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Effect of the Molecular Structure on the Strength of the C–NO_2 Bond in a Series of Monofunctional Nitrobenzene Derivatives

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Abstract—Geometric parameters and formation enthalpy and the enthalpy of the radicals formed during the homolytic breakage of C–NO_2 bond in 37 aromatic nitro compounds were calculated using different bases of the hybrid density functional method B3LYP, as well as the composite CBS-QB3 methods. On the basis of thermochemical data, were calculated the C–NO_2 bond dissociation energy and the activation energy of the radical gas-phase decomposition. Donor substituents were shown to cause an increase in the C–NO_2 bond dissociation energy, while the acceptors decrease it. The values of activation energies of gas-phase decomposition of aromatic nitro compounds calculated basing on the C–NO_2 bond dissociation energy are in good agreement with experiment.

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Aromatic nitro compounds are widely used as brizant explosives, intermediates in the synthesis of dyes, medicines, and several others industrial products [1]. Ability to decompose at relatively low temperatures made it necessary to study the kinetics and mechanism of thermal decomposition of nitroarenes [2]. Of great scientific and practical interest is the problem of the influence of molecular structure changes in a series of Arrhenius parameters of the primary act of the gas-phase monomolecular decomposition reactions. Currently, there are sufficiently detailed data on the kinetics of gas-phase decomposition of nitrobenzene and its simple derivatives, however, to interpret them in terms of one or another mechanism of the primary act of reaction is quite difficult [2–8].

It is assumed [2, 3] that nitrobenzene and the majority of its monofunctional derivatives decompose along the radical mechanism with the homolytic cleavage of the C–NO_2 bond:

$$R–NO_2 \rightarrow R^{\bullet} + NO_2^{\bullet}. \quad (1)$$

Decomposition of some nitroarenes with the hydrogen-containing substituents (CH_3, NH_2, OH) in *ortho*-position [2, 3], as well as, obviously, dinitrobenzene [3, 9] and several other polynitrobenzenes with nitro groups in *ortho*-position apparently follows to various non-radical mechanisms.

In the case of radical mechanism, the dissociation energy (D(C–N)) of the cleaving bond in the primary act of the reaction can be determined with the equation [2]:

$$D(\text{C–N}) = E - RT, \quad (2)$$

where E is activation energy, T is average temperature of the range in which was carried out experimental study, R is universal gas constant.

However, the calculation of the dissociation energy with Eq. (2) is associated with considerable difficulties, both technical and fundamental nature [3]. The process of thermal decomposition of aromatic compounds in the gaseous state is quite complicated [2, 4]. Due to many concurrent secondary reactions, as well as high rate of the process of decomposition on the walls of the reaction vessel, obtaining the Arrhenius parameters of the reaction primary act is very difficult. Perhaps for this reason, experimental

data on the kinetics of gas-phase decomposition obtained in different research groups vary considerably [2–4]. The most reliable results were obtained for a large number of aromatic nitro compounds in [5, 6, 10, 11].

There is another serious problem hindering the calculation of D(C–N) from the experimental data on the kinetics of gas-phase decomposition using Eq. (2). The issue is that the experimentally measured effective rate constant for the reaction of thermal decomposition used at the calculation of the Arrhenius parameters may include the parallel alternative processes of thermal decomposition. According to experimental [8, 12] and theoretical investigations, the monomolecular decomposition of nitrobenzene and its derivatives may include a nitro-nitrite rearrangement (NNR), which activation enthalpy, according to quantum-chemical calculations, is below than the D(C–N). In addition, quite recently [3, 9] was shown that with the radical mechanism of the primary act of the nitrobenzene decomposition may compete a reaction of formation of a bicyclic compound which then decomposes by multistage biradical mechanism.

Thus, for correct interpretation of the results of the experiment is needed a reliable, independent determination of barriers and rate constants of alternative reactions.

Thermochemical methods for determining the D(C–N) are not very useful due to the lack of reliable data on the formation enthalpy of aromatic radicals formed during the homolytic cleavage of C–NO_2 bond. The estimates obtained using different quantum-chemical methods are poorly mutually consistent. The values of activation energy D(C–N) sufficiently fitting the experimental data were obtained by B3LYP/6-31G(d) calculations [13–16]. However, this method is not good for the finding formation enthalpy, and a satisfactory agreement with experiment is achieved by partial compensation of errors in the formation enthalpy of initial compounds and reaction products using Eq. (3):

$$D(\text{C–N}) = \Delta_f H^0_{\text{R}\cdot} + \Delta_f H^0(\text{NO}_2) - \Delta_f H^0(\text{R–NO}_2). \qquad (3)$$

In this regard, our work was undertaken a study of the possibility to calculate the formation enthalpy of aromatic nitro compounds and D(C–N) different bases of B3LYP method. In addition, we consider the possibility of using for this purpose the multistep composite quantum-chemical methods on the example of CBS-QB3. In recent years such methods were widely used to study hydrocarbons and some other classes of organic compounds [22, 23].

