2	222.454771	222.444693	0.20	0.14	0.51	0.35	0	8.0
	CCSD	222.459283	222.448466	0.15	0.10	0.43	0.27	0	8.9
Ic, C_s	MP2	222.454916	222.444679	0.11	0.15	0.60	0.34	0	33.2
	CCSD	222.459410	222.448435	0.07	0.12	0.51	0.25	0	33.2
Id, C_s	MP2	222.454923	222.444793	0.10	0.08	0.61	0.41	0	23.4
	CCSD	222.459378	222.448565	0.09	0.03	0.49	0.33	0	10.5
Ie, C_s	MP2	222.454761	222.444671	0.20	0.15	0.50	0.33	0	10.7
	CCSD	222.459275	222.448440	0.15	0.11	0.42	0.25	0	14.0
If, $C_{\infty v}$	MP2	222.454526	222.444259	0.35	0.41	0.36	0.07	0	29.0
	CCSD	222.459054	222.448056	0.29	0.35	0.28	0.01	0	24.9
Ih, C_s	MP2	222.454802	222.444754	0.18	0.10	0.53	0.38	1	*i*24.5
	CCSD	222.459320	222.448510	0.13	0.07	0.45	0.30	1	*i*18.9
Ij, C_s	MP2	222.454734	222.444645	0.22	0.17	0.49	0.32	1	*i*19.3
	CCSD	222.459233	222.448416	0.18	0.13	0.40	0.24	1	*i*16.5
IVa, C_s	MP2	331.795808	331.780211	0	0	1.86	1.35	0	24.9
IVb, C_s	MP2	331.795652	331.779927	0.10	0.18	1.76	1.17	0	20.1
IVc, C_s	MP2	331.795472	331.779882	0.21	0.21	1.65	1.14	0	9.6
VIa, C_s	MP2	441.136226	441.115006	1.12	1.13	2.82	1.90	0	3.0
VIb, C_s	MP2	441.136550	441.115289	0.91	0.95	3.02	2.08	0	3.4
VIc, C_1	MP2	441.138004	441.116801	0	0	3.93	3.03	0	19.5
VId, C_1	MP2	441.137691	441.116512	0.20	0.18	3.74	2.84	0	13.0

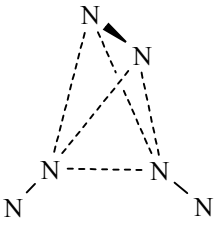
[a] (E_{tot}, au) is total energy (1au = 627.5095 kcal mol^{-1}); (E_{tot} + ZPE, au) is total energy corrected for the energy of zero harmonic vibrations; (ΔE, kcal mol^{-1}) is relative energy; (ΔE_{ZPE}, kcal mol^{-1}) is relative energy corrected to the energy of zero harmonic vibrations; (E_f, kcal/mol^{-1}) is energy of complex formation; ($E_{f\,ZPE}$, kcal mol^{-1}) is energy of complex formation corrected for the energy of zero harmonic vibrations; (λ) is the number of negative eigenvalues of Hessian; (ω_1, cm^{-1}) is minimal harmonic vibrational frequency. The same in Tables 2, 3.

plex N_2···CO. Thus, interconversion of the conformers **Id** ↔ **Ic** ↔ **Ie**, according to calculations, proceeds with the barriers not exceeding 0.07 kcal mol^{-1}. Therefore, the internal movement of the molecules in the system N_2···CO is practically free, which is also proved by the experimental data [10, 21, 32–34].

Trimer systems. Replacement of one of the N_2 molecules in the earlier found [26] stable trimers of nitrogen **III** by the isoelectronic molecule CO does not violate the stability of the systems. The so formed mixed heteromolecular clusters **IVa–IVc** correspond to energy minima (λ = 0) on the PES. The structural and energy characteristics of systems **IV** are given in Fig. 1 and Table 1.



IIIa, C_{3h}



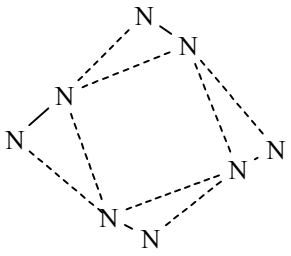
IIIb, C_{2v}

On the basis of cluster **IIIa** planar systems **IVa** and **IVb** are formed, in which the centers of mass of molecules N_2 and CO form equilateral triangle. The N···O(C) bond distances in these complexes are slightly elongated relative to dimers **I**. System **IVa**

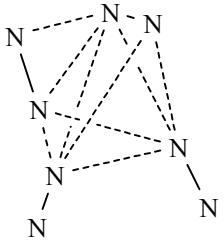
with the endocyclic oxygen atom forming more stabilizing contacts is by 0.18 kcal mol^{-1} lower in energy than system **IVb** with the exocyclic oxygen atom. Nonplanar system **IVc** formed on the basis of the nitrogen cluster **IIIb** is somewhat less stable than planar structures **IVa** and **IVb**. The calculated energies of formation for complexes **IVa–IVc** are 1.14–1.35 kcal mol^{-1} (Table 1), which is slightly higher than for the dimer complexes **I** although lower as compared to the isostructural homomolecular nitrogen clusters **III** (1.40–1.41 kcal mol^{-1} [26]).

