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QUANTUM CHEMICAL STUDY OF THE NATURE OF REGIOSELECTIVITY IN REACTIONS OF 2,4,6-TRIAZIDOPYRIDINES WITH *tert*-BUTYLPHOSPHAACETYLENE

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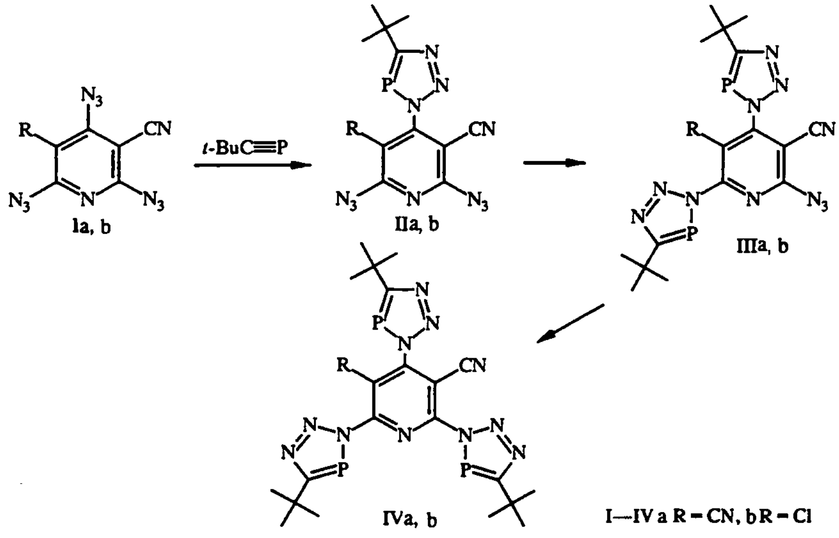
We have performed PM3 calculations for 2,4,6-triazido-3,5-dicyanopyridine and 2,4,6-triazido-3-chloro-5-cyanopyridine, and also the cycloadducts of these compounds with one and two tert-butylphosphaacetylene molecules. We have established that the selectivity of addition of a phosphaacetylene molecule at the γ-azido group of triazidopyridines is due to the specifics of the electronic properties and geometry of these groups, characterized by enhanced electrophilicity of the terminal nitrogen atoms, a greater contribution from atomic orbitals to the LUMO (lowest unoccupied molecular orbital), and greater bending of the chain of N—N—N atoms. The cycloaddition itself corresponds to the dipole—LUMO-controlled reaction type, and sequential addition of phosphaacetylene molecules at the azido groups of pyridines leads to formation of cycloadducts having lower LUMO energies. Nevertheless, the γ-azido groups of the triazidopyridines can remain stronger dipoles than the azide groups of the cycloadducts when the difference between the LUMO energies in the triazidopyridines and cycloadducts is no greater than 10 kcal/mole.

This paper is a continuation of our investigations on determination of the characteristics of selective addition of dipolarophiles at the azido groups of 2,4,6-triazidopyridines [1-3].

Earlier we showed that 1,3-dipolar cycloaddition of compounds Ia, b to *tert*-butylphosphaacetylene occurs regioselectively at the azido group in the 4 position of the pyridine ring, leading to cycloadducts IIa, b [3]. However, it proved possible to stop these reactions at the step of addition of only one dipolarophile molecule only in the case of compound IIa. Diazidopyridine IIb reacted so easily with two phosphaacetylene molecules that practically at the very beginning of the reaction of compound Ib, we observed simultaneous formation of the monoadduct IIb and the *tris*-adduct IVb [3].



I—IV a R = CN, b R = Cl

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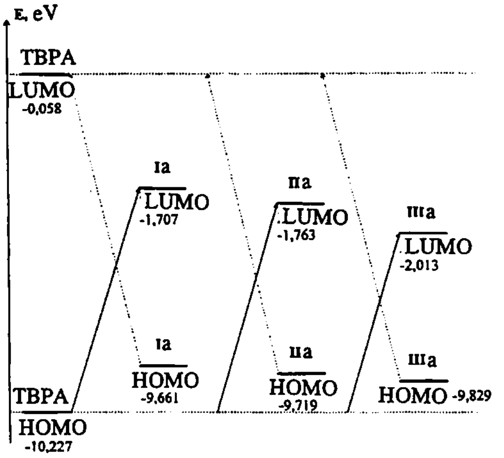

Fig. 1. LUMO and HOMO energy level diagram for azidopyridines Ia-IIIa and TBPA.