The calculations were performed using quantum-chemical programs Gaussian98 and Gaussian03 [24, 25] by the hybrid DFT method B3LYP with different basis sets [6-31G(d), 6-31G(d,p), 6-31G(df,p), 6-31G(d',p'), 6-31G(d'f,p'), 6-31+G(d,p), 6-311G(df,p), 6-311G(2df,p), 6-311++G(df,p), and 6-311++G(3df,3pd)], as well as the composite method CBS-QB3. The formation enthalpies of compounds and radicals were estimated using standard methods from their total electronic energy on the basis of the formation enthal-pies of atoms and calculation of the zero vibrations energy.

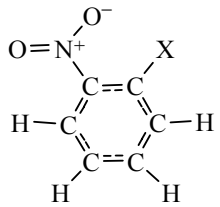
Table 1 shows the main geometric parameters of the two molecules (nitrobenzene and *ortho*-chloro-nitrobenzene) as an example for the analysis of influence of using different basis sets on the geometric parameters.

The geometry of aromatic nitro compounds is defined by the mutual influence in the "nitro group–benzene ring–substituent" system. For all compounds of this type is typical the benzene ring deformation under the influence of nitro groups and substituents.

The potential of internal rotation of NO_2 group in nitrobenzene molecule, according to the microwave data [18], has a minimum at $\varphi(NO_2) = 0°$, that is, at the planar configuration of the molecule. Electronography study allows to determine the average value of the dihedral angle between the planes of benzene ring and nitro group, which for nitrobenzene is 13°, which does not coincide with the equilibrium value. The same situation appears to be the case for the nitrobenzene *meta*- and *para*-derivatives, where the minimum of the internal rotation potential of NO_2 group corresponds to 0°, while the non-planar conformation determined by electronography are associated with torsional vibrations of nitro groups.

A systematic study of the geometry of aromatic nitro compounds was initiated in the sixties. To the moment, the geometrical parameters of more than 100 molecular crystals were revealed by X-ray diffraction. The number of compounds studied in the gaseous state is much smaller. Owing to a considerable uncertainty in the bond lengths and angles of the free molecules it is impossible to trace the effect of structural changes on the parameters of the reaction center (C–NO_2 group) in this series [17, 18]. In a review of experimental data [18] is noted that the values of C–N

Table 1. The geometric parameters of the reaction center of the nitrobenzene and *o*-chloronitrobenzene molecules in the gas phase from experimental data [17] and quantum-chemical calculations, obtained by CBS-QB3 and B3LYP with different basis sets



Method, basis	Bond lengths, pm				Bond angles, deg			φ(NO_2), deg[d]
	C–C[a]	C–N	N–O[b]	C–X[c]	ONO	CC_NC	CC_XC	
Nitrobenzene								
Experiment	139.9	148.6	122.3	–	125.3	123.4	–	13.0
B3LYP/6-31G(d)	139.4	147.4	123.1	–	124.6	122.3	–	0.0
B3LYP/6-31G(d,p)	139.4	147.4	123.1	–	124.6	122.3	–	0.0
B3LYP/6-31G(df,p)	139.3	147.4	122.9	–	124.6	122.4	–	0.0
B3LYP/6-31G(d',p')	139.4	147.8	122.5	–	124.8	122.3	–	0.0
B3LYP/6-31G(d'f,p')	139.3	147.8	122.5	–	124.8	122.3	–	0.0
B3LYP/6-31+G(d,p)	139.4	147.4	123.1	–	124.6	122.3	–	0.0
B3LYP/6-311G(df,p)	138.8	148.0	122.2	–	124.8	122.3	–	0.0
B3LYP/6-311G(2df,p)	138.7	147.7	122.1	–	124.8	122.2	–	0.0
B3LYP/6-311++G(df,p)	138.9	148.0	122.3	–	124.6	122.3	–	0.0
B3LYP/6-311++G(3df,3pd)	138.8	147.7	122.1	–	124.7	122.3	–	0.0
CBS/B7 (CBS-QB3)	139.1	148.1	122.3	–	124.9	122.3	–	0.0
o-Chloronitrobenzene								
Experiment	138.7	146.2	122.6	172.1	123.6	121.4	121.7	34.0
B3LYP/6-31G(d)	140.3	147.4	123.1	174.3	125.1	120.6	118.7	33.2
B3LYP/6-31G(d,p)	140.3	147.4	123.1	174.3	125.1	120.6	118.7	33.1
B3LYP/6-31G(df,p)	140.2	147.4	123.0	174.1	125.2	120.7	118.6	34.0
B3LYP/6-31G(d',p')	140.3	147.8	122.6	174.5	125.4	120.6	118.7	33.8
B3LYP/6-31G(d'f,p')	140.2	147.8	122.6	174.3	125.4	120.6	118.7	34.5
B3LYP/6-31+G(d,p)	140.3	147.4	123.3	174.2	125.2	120.9	118.6	39.3
B3LYP/6-311G(df,p)	139.6	147.8	122.3	174.1	125.5	120.7	118.7	38.3
B3LYP/6-311G(2df,p)	139.5	147.6	122.2	173.6	125.4	120.7	118.7	37.3
B3LYP/6-311++G(df,p)	–	–	–	–	–	–	–	–
B3LYP/6-311++G(3df,3pd)	139.6	147.5	122.1	172.9	125.5	121.0	118.4	40.8
CBS/B7 (CBS-QB3)	139.9	148.0	122.4	174.1	125.5	120.7	118.7	37.1