System **IVa** is formed by means of three intermolecular interactions NN···N_2, CO···N_2 and NN···CO, which in the "isolated" manner are realized in the T-shape dimers **Ia**, **Ic** and **IIb**. In this connection, it is interesting to analyze the possibility of manifestation of the cooperative effect related with nonadditive increase in the energy of intermolecular interactions. According to calculations, the cooperative effect of the formation of complex **IVa** estimated as the difference between the energy of formation of **IVa** and the sum of the energies of formation of **Ia**, **Ic,** and **IIb** is 0.07 kcal mol^{-1} (5.2%) which is somewhat higher than for the starting homomolecular cluster **IIIa** (3.6% [26]) For a less stable system **IVb** the value of the cooperative effect is lowered and amounts to 0.03 kcal mol^{-1} (2.6%).

Tetramer systems. Replacement of one of the N_2 molecules by the CO molecule in stable tetramer homomolecular complexes **V** leads to the formation of heteromolecular complexes **VIa–VId**, corresponding to energy minima on the PES. Structural and energy characteristics of systems **VIa–VId** are given in Fig. 2 and Table 1.



Va, C_{4h}



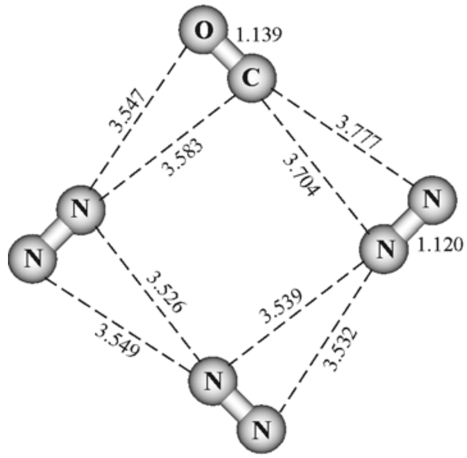
Vb, C_s

Clusters **VIa** and **VIb** are characterized by planar structure, in which the centers of mass of the interacting molecules form a slightly distorted square. Complex **VIb** with the endocyclic oxygen participating in several stabilizing interactions is by 0.18 kcal mol^{-1} more stable than complex **VIa** with the exocyclic oxygen forming only one stabilizing contact.

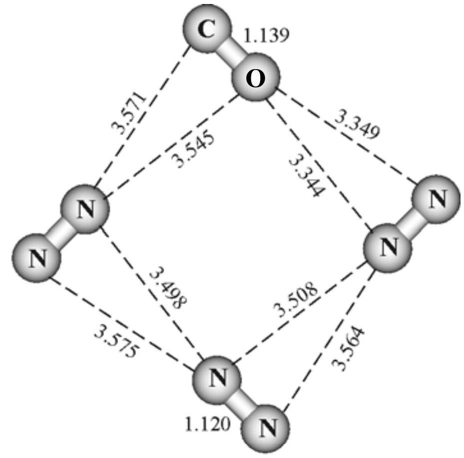
The calculated stabilization energies of complexes **VIa** and **VIb** are somewhat lower than that of the parent homomolecular complex **Va** (2.15 kcal mol^{-1} [26]) and amount to 1.90 and 2.08 kcal mol^{-1}, respectively. Therefore, the tendency of lowering the energy of stabilization caused by incorporation of the CO molecule found for trimers **IV** is retained for planar tetramers. The cooperative effect for system **VIa** calculated as the difference between the energy of formation of the cluster and the sum of the energies of formation of complexes **Ib**, **Ic** and two dimers **IIb** is 0.31 kcal mol^{-1} (16.3%). The cooperative effect for system **VIb** calculated as the difference between the energy of formation of the cluster and the sum of the energies of formation of complexes **Ia**, **Ic** and two dimers **IIb** is 0.35 kcal mol^{-1} (16.8%).

Unlike trimers **IV**, for which the most stable forms correspond to planar systems, in the case of tetramers $3N_2$-CO spatial clusters are more stable, e.g., systems **VIc** and **VId** (Fig. 2). The most stable cluster **VIc** is energetically preferable relative to the planar systems **VIa** and **VIb** by about 1 kcal mol^{-1} (Table 1), and its energy of formation (3.03 kcal mol^{-1}) is almost the same as that of the parent homomolecular complex **Vb** (3.10 kcal mol^{-1} [26]).

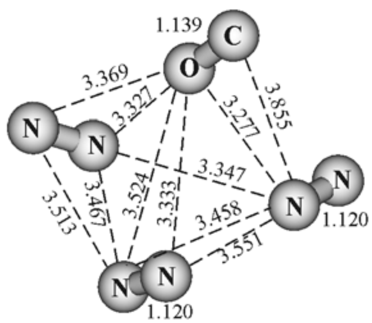
Replacement of the two nitrogen molecules by the CO molecules in complex **Va** leads to the formation of heteromolecular complexes **VIIa–VIId** (Fig. 3), among which the most stable is complex **VIIa** characterized by the diagonal arrangement of the CO molecules and endocyclic oxygen atom. The least stable is complex **VIIb** with the diagonal arrangement of the CO molecules and exocyclic oxygen atoms. The calculated stabilization energies for complexes **VIIa–VIId** (1.66–2.01 kcal mol^{-1}) are reduced as compared both with the parent homomolecular complex **Va** (2.15 kcal mol^{-1} [26]) and with the monosubstituted systems **VIa, VIb**. The cooperative effect for system **VIIa** calculated as the difference between the energy of formation of the cluster and the sum of the energies of formation of two complexes **Ia** and two complexes **Ic** is 0.35 kcal mol^{-1} (16.8%). The cooperative effect for system **VIIb** calculated as the difference between the energy of formation of the cluster and the sum of the energies of formation of two complexes **Ib** and two complexes **Ic** is 0.28 kcal mol^{-1} (16.9%). Therefore, cooperative effects in the tetramer systems **VII** are