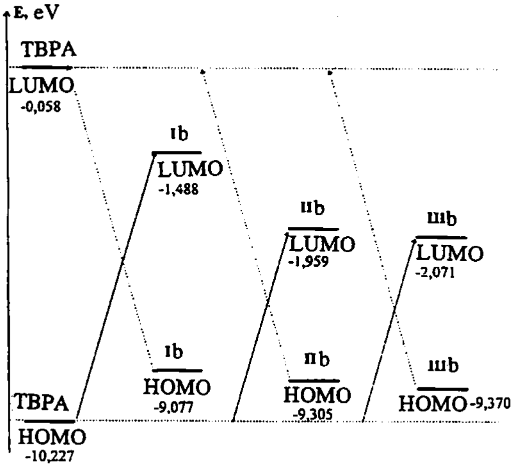

Fig. 2. LUMO and HOMO energy level diagram for azidopyridines Ib-IIIb and TBPA.

Observation of the regioselectivity effect in reactions of triazidopyridine Ia, b with phosphaacetylene and the significant differences in reactivity of the intermediate cycloadducts posed fundamentally new problems for azide chemistry, connected with determination of the possibility of selective addition of dipolarophiles at the azido groups in polyazide molecules. It was known that arylazides whose molecules contain electron-acceptor substituents react with dipolarophiles more easily as the LUMO energy of the azides is lowered (dipole–LUMO-controlled reactions) [4-7]. In turn, lower values of the LUMO energies corresponded to those azides whose molecules contained stronger electron-acceptor substituents [4]. These data made it possible to reliably describe reactions of 1,3-dipolar cycloaddition of monoazides. However, when several azide groups are present in the azide molecule, the value of the LUMO energy of the azide made it possible to estimate only the total reactivity of such a compound, but not the reactivity of its individual azido groups. Moreover, it did not seem possible earlier to trace the effect of other factors on the chemical properties of azide groups because of the dependence of the reactivity of monoazides on the LUMO energy. Theoretical studies only predicted that such determining factors for azido groups may be the charge distribution on their N(α) and N(γ) atoms [4-9], the contribution of the atomic orbitals (AO's) of the N(β) and N(γ) atoms to the LUMO [4-9], and the geometry of the given groups [10,11]. We can reliably assess the actual significance of each of these factors only by comparing calculated data on the geometry and electronic properties for azide groups whose difference in reactivity is not connected with the values of the LUMO energies. Such an investigation became possible for the first time due to the significantly different reactivities of the α and γ azido groups of pyridine derivatives Ia, b.

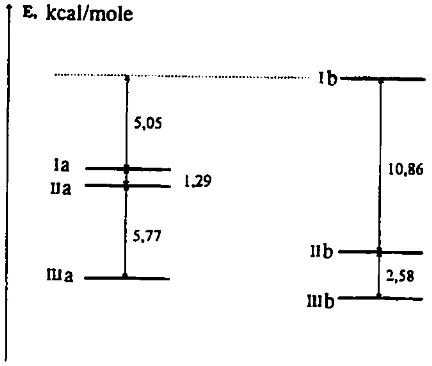

Fig. 3. LUMO energy level diagram for azidopyridines Ia, b-IIIa, b.

Our goal was to determine the characteristic features of the geometry and electronic properties of azido groups of compounds Ia, b, which are responsible for the selectivity in reactions of the given compounds with phosphaacetylene. Since the selectivity of addition of the latter at the γ-azido groups of compounds Ia, b also depends on the properties of the cycloadducts formed, one of our tasks was to determine the nature of the effects which do not allow reactions of triazidopyridines Ia, b with *tert*-butylphosphaacetylene to stop at the step of addition of a single dipolarophile molecule. With this goal, we carried out a quantum chemical study of the geometry and electronic properties of dipoles Ia, b and cycloadducts IIa, b-IIIa, b.

In this work, we used the PM3 semiempirical calculation method [12] included in the Spartan program package [13]; nonempirical calculations were done using the Games program [14]. The molecular structures of the azides were calculated with full optimization of the geometric parameters. Application of the PM3 calculation method made it possible to do a comparative analysis of the characteristics we obtained with literature calculations of the geometry and electronic properties for a whole series of other aryl- and hetarylazides [4-11,15]. Furthermore, we knew that the PM3 method very accurately describes the geometric characteristics of *para*-nitrophenylazide [15], studied earlier by x-ray diffraction [16].