[a] Bond length, adjacent to the nitro group. [b] Length of the longest bond in the case of asymmetry in the bond lengths, [c] X is a substituent, not NO_2 group (X = OH, NH_2, CH_3). [d] The angle of turn of the nitro group from the plane of benzene ring.

bond length in the series of aromatic nitro compounds have been determined with rather large errors. For this reason the effect of substituents on the length of this bond can not reveal basing on the analysis of experimental data. In this regard, we shall not give the results of the experimental studis for other monofunctional nitrobenzene derivatives.

Experimental values of formation enthalpies of free molecules of nitroarenes also not enough precise: in some cases the results obtained by different authors differ by 15–20 kJ mol^{-1} [19–21].

In the molecules of *ortho*-derivatives of nitrobenzene due to a considerable steric hindrance the equilibrium configurations are essentially nonplanar. Therefore, we can assume that in the *ortho*-derivatives of nitrobenzene experimentally determined conformations are close to equilibrium.

Using different bases within the B3LYP method leads to quite similar results, however, according to the calculation one can reveal certain trends in changing values of geometric parameters. For example, the extension of the basis by introducing splitting and adding polarization orbitals [6-311G(2df,p) and 6-311++G(3df, 3pd)] leads to a decrease in the predicted values for the lengths of the bonds CC adjacent to the reaction center (the C–NO_2 group) and of *r*(NO). It is worth noting a significant differences in the values of the dihedral angle, which are mainly observed in the *ortho*-substituted derivatives of nitrobenzene when the NO_2 group is turned out of the plane of the molecule. In this case, there is a tendency to increase the rotation angle at extension the basis. Inclusion of diffuse functions to the basic set leads to greater turn the NO_2 group out of the plane of the molecule.

As the different bases in the B3LYP method give similar values of key geometric parameters of the reaction center, in the Table 2 we present the data on the geometry of the studied compounds obtained with the 6-31G(d,p) basis. Table 1 shows that this basis gives the basic geometric parameters of nitrobenzene close to the experimental values. From the data presented in Table 2 follows that the estimates obtained by this method are in satisfactory agreement with the experimental data on the geometry of benzene, halobenzenes, phenol, aniline and toluene.

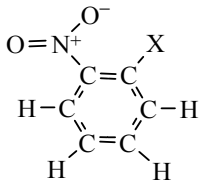
Our results show that substitution of hydrogen atoms in the nitrobenzene molecule by the donor substituents F-, Cl-, Br-, H_2N-, HO-, H_3C-, the *r*(C–N) magnitude decreases, the effect being most strongly pronounced for *ortho*- and *para*-isomers. A similar trend in *r*(C–N) is obviously connected with the direct polar conjugation of the donor substituent with the acceptor (NO_2 group). In the molecules of *ortho*-halonitrobenzene and *ortho*-nitrotoluene the conjuga-tion is violated by the steric factors, as indicated by the out of plane turn of NO_2 group, and in the case of fluorine this violation is manifested in the least degree, due to the relatively small size of fluorine atom. In the *meta*-isomers, the direct polar conjugation is absent and the value of *r*(C–N) for them is little different from that of nitrobenzene.

The existence of strong intramolecular hydrogen bond in *ortho*-nitrophenol has long been demonstrated experimentally, including using the methods of IR and NMR spectroscopy, as well as an analysis of some physical and physico-chemical properties. For example, a possibility of formation of intermolecular hydrogen bonds in the *ortho*-isomers is significantly reduced, the boiling point of *ortho*-nitrophenol (215°C) is significantly lower than that of *para*-nitrophenol (279°C). Formation of sixmembered ring favors the stability of intramolecular hydrogen bond in *ortho*-nitrophenol. Note that the results of our calculations for a model structure of *ortho*-nitrophenol in which the OH group was oriented in such a way as to preclude the formation of intramolecular hydrogen bond led to the conformation in which the value of *r*(C–N) does not differ from the calculated values for nitrobenzene and *meta*-nitrophenol.

Analysis of the geometric parameters of *ortho*-nitroaniline also indicates the formation in this molecule of the intramolecular hydrogen bond. In particular, *r*(C–N) in *ortho*-nitroaniline is significantly reduced compared with the *meta*- and *para*-isomers, while *r*(NO) is significantly increases. This trend, but even more strongly pronounced, is observed for *ortho*-nitrophenol.