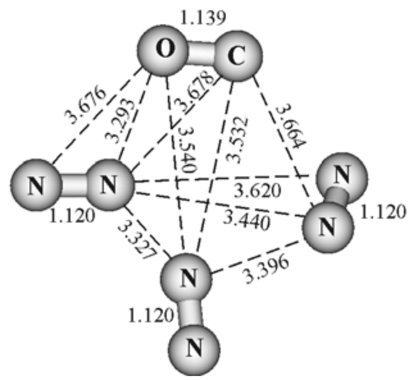
VIa, C_s



VIb, C_s



VIc, C_1



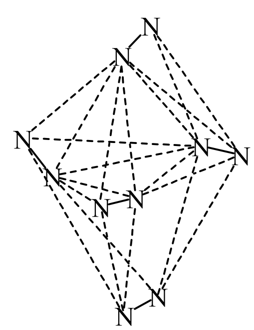
VId, C_1

Fig. 2. MP2(full)/6-311+G* geometrical characteristics of systems **VI**.

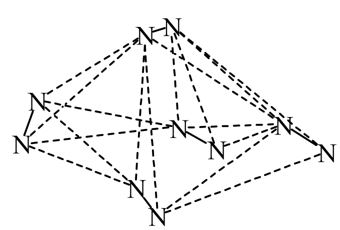
more manifested as compared with those for the trimer complexes **VI**.

Formation of the 2:2 complexes on the basis of the nonplanar form of the nitrogen tetramer **Vb** is also possible: examples are isomers **VIII** (Fig. 4, Table 2) corresponding to energy minima on the PES. As follows from Table 2, nonplanar conformers **VIII** are notably more stable as compared to planar systems **VII**. The most stable conformer corresponds to complex **VIIIe**: its energy of formation is 3.01 kcal mol^{-1} and only slightly exceeds the energy of formation of the parent nitrogen tetramer.

Pentamer systems. Earlier, we have found for the nitrogen pentamer $(N_2)_5$ two main structural types of complexes: complex **IXa**, in which the centers of mass of the nitrogen molecules are located in the vertices of a trigonal bipyramid, and complex **IXb**, where they form a square pyramid [26].



IXa, C_1



IXb, C_1

Replacement of either of the molecules of nitrogen in systems **IX** by the CO molecule does not violate the stability of the system and gives rise to formation of several types of clusters: as an example, in Fig. 5 are shown structures **Xa** and **Xb**, the latter being the most stable. The calculated energy of formation for **Xb** is somewhat smaller than for **IXa** (4.90 kcal mol^{-1} [26])

Table 2. Energy characteristics of compounds **VII, VIII, IX, XI** calculated by the MP2(full)/6-311+G* method

Structure	$-E_{tot}$	$-(E_{tot} + ZPE)$	ΔE	ΔE_{ZPE}	E_f	$E_{f\,ZPE}$	λ	ω_1
VIIa, C_{2h}	444.912490	444.891492	1.02	1.00	2.87	2.01	0	4.1
VIIb, C_{2h}	444.911847	444.890934	1.46	1.35	2.43	1.66	0	2.2
VIIc, C_s	444.912250	444.891235	1.17	1.16	2.72	1.85	0	2.4
VIId, C_s	444.911928	444.890998	1.37	1.31	2.52	1.70	0	1.5
VIIIa, C_1	444.913978	444.892875	0.09	0.13	3.80	2.88	0	15.9
VIIIb, C_1	444.913447	444.892420	0.42	0.42	3.47	2.59	0	20.8
VIIIc, C_1	444.913066	444.892070	0.66	0.64	3.23	2.37	0	8.3
VIIId, C_1	444.913573	444.892486	0.34	0.38	3.55	2.63	0	20.1
VIIIe, C_1	444.914117	444.893088	0	0	3.89	3.01	0	20.8
Xa, C_1	550.479926	550.453117	0.01	0.06	5.83	4.53	0	16.9
Xb, C_1	550.479941	550.453218	0	0	5.84	4.59	0	10.8
XIa, C_1	554.256186	554.229553	0	0	5.89	4.61	0	16.5
XIb, C_1	554.255090	554.228475	0.69	0.68	5.20	3.93	0	3.8
XIc, C_1	554.254998	554.228387	0.74	0.73	5.14	3.88	0	11.5

and amounts to 4.59 kcal mol^{-1}. All clusters $4N_2$-CO formed by the trigonal bipyramid type are more stable than those formed on the basis of the square pyramid.

Introduction of the second CO molecule also results in the formation of numerous isomeric complexes, but it is followed by reduction of the energy of