The calculated data are presented in Figs. 1-4 and Tables 1-4.

In Figs. 1 and 2, we present the energy characteristics of the HOMO and LUMO of compounds Ia, b-IIIa, b and phosphaacetylene. From comparison of these characteristics, we see that for each studied azide–dipolarophile pair, the difference between the values of the LUMO energy of the azide and the HOMO energy of the dipolarophile is substantially less than the differences between the LUMO energy of the dipolarophile and the HOMO energy of the azide. These data, according to the general theory of 1,3-dipolar cycloaddition reactions [4-7], indicate that the reaction of compounds Ia, b-IIIa, b with phosphaacetylene are classified as dipole–LUMO-controlled reactions. The lower the LUMO energy of the azide, the higher its reactivity relative to the dipolarophile.

As we see from the data in Figs. 1 and 2, addition of each new phosphaacetylene molecule at the azido groups leads to formation of compounds having lower values of the LUMO energies. In fact, in the experiment the reactivity of azidopyridines increased as the number of triazaphosphole substituents in their pyridine ring increased [3]. The values of the LUMO energies of azidopyridines Ia, b-IIIa, b calculated by the PM3 method also allow us to compare the reactivity of these compounds with known aromatic azides. Thus our calculations showed that the LUMO energies of phenylazide, its *para*-nitro-substituted derivative, and 4-pyridylazide respectively have values of −0.293, −1.421, and −0.622 eV [15]. The markedly lower values of the LUMO energies for azidopyridines Ia, b-IIIa, b (Figs. 1 and 2) provide a basis for assuming that these compounds should have considerably higher reactivity relative to dipolarophiles than most previously known aromatic azides [4-7].

Comparison of the LUMO energies for the original azidopyridines Ia, b and the compounds IIa, b formed from them also allows us to establish the reason why the reactions of triazidopyridines Ia, b with *tert*-butylphosphaacetylene stops at different stages of cycloaddition. As we see from the diagram in Fig. 3, addition of a single molecule of dipolarophile at the γ-azido group of pyridine Ia leads to formation of cycloadduct IIa, the LUMO energy of which is only 1.29 kcal/mole lower than the LUMO energies of the original compound. In contrast, in the case of addition of a single molecule at the γ-azido group of pyridine Ib, the difference in LUMO energies of the cycloadduct formed and the original azide reaches 10.86 kcal/mole. According to the values of the LUMO energies, compound IIb should have significantly greater reactivity than cycloadduct IIa and should approximately correspond to the very reactive compound IIIa (Fig. 3). From these comparisons, it becomes

TABLE 1. Torsional Angles (φ, degrees) in Azide Molecules IIa, b-IIIa, b

Compound	Parameter	φ
IIa	$C_{(3)}—C_{(4)}—N—P$	90,18
IIb	$C_{(3)}—C_{(4)}—N—P$	14,62
IIIa	$C_{(3)}—C_{(4)}—N—P$	91,06
	$C_{(3)}—C_{(2)}—N—P$	-52,96
IIIb	$C_{(3)}—C_{(4)}—N—P$	16,85
	$C_{(3)}—C_{(2)}—N—P$	-21,86

TABLE 2. AO Coefficients for Atoms of Azide Groups in LUMO of Compounds Ia, b-IIIa, b

Compound	Group	Atom					
		$N\alpha$		$N\beta$		$N\gamma$	
		Calculation method					
		PM3	STO-3G	PM3	STO-3G	PM3	STO-3G
Ia	$2-N_3$	0,05	-0,05	0,26	0,39	-0,27	-0,39
	$4-N_3$	-0,04	0,07	-0,23	-0,44	0,23	0,45
	$6-N_3$	-0,01	0,01	-0,08	-0,03	0,08	0,03
Ib	$2-N_3$	0,04	-0,04	0,26	0,36	-0,25	-0,37
	$4-N_3$	-0,04	0,06	-0,25	-0,44	0,25	0,45
	$6-N_3$	0,00	0,00	-0,06	-0,02	0,06	0,02
IIa	$2-N_3$	0,03	—	0,13	—	-0,13	—
	$6-N_3$	0,02	—	0,12	—	-0,12	—
IIb	$2-N_3$	-0,03	—	-0,08	—	0,09	—
	$6-N_3$	-0,02	—	-0,05	—	0,05	—
IIIa	$6-N_3$	-0,04	—	-0,12	—	0,12	—
IIIb	$2-N_3$	0,00	—	-0,01	—	0,01	—