However, the theoretically possible formation of intramolecular hydrogen bond in *ortho*-nitrotoluene is not confirmed by the calculations. In this case, no significant increase in *r*(NO) compared with the *meta*- and *para*-isomers is obtained. The C–N not decreases, but rather increases, indicating the internal stresses in the molecule causing repulsion. This conclusion is confirmed by the significant value of the angle of rotation of NO_2 group relative to the plane of the ring, which probably can lead to a lower barrier for the radical cleavage of C–N bond.

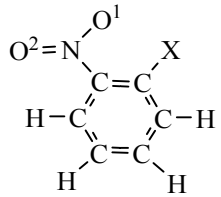
Table 2. Principal geometric parameters of molecules of some arenes, nitrobenzene and some of its monofunctional derivatives according to the method B3LYP/6-31G(d,p)



Comp. no.	Compound	Bond lengths pm				Bond angles, deg			φ(NO_2), deg[d]
		C–C[a]	C–N	N–O[b]	C–X[c]	ONO	CC_NC	CC_XC	
I	Benzene	139.6 (139.7)	–	–	–	–	–	–	–
II	Fluorobenzene	139.0 (138.3)	–	–	135.1 (135.4)	–	–	122.3 (123.4)	–
III	Chlorobenzene	139.4 (140.2)	–	–	176.1 (172.5)	–	–	121.4 (120.4)	–
IV	Bromobenzene	139.3 (142.0)	–	–	191.4 (185.0)	–	–	121.5 (117.4)	–
V	Phenol	139.9 (139.8)	–	–	136.8 (135.4)	–	–	120.1	–
VI	Aniline	140.5 (139.2)	–	–	139.8 (143.1)	–	–	118.6	–
VII	Toluene	140.1 (139.4)	–	–	151.1 (151.3)	–	–	118.2 (119.0)	–
VIII	Benzaldehyde	140.3	–	–	148.0	–	–	119.9	–
IX	Benzoic acid	140.2	–	–	148.7	–	–	120.0	–
X	Nitrobenzene	139.4	147.4	123.1	–	124.6	122.3	–	0.0
XI	*o*-Fluoronitrobenzene	140.2	146.9	123.2	133.4	124.8	119.8	120.0	12.8
XII	*m*-Fluoronitrobenzene	139.3	147.5	123.0	134.5	124.9	122.8	122.3	0.0
XIII	*p*-Fluoronitrobenzene	139.5	146.9	123.1	134.2	124.7	122.1	122.5	0.0
XIV	*o*-Chloronitrobenzene	140.3	147.4	123.1	174.3	125.1	120.6	118.7	33.1
XV	*m*-Chloronitrobenzene	139.3	147.6	123.0	175.3	124.9	122.8	121.3	0.0
XVI	*p*-Chloronitrobenzene	139.3	147.1	123.1	175.0	124.8	122.1	121.5	0.0
XVII	*o*-Bromonitrobenze	140.1	147.5	123.1	189.8	125.1	120.6	118.7	33.2
XVIII	*m*-Bromonitrobenze	139.3	147.6	123.0	190.6	124.9	122.7	121.3	0.0
XIX	*p*-Bromonitrobenze	139.3	147.1	123.1	190.3	124.8	122.1	121.5	0.0
XX	*o*-Nitrophenol	141.8	144.6	125.4	133.5	122.4	121.3	117.6	0.0
XXI	*m*-Nitrophenol	139.4	147.6	123.0	136.2	124.6	123.1	120.0	0.0
XXII	*p*-Nitrophenol	139.7	146.2	123.3	135.7	124.4	121.5	120.3	0.0
XXIII	*o*-Nitroaniline	142.5	144.8	124.7	135.5	122.4	121.2	116.3	0.0
XXIV	*m*-Nitroaniline	139.2	147.5	123.2	138.9	124.4	123.1	118.5	0.4
XXV	*p*-Nitroaniline	139.7	145.6	123.4	137.8	124.2	121.0	118.8	0.1
XXVI	*o*-Nitrotoluene	141.0	147.5	123.2	150.9	123.8	122.5	115.8	13.0
XXVII	*m*-Nitrotoluene	139.3	147.3	123.1	151.0	124.5	122.5	118.3	0.3
XXVIII	*p*-Nitrotoluene	139.3	146.9	123.1	150.9	124.5	121.8	118.5	0.1
XXIX	*o*-Nitrobenzoic aldehyde	140.7	147.5	123.2	150.3	124.7	122.0	117.2	25.8
XXX	*m*-Nitrobenzoic aldehyde	139.3	147.4	123.0	148.6	124.9	122.1	120.1	0.0
XXXI	*p*-Nitrobenzoic aldehyde	139.6	147.7	123.0	148.7	124.9	122.7	120.2	0.0
XXXII	*o*-Nitrobenzoic acid	140.2	147.4	123.0	150.1	125.2	121.9	117.8	31.8
XXXIII	*m*-Nitrobenzoic acid	139.4	147.5	123.0	149.1	124.9	122.4	120.1	0.0
XXXIV	*p*-Nitrobenzoic acid	139.4	147.6	123.0	149.2	124.9	122.5	120.3	0.0
XXXV	*o*-Dinitrobenzene	139.8	147.5	122.8	–	126.1	120.2	–	40.1
XXXVI	*m*-Dinitrobenzene	139.3	147.0	122.9	–	125.4	119.9	–	0.0
XXXVII	*p*-Dinitrobenzene	139.3	147.8	122.9	–	125.2	122.7	–	0.0