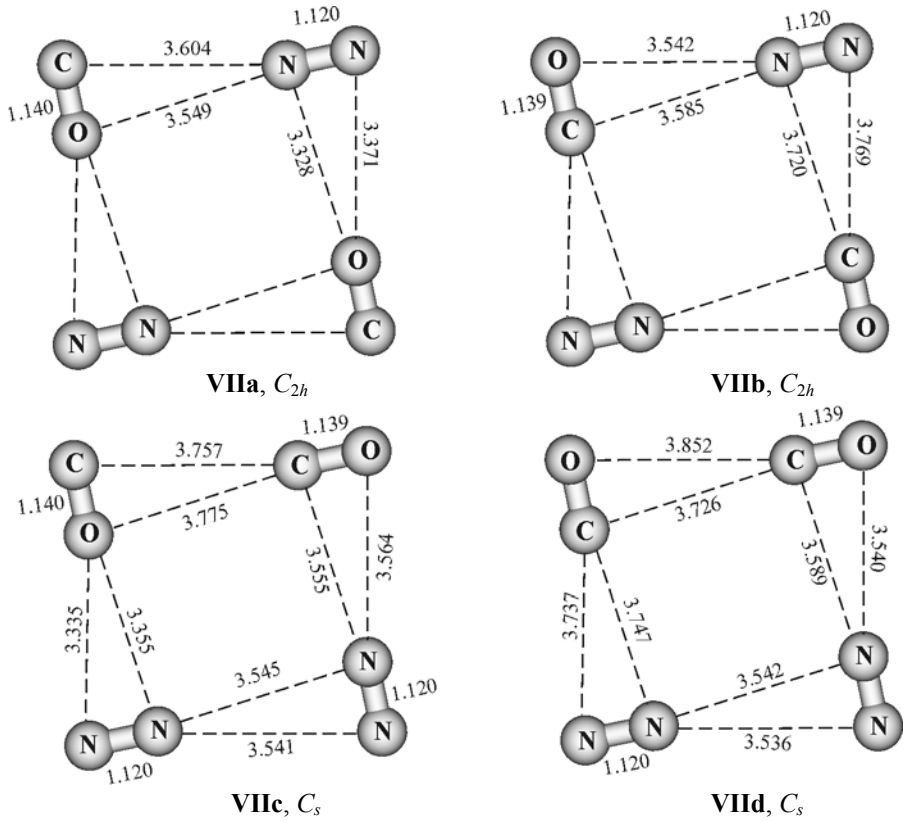


Fig. 3. MP2(full)/6-311+G* geometrical characteristics of systems **VII**.

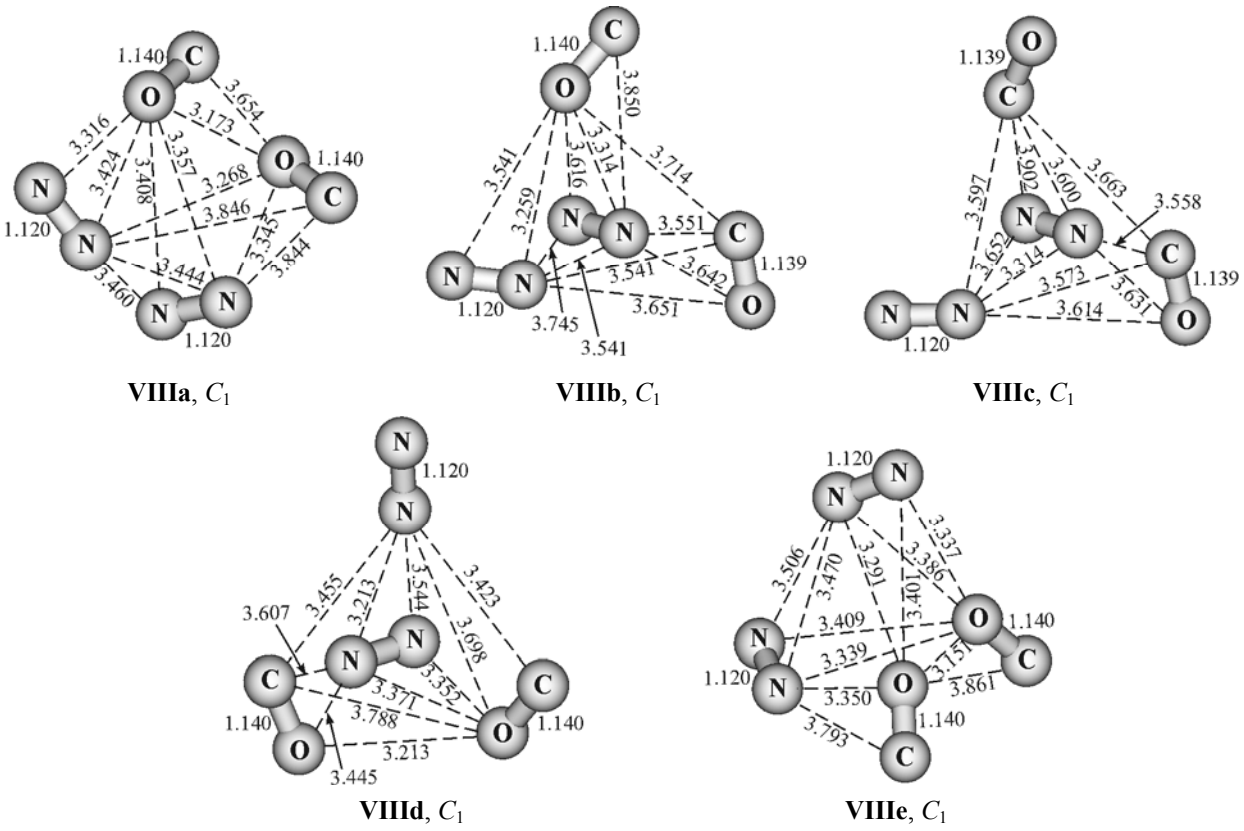
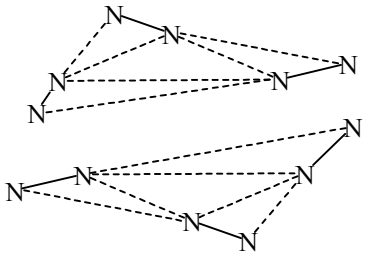


Fig. 4. MP2(full)/6-311+G* geometrical characteristics of systems **VIII**.

stabilization. In Fig. 5 the most stable complex **XIa** is shown, in which the CO molecules are located in the axial positions of the trigonal bipyramid with the endocyclic oxygen atoms. The least stable is structure **XIc** with the CO molecules located in the basal ring. The calculated energies of stabilization of clusters **XIa** and **XIc** are 4.61 and 3.88 kcal mol^{-1}, respectively. Other possible forms (for example, **XIb** are characterized by the energies of complex formation intermediate between **IXa** and **IXc**).