TABLE 3. Bond Lengths in Azide Groups of Pyridines Ia, b-IIIa, b

Compound	Group	Bond length		
		$C—N_{(\alpha)}$	$N_{(\alpha)}—N_{(\beta)}$	$N_{(\beta)}—N_{(\gamma)}$
Ia	$2-N_3$	1,4126	1,2809	1,1211
	$4-N_3$	1,4111	1,2807	1,1218
	$6-N_3$	1,4135	1,2818	1,1207
Ib	$2-N_3$	1,4167	1,2777	1,1221
	$4-N_3$	1,4152	1,2773	1,1228
	$6-N_3$	1,4173	1,2790	1,1216
IIa	$2-N_3$	1,4128	1,2817	1,1208
	$6-N_3$	1,4128	1,2817	1,1208
IIb	$2-N_3$	1,4169	1,2791	1,1215
	$6-N_3$	1,4159	1,2789	1,1217
IIIa	$6-N_3$	1,4131	1,2830	1,1205
IIIb	$6-N_3$	1,4162	1,2796	1,1215

understandable that with the appearance of the intermediate cycloadduct IIb in the reaction of pyridine Ib with phosphaacetylene, the preferred process then should be reaction of the dipolarophile molecule with compound IIb, having a much lower LUMO energy.

A central question in analysis of the factors which prevent the reactions of compound IB from stopping in the stage of addition of a single dipolarophile molecule was determination of the nature of the anomalously low LUMO energy for the intermediate cycloadduct IIb. We could obtain an answer to this question by comparing the geometric and electronic characteristics of the given cycloadduct and its derivative IIa. Such an investigation was especially timely since according to purely formal indices, of the two diazidopyridines IIa and IIb, the higher reactivity should be expected from azide IIa, whose molecule contains two strong electron-acceptor cyano groups.

TABLE 4. Bond Angles (ω, degrees) in Azide Groups of Compounds Ia, b-IIIa, b

Compound	Parameter	Group		
		$2-N_3$	$4-N_3$	$6-N_3$
Ia	N—N—N	169,68	166,29	169,70
	C—N—N	122,27	126,59	122,15
Ib	N—N—N	169,67	166,35	169,70
	C—N—N	122,04	126,28	122,04
IIa	N—N—N	169,75	—	169,75
	C—N—N	122,31	—	122,32
IIb	N—N—N	169,73	—	169,72
	C—N—N	121,86	—	122,29
IIIa	N—N—N	—	—	169,46
	C—N—N	—	—	122,18
IIIb	N—N—N	—	—	169,35
	C—N—N	—	—	123,34

As shown by the calculation data (Table 1), a fundamental difference in the geometric structure of the molecules of compounds IIa, b is the different spatial orientation of their triazaphosphole rings relative to the plane of the pyridine ring. In the case of the molecule of the less reactive cycloadduct IIa, the planes of both rings are in fact perpendicular to one another ($\varphi = 90.18°$), while in the molecule of compound IIb the torsional angle $C_{(3)}-C_{(4)}-N-P$ is equal to 14.62°. The reason for such substantial differences in the geometry of molecules of compounds IIa, b is the specific steric interaction of the Cl and P atoms in the molecule of cycloadduct IIb. The existence of such an interaction in particular is suggested by the relative redistribution of electron density on these atoms. Thus compared with the original compound Ib, the molecule of compound IIb is characterized by a higher positive charge on the chlorine atom (respectively +0.17 and +0.22, Fig. 4), and a lower positive charge on the phosphorus atom compared with cycloadducts IIa and IIIa (+0.42 vs. +0.49-0.51). It is important to note that the effect of a decrease in electron density at the chlorine atom in the molecule of cycloadduct IIb is not connected with enhancement of the conjugation of this atom with the pyridine ring. In contrast, from analysis of the $C_{(3)}-Cl$ bond lengths in the molecules of pyridines Ib and IIb (respectively 1.6735 and 1.6787 Å) we see that the decrease in the electron density at the chlorine atom of cycloadduct IIb is accompanied by simultaneous elongation of the bond of this atom with the pyridine ring.