[a] In parentheses are the experimental values [26–33]. [b] Length of the longest bond in the case of asymmetry in the bond lengths, [c] X is a substituent, not NO_2 group (X = OH, NH_2, CH_3). [d] The angle of turn of the nitro group from the plane of benzene ring.

Table 3. Parameters of the electronic structure of aromatic nitro compounds according to the method B3LYP/6-31G(d,p) (atomic charges in units of electron charge, dipole moments in D)



Comp. no.	q_C, *e*	q_N, *e*	q_{O1}, *e*	q_{O2}, *e*	μ_{calc}, D
X	0.242	0.387	–0.395	–0.395	4.56
XI	0.196	0.384	–0.380	–0.395	5.13
XII	0.241	0.390	–0.390	–0.390	3.95
XIII	0.241	0.388	–0.397	–0.397	3.34
XIV	0.251	0.359	–0.363	–0.380	4.96
XV	0.240	0.393	–0.389	–0.390	3.85
XVI	0.240	0.389	–0.394	–0.394	2.92
XVII	0.228	0.360	–0.365	–0.380	4.77
XVIII	0.238	0.393	–0.389	–0.390	3.87
XIX	0.243	0.389	–0.394	–0.394	3.12
XX	0.229	0.387	–0.454	–0.386	3.60
XXI	0.240	0.387	–0.392	–0.394	5.80
XXII	0.241	0.382	–0.406	–0.404	5.34
XXIII	0.239	0.367	–0.449	–0.406	4.73
XXIV	0.239	0.385	–0.400	–0.396	5.66
XXV	0.239	0.375	–0.413	–0.413	7.16
XXVI	0.197	0.375	–0.402	–0.395	4.30
XXVII	0.244	0.387	–0.397	–0.397	4.88
XXVIII	0.239	0.385	–0.399	–0.399	5.21
XXIX	0.200	0.362	–0.386	–0.375	4.55
XXX	0.235	0.393	–0.391	–0.391	2.19
XXXI	0.249	0.393	–0.389	–0.387	2.51
XXXII	0.226	0.365	–0.382	–0.378	4.03
XXXIII	0.231	0.394	–0.390	–0.393	2.72
XXXIV	0.252	0.391	–0.389	–0.390	3.68
XXXV	0.255	0.368	–0.364	–0.367	6.65
XXXVI	0.245	0.390	–0.380	–0.386	4.22
XXXVII	0.261	0.395	–0.384	–0.384	0.00

Effect of molecular structure can be seen also in the change of bond angles, although their changes in the series predicted by calculations are not large. For example, the ONO angle in the *ortho*-nitroaniline and *ortho*-nitrophenol is considerably less than in the *meta*- and *para*-isomers, due obviously to the formation of intramolecular hydrogen bonds. At the same time, the calculation predicts the largest in a series of isomers ONO angle in the *ortho*-nitrotoluene. In the most of the studied compounds the ONO angle of *para*-isomer is substantially less than of the respective *meta*-isomer.

Introduction to the molecule of an acceptor substituent (COH, COOH and NO_2 groups) causes a slight increase in *r*(C–N). In contrast to other aromatic nitro compounds presented in Table 2, for dinitrobenzenes observed though poorly marked, but quite a noticeable decrease in *r*(NO). In contrast to the compounds with donor substituents, the length of the C–X bond for the acceptor groups in *ortho*-position does not decreases but significantly increases compared with the *meta*- and *para*-isomers.

Charges on the atoms of the reaction center in the studied compounds vary slightly (Table 3).

For *ortho*-halonitrobenzenes and *ortho*-dinitrobenzene can be noted a slight decrease in the negative charge on the oxygen atoms of NO_2 group compared with the corresponding *meta*- and *para*-isomers. In these compounds the nitro group is turned significantly relative to the plane of the benzene ring. Conversely, the negative charge increases significantly in the compounds where the hydrogen bond is formed (*ortho*-nitroaniline and *ortho*-nitrophenol).