Hexamer systems. Earlier, we have found for the nitrogen hexamer $(N_2)_6$ several structural types of complexes [26], the most stable being complex **XII** having the C_3–symmetry of the type of trigonal antiprism, whose formation can be the result of parallel rapprochement of two trimers.



XII, C_3

Replacement of either of the molecules of nitrogen in systems **XII** by the CO molecule does not violate the stability of the system and gives rise to formation of numerous isomeric clusters (as an example, in Fig. 6 is shown cluster **XIIIa**). The energy of formation of cluster **XIIIa** is 6.54 kcal mol^{-1}, which is somewhat lower than that of **XII** (7.04 kcal mol^{-1} [26]). Formation of heteromolecular clusters of the 5:1 composition is also possible: an example is system **XIIIb**.

Replacement of one more nitrogen molecule in the hexamolecular complex **XII** by the CO molecule substantially increases the number of isomers: as an example, in Fig. 6 are shown complexes **XIVa–XIVc**. In general, the energies of formation of the disubstituted clusters are somewhat lower than of monosubstituted. Replacement of the third nitrogen molecule (in Fig. 6 are shown clusters **XV**) is followed by further lowering of the energy of complex formation.

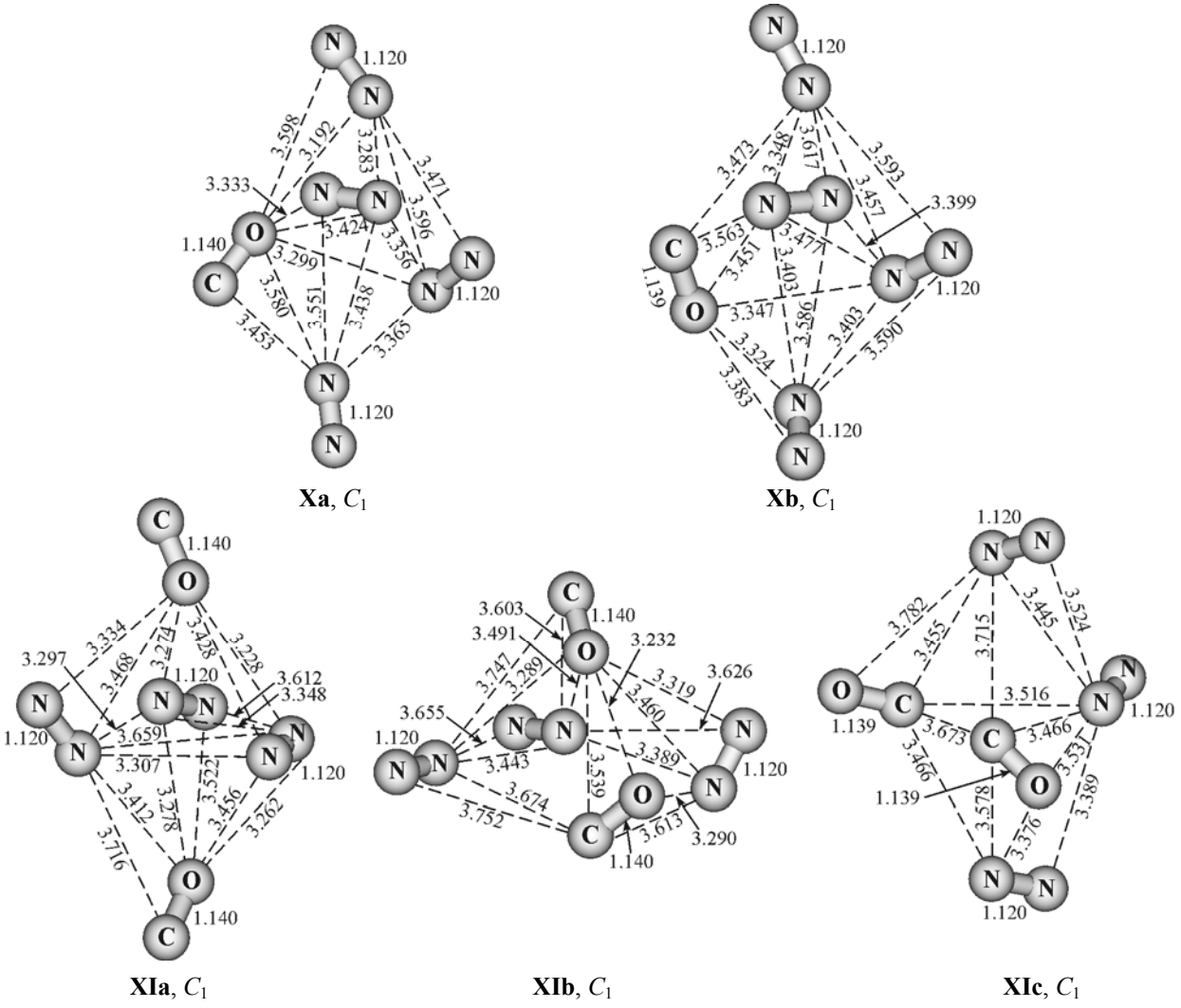


Fig. 5. MP2(full)/6-311+G* geometrical characteristics of systems **X** and **XI**.