The electronic charge distribution in the molecules of compounds Ia, b-IIIa, b (Fig. 4) also shows that the triazaphosphole rings are classified as electron-donor substituents relative to their effect on the pyridine ring. This is suggested in particular by the decrease in positive charge at the $C_{(4)}$ atoms in the molecules of cycloadducts IIa, b compared with the original pyridines Ia, b, and this effect is most pronounced in the case of the more coplanar molecule of compound IIb. Another confirmation of the electron-donor character of the triazaphosphole substituents is the characteristic electron density distribution at the $N_{(3)}$ atoms of the triazaphosphole rings in molecules of IIa, b. From the data in Fig. 4, we see that it is specifically the molecule of cycloadduct IIb which is characterized by a lower negative charge on the $N_{(3)}$ atom, due to the stronger conjugation of its triazaphosphole ring with the pyridine ring. Generalizing these data, we can conclude that the lowering of the LUMO energy of the cycloadducts with an increase in the number of triazaphosphole substituents in their pyridine ring is due not to the electron-acceptor effect of these substituents on the pyridine ring, but rather exclusively to the specific characteristics of the electronic properties of the triazaphosphole rings themselves. Cycloadduct IIb is a separate case: in its molecule, the triazaphosphole ring actually withdraws some of the electron density of the pyridine ring as a result of the steric interaction between the Cl and P atoms. It is specifically such a redistribution of electron density which probably is the main reason for the lower LUMO energy of cycloadduct IIb compared with its derivative IIa, despite the fact that in the molecule of the latter there are formally stronger electron-acceptor substituents.

The nature of the exceptionally high reactivity of the γ-azido groups of compounds Ia, b was determined by determining the strongest differences in electronic properties and geometry for the given groups compared with the α-azido groups of compounds Ia, b and compounds IIa, b-IIIa, b. The calculations for charge redistribution, the contribution of AO's to the LUMO, and the geometric parameters for the azide groups of pyridines Ia, b-IIIa, b are presented in Fig. 4 and in Tables 2-4.

From the data in Fig. 4 we see that independently of the position of the azide groups in the pyridine ring of compounds Ia, b-IIIa, b and also the nature of the substituents in molecules of these compounds, all the azido groups of pyridines Ia, b-IIIa,