Table 4 shows the comparison of experimental data and quantum-chemical estimates of the values of formation enthalpy calculated by usual methods from the total electronic energy on the basis of the enthalpies of formation of atoms and calculated energy of zero vibrations. Comparison with experimental data shows that in most cases the calculation satisfactorily reproduces both the absolute values of formation enthalpy, and in particular the tendency of their change in the series. Note that the accuracy of experimental determination of formation enthalpy in a series of aromatic nitro compounds is low.

Analysis of the results presented in Table 4 shows that the best consistence with experimental values is obtained with the bases 6-31G(d,p), 6-31G(df,p) and 6-31G(d'f,p') in the DFT-B3LYP method: the average errors for the studied compounds are 12.9, 11.7, and 8.1 kJ mol^{-1} respectively, which is comparable to the differences of experimental evaluations obtained by different authors [19,38]. As to the used by us composite method CBS-QB3, one can also note a good agreement with available experimental data (average error amounts to 13.0 kJ mol^{-1}). But this method consumes much more computational time than the DFT methods. Therewith, the results obtained with this complicated method, are on the level of the results

obtained by simpler methods of density functional, or sometimes even worse.

Of the other bases used in the study, the results close to the experimental points give considerably extended bases, such as 6-311G(2df,p) and 6-311++G (3df, 3pd) (average error 20.3 and 25.1 kJ mol^{-1}, respectively). It is interesting that the majority of bases used in the work overstate the value of the formation enthalpy in comparison with the experimental data, and the bases 6-31G(df,p) and CBS-QB3 understate it.

While discussing above the data on the geometry of *ortho*-nitrotoluene, *ortho*-nitroaniline and *ortho*-nitrophenol, we mentioned a possibility of intramolecular hydrogen bonding in these compounds. The findings

Table 4. Formation enthalpies of aromatic nitro compounds (kJ mol^{-1}) from experimental data [19, 34–38] and quantum-chemical calculations, obtained by CBS-QB3 and B3LYP with different basis sets

Comp. no.	B3LYP/6-31G(d)	B3LYP/6-31G(d,p)	B3LYP/6-31G(df,p)	B3LYP/6-31G(d',p')	B3LYP/6-31G(d'f,p')	B3LYP/6-31 +G(d,p)
I	116.6	91.2	78.7	103.5	89.2	143.6
II	–90.1	–111.3	–128.0	–95.9	–117.4	–42.3
III	101.7	80.5	65.4	91.1	75.0	138.9
IV	123.5	102.1	78.4	110.8	88.7	139.5
V	–35.7	–71.4	–87.2	–59.2	–77.9	–15.0
VI	138.0	98.9	81.9	110.2	91.4	148.6
VII	90.9	58.3	45.0	72.3	56.9	122.9
VIII	2.4	–22.3	–39.1	–9.2	–29.7	48.2
IX	–231.7	–266.8	–286.1	–253.2	–277.7	–190.0
X	92.0	70.8	50.4	82.3	58.8	144.0
XI	–85.8	–102.8	–128.0	–88.2	–119.7	–8.5
XII	–108.4	–125.4	–150.1	–110.9	–141.8	–34.3
XIII	–112.6	–129.7	–154.4	–115.1	–146.1	–38.7
XIV	115.1	98.1	74.4	107.6	81.6	176.3
XV	85.2	68.1	45.1	77.9	52.6	147.2
XVI	82.2	65.1	42.0	74.9	49.5	143.8
XVII	133.1	116.0	82.7	124.4	91.9	169.6
XVIII	106.6	89.3	57.4	96.8	65.3	141.8
XIX	104.0	86.7	54.6	94.0	62.5	139.6
XX	–84.2	–116.4	–139.4	–103.9	–131.5	–34.3
XXI	–58.2	–89.7	–113.3	–78.3	–106.4	–11.8
XXII	–66.0	–97.5	–121.1	–86.0	–114.0	–19.9
XXIII	97.7	61.7	36.6	73.3	44.8	133.5
XXIV	110.0	74.9	50.0	85.6	57.4	145.8
XXV	100.2	65.2	40.0	76.2	48.0	135.1
XXVI	76.0	47.3	26.1	60.2	35.5	133.4
XXVII	64.8	36.4	15.3	49.6	25.1	121.5
XXVIII	63.3	34.9	13.8	48.2	23.6	119.7
XXIX	8.4	–12.6	–37.5	–0.7	–30.5	80.4
XXX	–14.5	–35.2	–59.9	–23.0	–52.7	56.6
XXXI	–12.3	–33.1	–57.8	–21.0	–50.7	58.8
XXXII	–215.6	–246.6	–274.9	–233.9	–268.7	–148.8
XXXIII	–249.6	–280.6	–307.8	–268.0	–301.7	–182.3
XXXIV	–248.1	–279.1	–306.4	–266.6	–300.2	–180.8
XXXV	126.5	109.5	80.2	119.9	86.3	202.6
XXXVI	83.0	69.0	37.6	76.4	43.7	164.0
XXXVII	83.6	66.3	37.9	76.7	44.1	161.1

Table 4. (Contd.)