The calculations show that the effect of the decrease of stability and increase in stereochemical nonrigidity of clusters with increase in the fraction of carbon monooxide in the mixture is observed also for more complex systems. In Fig. 7 and Table 3 are given the structural and energy characteristics of tenmolecular clusters **XVI–XVIII** of the composition 1:9, 2:8 and 3:7, respectively. The energy of stabilization of these clusters decreases with the degree of substitution, simultaneously increases the number of possible isomers and stereochemical nonrigidity of the complexes.

Therefore, the performed calculations show that on going from homomolecular nitrogen complexes to heteromolecular mixtures of nitrogen with carbon monooxide the polyhedron structure of the clusters is retained: globular forms, which are more spatially favorable for realization of nonvalent interactions, are characterized by a larger stability as compared to planar forms. The increase in percentage of carbon monooxide in the mixture is followed by lowering of the complex formation energy and increase in stereochemical nonrigidity of complexes. As in the case of homomolecular systems, the increase in the number of interacting molecules in heteromolecular systems results in strengthening of intermolecular contacts, increase in "compactness" of the cluster and appearing of cooperative effects.

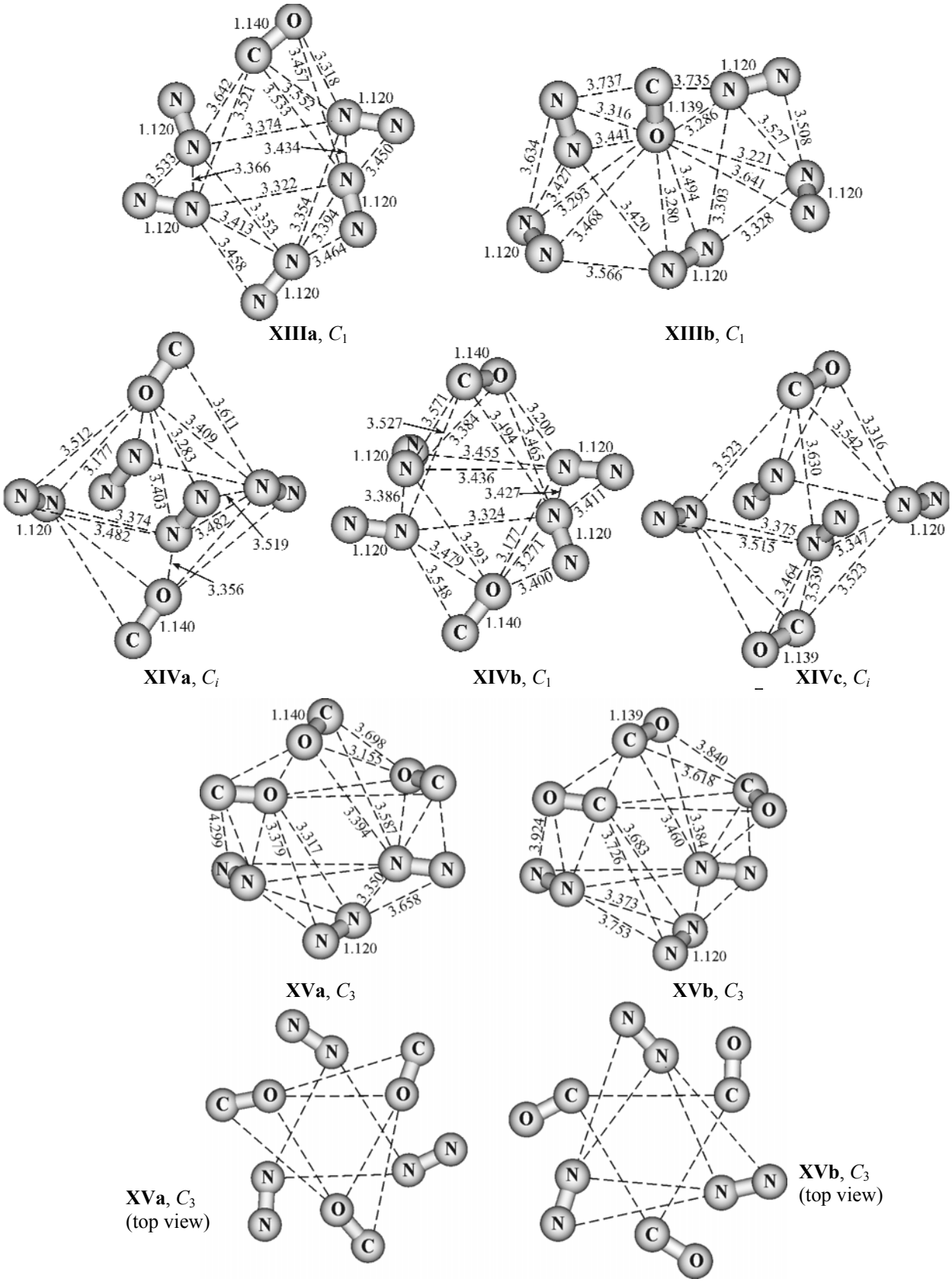


Fig. 6. MP2(full)/6-311+G* geometrical characteristics of systems **XIII–XV**.