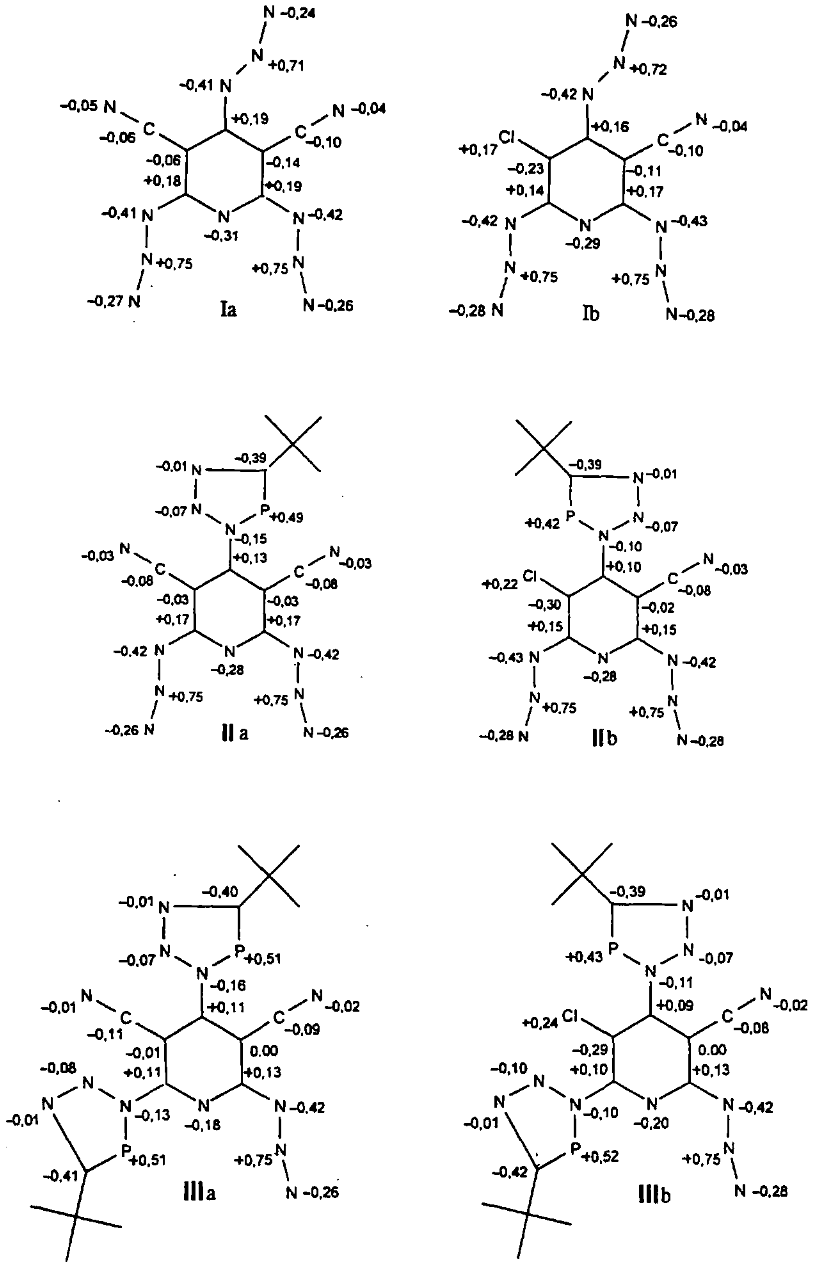

Fig. 4. Electronic charges at atoms of compounds Ia, b-IIIa, b.

b are characterized by approximately identical charges on the $N_{(\alpha)}$ atoms. Some difference between the α- and γ-azido groups of compounds Ia, b is apparent only in the somewhat lower values of the positive charge on the $N_{(\beta)}$ atoms and the negative charge on the $N_{(\gamma)}$ atoms for the more reactive γ-azide groups. In this case, the charge distribution on the terminal atoms of the azido groups is of fundamental importance. Detailed study of the mechanism of dipole–LUMO-controlled cycloaddition reactions has shown that it is specifically nucleophilic attack by the dipolarophile molecules on the $N_{(\gamma)}$ atom of the azido group that is the initial step of such reactions [9]. According to these data, the lower negative charge on the $N_{(\gamma)}$ atoms for γ-azido groups of the pyridines Ia, b in fact can be one of the reasons for the elevated reactivity of these groups in reactions with *tert*-butylphosphaacetylene. Moreover, it seems not very likely to us that specifically such a small change in electron density distribution on the $N_{(\gamma)}$ atoms in α- and γ-azide groups of compounds Ia, b would be the main reason for such strong differences in reactivity of these dipoles.

Analysis of the electronic charge distribution on atoms of the azido groups of pyridines Ia, b-IIIa, b (Fig. 4) also allows us to understand the reason for the regioselectivity of the reactions of azides with phosphaacetylene occurring with formation of exclusively 3H-1,2,3,4-triazaphosphole rings [3]. According to PM3 calculations, charges on the P and $C_{(2)}$ atoms in the dipolarophile molecule are respectively +0.393 and −0.497 [17]. Obviously on reaction with the azide group, the preferred orientation of the dipolarophile molecule should be to approach the nucleophilic $C_{(2)}$ atom with the less negatively charged terminal atom of the azido group, followed by closure of the ring with formation of $N_{(\gamma)}-C$ and $N_{(\alpha)}-P$ bonds.

The data in Table 2 allow us to compare the AO coefficients for atoms of the α- and γ-azide groups in the LUMO of compounds Ia, b. The AO coefficients were calculated by both the semiempirical PM3 method and nonempirically in an STO-3G basis. We know that dipole−LUMO-controlled cycloaddition of azides to dipolarophiles occurs more easily as the contribution of AO's of the atoms of the azido groups to the LUMO of the azides increases [4]. The large difference in reactivity of the α- and γ-azide groups of pyridines Ia, b in the reaction with phosphaacetylene allowed us to expect that the values of the AO coefficients for atoms of these azido groups also should be significantly different from each other. Moreover, from PM3 calculations (Table 2) it follows that addition to dipoles Ia, b should occur preferably at one of the azido groups in position 2 of the pyridine ring, the $N_{(\beta)}$ and $N_{(\gamma)}$ atoms of which are characterized by somewhat higher values of the AO coefficients. Analogous comparison of the AO coefficients for atoms of two nonequivalent azide groups in the molecule of cycloadduct IIb provides a basis for assuming that the reaction of this compound with phosphaacetylene should occur at the azido group located in the *ortho* position to the chlorine atom, giving the bisadduct IIIb as an intermediate product.