Comp. no.	B3LYP/6-311G(df,p)	B3LYP/6-311G(2df,p)	B3LYP/6-311++G(df,p)	B3LYP/6-311++G(3df,3pd)	B3LYP/CBSB7	CBS-QB3	Experiment
I	118.9	110.6	133.2	110.5	140.5	90.6	82.8
II	–80.6	–93.7	–61.5	–87.9	–51.7	–112.0	–110.8
III	107.9	92.2	120.9	91.8	127.2	49.9	54.4
IV	145.4	134.7	159.9	138.4	171.0	90.1	105.4
V	–43.8	–56.4	–29.3	–59.7	–17.8	–88.7	–96.2
VI	124.3	113.8	135.6	106.8	151.1	95.4	87.0
VII	100.5	90.1	118.3	91.4	124.1	59.3	50.2
VIII	9.5	–4.7	29.3	–1.2	38.8	–33.2	–37.2
IX	–236.4	–253.8	–212.0	–250.0	–202.9	–296.4	–278.2
X	102.3	76.1	125.4	82.5	134.9	55.4	62.8
XI	–67.0	–98.2	–36.8	–84.9	–26.0	–116.5	–
XII	–91.0	–122.2	–61.8	–109.5	–50.7	–142.3	–
XIII	–95.2	–126.5	–66.3	–114.3	–54.8	–144.1	–
XIV	128.2	93.8	–	98.3	158.7	44.2	–
XV	99.2	65.3	–	71.0	129.6	20.8	–
XVI	96.0	62.2	117.3	67.2	126.5	18.9	–
XVII	165.2	136.1	–	145.5	–	–	–
XVIII	136.1	107.5	–	117.5	–	–	–
XIX	133.5	104.9	–	114.2	–	–	–
XX	–81.8	–112.5	–54.4	–106.6	–44.8	–137.0	–128.8
XXI	–58.6	–89.1	–34.4	–85.5	–21.3	–123.6	–105.5
XXII	–66.1	–96.7	–42.2	–93.7	–28.9	–126.9	–114.7
XXIII	91.7	64.6	113.8	64.9	130.0	52.1	63.6
XXIV	103.7	75.7	124.7	75.6	141.8	56.8	69.0
XXV	93.9	66.1	114.1	65.3	132.3	52.1	67.8
XXVI	93.1	65.5	120.5	73.3	127.9	30.5	38.9
XXVII	82.1	54.1	108.7	61.3	116.8	21.8	17.2
XXVIII	80.7	52.6	106.9	59.6	115.4	21.5	31.0
XXIX	22.2	–9.6	52.5	1.1	62.7	–44.8	–
XXX	–0.4	–32.5	–	–22.3	40.0	–62.9	–
XXXI	1.6	–30.5	–	–20.1	42.0	–61.8	–
XXXII	–214.0	–249.4	–	–239.8	–168.4	–301.2	–278.2
XXXIII	–247.2	–282.6	–	–271.7	–202.6	–326.4	–295.0
XXXIV	–245.8	–281.2	–	–270.3	–201.3	–325.8	–295.8
XXXV	141.0	95.9	172.5	108.9	186.0	66.2	84.9
XXXVI	100.0	55.4	133.4	69.3	143.9	33.4	54.0
XXXVII	100.2	55.6	134.1	69.0	144.1	32.0	50.2

based on the analysis of the geometric parameters are quite consistent with the calculated and experimental estimates of enthalpies of isomeric nitrophenols. For example, according to the data obtained with different bases used in our work, the formation enthalpy of *para*-nitrophenol by 10–20 kJ mol^{-1} higher compared to *ortho*-nitrophenol. Thermochemical estimation (14.1 kJ mol^{-1}) is also consistent with this trend. A similar trend can be observed for nitroaniline. Differences in the experimental values of the formation enthalpy of *ortho*-nitroaniline and *para*-nitroaniline is 4.2 kJ mol^{-1} [19]. In various bases the formation enthalpy of *ortho*-nitroaniline is by about 0.5–3.5 kJ mol^{-1} lower than that of *para*-nitroaniline. This indicates that intramolecular bonding in the latter is significantly weaker than in *ortho*-nitrophenol. This conclusion is

also consistent with the data on the geometry and electron density distribution in these molecules. Interestingly, that the extension of the base, as well as the use of CBS–QB3 method, leads to much smaller differences in the energy of these isomers.

In *ortho*-nitrotoluene the formation enthalpy is maximal in the series of isomers according both to a calculation using different bases, and the results of the experiment. From these data we can conclude the absence in *ortho*-nitrotoluene of intramolecular hydrogen bonding and manifestation in this molecule of the steric stress. The latter can also be judged from the turn of the nitro group relative to the plane of the ring. A bulky functional group in the *ortho* position may cause an increase in the formation enthalpy of other nitroarenes, for example, in dinitrobenzene and halonitrobenzenes.