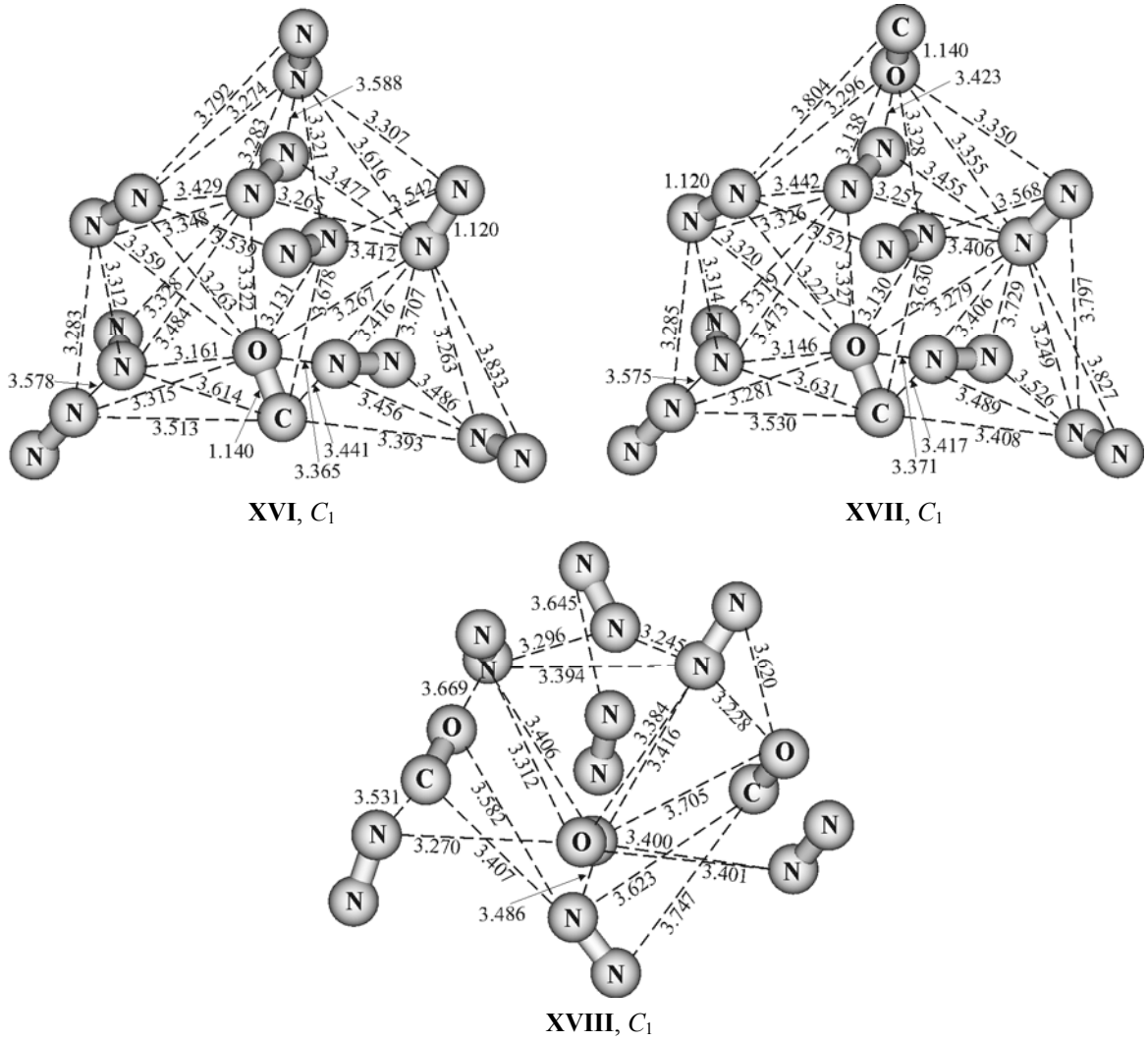


Fig. 7. MP2(full)/6-311+G* geometrical characteristics of systems **XVI–XVIII**.

Table 3. Energy characteristics of compounds **XIII–XVIII** calculated by the MP2(full)/6-311+G* method

Structure	$-E_{tot}$	$-(E_{tot} + ZPE)$	ΔE	ΔE_{ZPE}	E_f	$E_{f\,ZPE}$	λ	ω_1
XIIIa, C_1	659.822774	659.790232	0	0	8.32	6.54	0	18.6
XIIIb, C_1	659.822489	659.790103	0.18	0.08	8.14	6.46	0	12.4
XIVa, C_i	663.598765	663.566519	0	0	8.20	6.52	0	17.3
XIVb, C_1	663.598683	663.566235	0.05	0.18	8.15	6.35	0	22.8
XIVc, C_i	663.598124	663.565638	0.40	0.55	7.80	5.97	0	19.0
XVa, C_3	667.374863	667.342733	0	0	8.15	6.46	0	24.7
XVb, C_3	667.373394	667.341157	0.92	0.99	7.23	5.48	0	25.7
XVI, C_1	1097.194241	1097.139049	–	–	18.31	14.78	0	13.1
XVII, C_1	1100.969986	1100.915095	–	–	18.04	14.62	0	9.9
XVIII, C_1	1104.743742	1104.689056	–	–	16.51	13.15	0	10.5