The disagreement between the values of the AO coefficients for the azido groups of pyridines Ia, b calculated by the PM3 method and the experimentally observed effects in the reactions of these compounds with phosphaacetylene [3] forced us to carry out a nonempirical calculation for molecules Ia, b in an STO-3G basis [14]. As we can see from such calculations (Table 2), the $N_{(\beta)}$ and $N_{(\gamma)}$ atoms of the more reactive γ-azido groups of compounds Ia, b in fact are characterized by a somewhat higher contribution of the AO's to the LUMO's of these compounds. However, the lack of any literature analogies for such reactions leaves the question open of how adequately the discrepancies of 0.05-0.06 for the AO coefficients of the N(β) and N(γ) atoms of the α- and γ-azido groups of pyridines Ia, b reflect a significant difference between the reactivities of these groups. In our opinion, the calculations in an STO-3G basis more likely indicate some preference for the reaction of the dipolarophile with the γ-azido groups of pyridines Ia, b rather than completely excluding the possibility of alternative addition of a molecule of *tert*-butylphosphaacetylene at the α-azido groups of these compounds.

The geometric parameters of the azide groups in molecules of compounds Ia, b-IIIa, b are presented in Tables 3 and 4. From these data we see that a distinguishing property of the highly reactive γ-azido groups of molecules Ia, b is their strong conjugation with the pyridine ring, which is apparent in the shortened $C-N_{(\alpha)}$ bond for the given groups compared with the α-azido groups of the same compounds. From comparison of the bond lengths in the azide groups of molecules Ia, b we also see that the degree of conjugation of the azide groups with the pyridine ring significantly increases with enhancement of the electron-acceptor properties of the substituents in the pyridine molecules. In this case, we find that the α-azido groups of dicyanopyridines Ia-IIIa are characterized by even stronger conjugation with the pyridine ring than the highly reactive γ-azido group of compound Ib (Table 3). This effect, and also on the whole the small difference in $C-N_{(\alpha)}$ bond lengths for the α- and γ-azide groups of compound Ib along with their significantly different reactivity [3] provides a basis for assuming that the dipolar activity of the azido groups depends weakly on the bond lengths in the N−N−N chain of atoms. Moreover, analysis of the bond lengths in the azide groups proves to be useful for comparing the degree of conjugation of these groups with the aromatic system, which may be of interest for determining the effect of such conjugation on other geometric characteristics of the azide groups.

One of the most important geometric parameters of the azide groups is the bond angle in the chain of atoms N−N−N, which characterizes the degree to which the geometry of the given groups approaches the geometry of the cyclic transition state [4,8]. Previous PM3 calculations showed that the bond angles in the azido groups of phenylazide, *para*-nitrophenylazide, and picrylazide are respectively equal to 169.6, 169.2, and 168.3° [15,18], and investigations of the reactions of these compounds with dipolarophiles revealed huge differences in their reactivity [4,8]. From these data, it was clear that the reactivity of azides in fact correlates with the magnitudes of the bond angles in the azido groups, and even a small increase in the bending in the chain of atoms N−N−N corresponds to a significant increase in the reactivity of the azides. However, the differences in the LUMO energies of the monoazides compared did not make it possible to give a quantitative assessment of these effects. The only work done in this direction was an investigation of the correlation between the geometries of the azido groups and their ability to undergo photolytic decomposition [9]. The calculations done in that paper showed that a decrease in the bond angle in the azido group from 180° to 150° promotes a 23 kcal/mole decrease in the activation energy for the process. Considering the absolutely identical nature of the change in reactivity of the azides in photolytic/thermal decomposition reactions and 1,3-dipolar cycloaddition [11], the data in [9] allow us to advance the hypothesis that cycloaddition reactions which occur without rupture of the $N_{(\alpha)}-N_{(\beta)}$ bonds of the azido groups are even more sensitive to a change in the bond angles in the azido groups.

The calculations suggest (Table 4) that the strongest difference between the characteristics of the γ-azido groups of pyridines Ia, b are the values of the bond angles for these groups (atypically small for azides), which are 3.32-3.41° smaller than the corresponding angles in α-azido groups of compounds Ia, b and are 1.95-2.01° smaller than the bond angle in the azide group of the exceptionally reactive picrylazide [18]. Considering that even a small decrease in bond angle in the azido group is connected with significant increase in reactivity of the azides in reactions with dipolarophiles [4,8], we can say that it is specifically the considerable (on the scale of such changes) difference in bond angles of the α- and α-azido groups of compounds Ia, b which is the main reason for the significantly different reactivity of these groups. It is important to note that a decrease in bond angles in the azide groups does not always correlate with the degree of conjugation of the given groups with the aromatic ring. Thus, according to the $C-N_{(\alpha)}$ and $N_{(\alpha)}-N_{(\beta)}$ bond lengths, the α-azido group in pyridines Ia-IIIa (Table 3) are characterized by stronger conjugation with the pyridine ring compared with the γ-azide group of pyridine Ib, although in this case there are large bond angles (Table 4). The most likely reason for the decrease in bond angles in the γ-azido group of pyridines Ia, b, in our opinion, is the steric effect of the substituents in positions 3 and 5 of the pyridine ring in molecules of these compounds. Thus, according to PM3 calculations, the bond angle in the azido group of 4-azidopyridine is only 169.44° [15]. One result of the effect of the *ortho* substituents on the geometry of the γ-azido groups of compounds Ia, b is a significant increase in the $C-N_{(\alpha)}-N_{(\beta)}$ bond angle, which is 2.94-4.44° higher than analogous angles for α-azido groups of compounds Ia, b-IIIa, b (Table 4). It is interesting that as a result of recent studies on the correlation between reactivity of hetaryl azides and the magnitude of the $C-N_{(\alpha)}-N_{(\beta)}$ angle in molecules of these compounds, the hypothesis has been discussed that the considered parameters have a marked influence on the dipolar activity of the azide groups, and it has been reported that an increase in the $C-N_{(\alpha)}-N_{(\beta)}$ angle by only 0.47° corresponds to a decrease in the activation energy for thermolysis of azides by 9 kcal/mole, while thermal decomposition of azides in turn can be a test reaction for assessing the reactivity of the same compounds relative to dipolarophiles [11]. Despite the obvious interconnection between the chemical properties of azides and the $C-N_{(\alpha)}-N_{(\beta)}$ bond angles in molecules of these compounds, it seems more correct to us to analyze the relationship between the reactivity of azides and the magnitude of the bond angle in the N–N–N chain, which directly characterizes the geometry of a given type of dipole.

Comparison of the energy characteristics of pyridines Ia, b-IIIa, b (Fig. 3) with the characteristics and geometry of the azide groups in molecules of these compounds (Fig. 4, Tables 2-4) allows us for the first time to analyze the interesting effect when two azides are competing in the dipole–LUMO-controlled cycloaddition reaction and the azide with the higher LUMO energy presents the higher reactivity. Thus, as has already been noted above, addition of a TBPA molecule at the γ-azido group of pyridine Ia yields cycloadduct IIa, the LUMO energy of which is 1.29 kcal/mole lower than for the starting compound Ia. Nevertheless, the reaction of compound Ia with *tert*-butylphosphaacetylene stops at the stage of formation of cycloadduct IIa [3]. The LUMO energies of azidopyridines Ib and IIb are even more different (10.86 kcal/mole). However, even in this case, the reaction of pyridine Ib with dipolarophiles led to a mixture of cycloadducts IIb and IVb, in which compound IIb was the major product [3]. All these data suggest that despite the lower values of the LUMO energies, azidopyridines IIa, b have proved to be either less reactive or comparable in reactivity with the original pyridines Ia, b. Fig. 4 and the data presented in Tables 2-4 provide supporting evidence that the observed effect is due to special electronic properties and geometry of the γ-azido groups of compounds Ia, b, which are distinguished by enhanced electrophilicity of the terminal nitrogen atoms, a greater contribution of their AO's to the LUMO's, and an enhanced degree of bending of the nitrogen atom chain. The overall effect of these factors proves to be so significant that it balances out the difference in LUMO energies for azidopyridines Ib and IIb and ensures an overwhelming advantage in reactivity of pyridines Ia over its derivatives IIa.

Comparison of the LUMO energies of pyridines Ib and IIb, equal in reactivity (Fig. 3), shows that the differences in electronic properties and geometry for the γ-azido groups of compound Ib and the azido groups of derivative IIb are manifested in an effect corresponding to a change in the LUMO energy of the azide by about 10 kcal/mole. In turn, the identical geometric and electronic characteristics of the α-azido groups of pyridines Ia, b-IIa, b allows us to say that addition of a molecule of *tert*-butylphosphaacetylene at the γ-azido groups of compounds Ia, b is a more favorable process than the reaction at the γ-azido groups of the same compounds, by about 10 kcal/mole.

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