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REFERENCES

1. Hobza, P. and Zahradník, R., *Intermolecular Complexes. The Role of van der Waals Systems in Physical Chemistry and in the Biodisciplines*, Prague: Academia, 1988.
2. Nemukhin, A.V., *Ross. Khim. Zh. (Zh. Ross. Khim. Ob–va im. D.I. Mendeleeva).,* 1996, vol. 40, no. 3, p. 48.
3. Tang, J. and McKellar, A.R.W., *J. Chem. Phys*., 2003, vol. 119, no. 2, p. 754.
4. Long, C.A., Henderson, G., and Ewing, G.E., *Chem. Phys*., 1973, vol. 2, no. 4, p. 485.
5. Thakkar, A.J. and Smith, V.H.Jr., *Mol. Phys*., 1975, vol. 29, no. 3, p. 731.
6. Carnovale, F., Peel, J.B., and Rothwell, R.G., *J. Chem. Phys*., 1988, vol. 88, no. 2, p. 642.
7. Vanden Bout, P.A., Steed, J.M., Bernstein, L.S., and Klemperer, W., *Astrophys. J*., 1979, vol. 234, no. 2, p. 503.
8. Xu, Y. and Jäger, W., *J. Chem. Phys*., 1999, vol. 111, no. 13, p. 5754.
9. Kawashima, Y. and Nishiza, K., *Chem. Phys. Lett*., 1996, vol. 249, nos. 1–2, p. 87.
10. Xu, Y. and McKellar, A.R.W., *J. Chem. Phys*., 1996, vol. 104, no. 7, p. 2488.
11. Colbourn, E.A. and Douglas, A.E., *J. Chem. Phys*., 1976, vol. 65, no. 5, p. 1741.
12. Jäger, W. and Gerry, M.C.L., *Chem. Phys. Lett*., 1992, vol. 196, nos. 3–4, p. 274.
13. Böhm, H. and Ahlrichs, R., *Mol. Phys*., 1985, vol. 55, no. 5, p. 1159.
14. Avoird, A., Wormer, P.E.S., and Jansen, A.P.J., *J. Chem. Phys*., 1986, vol. 84, no. 3, p. 1629.
15. LeSar, R. and Shaw, M.S., *J. Chem. Phys*., 1986, vol. 84, no. 10, p. 5479.
16. Bohr, J.E. and Hunt, K.L.C., *J. Chem. Phys*., 1987, vol. 87, no. 7, p. 3821.
17. Mack, H. and Oberhammer, H., *J. Chem. Phys*., 1987, vol. 87, no. 4, p. 2158.
18. Pol, A., Avoird, A., and Wormer, P.E.S., *J. Chem. Phys*., 1990, vol. 92, no. 12, p. 7498.
19. Brookes, M.D. and McKellar, A.R.W., *J. Chem. Phys*., 1999, vol. 111, no. 6, p. 7321.
20. Roth, D.A., Surin, L.A., Dumesh, B.S., Winnewisser, G., and Pak, I., *J. Chem. Phys*., 2000, vol. 113, no. 8, p. 3034.
21. Xu, Y., Jäger, W., Surin, L.A., Pak, I., Panfilov, L.A., and Winnewisser, G., *J. Chem. Phys*., 1999, vol. 111, no. 23, p. 10476.
22. Fernández, B., Koch, H., and Makarewicz, J., *J. Chem. Phys*., 1999, vol. 110, no. 7, p. 8525.
23. Plönjes, E., Palm, P., Lee, W., Chidley, M.D., Adamovich, I.V., Lempert, W.R., and Rich, J.W., *Chem. Phys*., 2000, vol. 260, no. 3, p. 353.
24. Plönjes, E., Palm, P., Lee, W., Lempert, W.R., and Adamovich, I.V., *J. Appl. Phys*., 2001, vol. 89, no. 11, p. 5911.
25. Lee, W., Adamovich, I.V., and Lempert, W.R., *J. Chem. Phys*. 2001, vol. 114, no. 3, p. 1178.
26. Gribanova, T.N., Milov A.A., Starikov A.G., Gapurenko O.A., Gurashvili, V.A., Minyaev, R.M., and Minkin, V.I., *Russ. Chem. Bull. Engl. Transl*., 2008, vol. 57, no. 10, p. 2037.
27. Foresman, J.B. and Frisch, E., *Exploring Chemistry with Electronic Structure Methods*, Pittsburg: Gaussian Inc., 1996, 2nd ed.
28. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., 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., Gonzalez, C., and Pople, J.A., *Gaussian-03. Rev.,* B.03, Pittsburgh (Pa): Gaussian Inc., 2003.
29. Hehre, W.J., Radom, L., Schleyer, P.v.R., and Pople, J.A., *Ab Initio Molecular Orbital Theory*, New York: Wiley, 1986.
30. Schaftenaar, G., *Molden 3.4. CAOS/CAMM Center*, The Netherlands, 1998.
31. Franken, K.A. and Dykstra, C.E., *J. Phys. Chem*., 1993, vol. 97, no. 44, p. 11408.
32. Xia, C., McKellar, A.R.W., and Xu, Y., *J. Chem. Phys*. 2000, vol. 113, no. 2, p. 525.
33. Xu, Y. and Jäger, W., *J. Chem. Phys*. 2000, vol. 113, no. 2, p. 514.
34. Surin, L.A., Potapov, A.V., Műller, H.S.P., Panfilov, V.A., Dumesh, B.S., Giesen, T.F., and Schlemmer, S., *J. Mol. Struct*., 2006, vol. 795, nos. 1–3, p. 198.
35. Fiser, J. and Polak, R., *Chem. Phys. Lett*., 2002, vol. 360, nos. 5–6, p. 565.