Another enough interesting result of the influence of molecular structure on the values of formation enthalpies of the studied nitroarenes is reducing the formation enthalpy of *para*-isomer compared to the *meta*-isomers of nitrobenzene derivatives with donor substituents. This difference can be attributed to a manifestation of direct polar conjugation of the donor substituent with the acceptor nitro group. This effect is not possible in the *meta*-isomers, while in *ortho*-isomers the formation of intramolecular hydrogen bonds and steric repulsion can compete with it.

We will not comment on the results of the calculation of formation enthalpies of radicals, since

Table 5. Formation enthalpies of NO_2 and radicals formed at homolytic cleavage of C–N bond (kJ mol^{-1}) from experimental data [1, 36] and quantum-chemical calculations by CBS-QB3 and B3LYP with different basis sets

Radical	B3LYP/6-31G(d)	B3LYP/6-31G(d,p)	B3LYP/6-31G(df,p)	B3LYP/6-31G(d',p')	B3LYP/6-31G(d'f,p')
NO_2	23.0	23.0	15.4	20.5	11.5
Phenyl	361.6	340.4	327.5	352.1	337.6
1-Fluorophenyl	166.2	149.2	132.0	163.7	141.8
2-Fluorophenyl	155.9	139.0	121.8	153.8	131.9
3-Fluorophenyl	159.5	142.5	125.5	157.3	135.6
1-Chlorophenyl	353.4	336.4	320.8	346.4	330.0
2-Chlorophenyl	347.4	330.5	315.0	340.5	324.2
3-Chlorophenyl	350.4	333.5	318.0	343.5	327.1
1-Bromophenyl	373.6	356.5	332.6	364.3	342.1
2-Bromophenyl	368.7	351.6	327.7	359.6	337.5
3-Bromophenyl	371.8	354.7	330.7	362.7	340.5
1-Hydroxyphenyl	218.9	187.4	171.3	198.9	180.0
2-Hydroxyphenyl	209.0	177.5	161.4	189.2	170.2
3-Hydroxyphenyl	214.1	182.7	166.6	194.3	175.5
1-Aminophenyl	385.3	350.5	333.2	361.1	342.1
2-AAminophenyl	381.6	346.7	329.2	357.5	338.4
3-Aminophenyl	387.8	353.0	335.8	363.7	344.8
1-Methylphenyl	335.0	306.6	292.9	320.0	304.3
2-Methylphenyl	335.1	306.8	293.2	320.3	304.6
3-Methylphenyl	337.2	308.9	295.3	322.4	306.8
1-Formylphenyl	250.2	229.5	212.4	241.9	221.3
2-Formylphenyl	249.2	228.7	211.5	241.0	220.5
3-Formylphenyl	248.4	227.8	210.6	240.2	219.6
1-Carboxyphenyl	16.8	–14.0	–33.8	–1.1	–25.7
2-Carboxyphenyl	14.9	–15.9	–35.6	–3.0	–27.6
3-Carboxyphenyl	14.2	–16.7	–36.4	–3.8	–28.4
1-Nitrophenyl	348.3	335.6	310.6	342.0	318.4
2-Nitrophenyl	340.8	323.8	303.0	334.6	311.0
3-Nitrophenyl	340.3	323.2	302.5	334.1	310.5

Table 5. (Contd.)

Radical	B3LYP/6-31+G(d,p)	B3LYP/6-311G (df,p)	B3LYP/6-311G(2df,p)	B3LYP/6-311++G(df,p)	B3LYP/6-311++G(3df,3pd)	B3LYP/CBSB7	CBS-QB3	Experiment
NO_2	37.5	20.4	4.9	28.0	6.4	31.0	25.3	33.5
Phenyl	391.5	363.2	354.7	376.6	355.7	385.1	355.6	330.2
1-Fluorophenyl	217.3	175.1	161.4	193.1	167.9	204.4	164.1	–
2-Fluorophenyl	207.3	165.1	151.6	183.8	158.5	194.4	153.7	–
3-Fluorophenyl	210.5	168.5	155.1	187.2	161.8	197.7	157.3	–
1-Chlorophenyl	393.6	359.2	343.2	371.1	343.6	379.0	323.9	–
2-Chlorophenyl	387.8	353.3	337.1	365.4	337.9	372.9	316.6	–
3-Chlorophenyl	390.8	356.2	340.0	368.4	340.8	375.7	319.2	–
1-Bromophenyl	392.3	393.9	383.1	–	387.5	–	–	–
2-Bromophenyl	387.5	390.1	379.1	–	383.7	–	–	–
3-Bromophenyl	391.2	393.3	382.2	–	386.8	–	–	–
1-Hydroxyphenyl	242.5	210.2	196.9	223.6	194.1	236.4	181.8	–
2-Hydroxyphenyl	233.0	200.3	187.4	214.3	185.2	226.7	171.9	–
3-Hydroxyphenyl	238.0	205.6	192.8	219.5	190.4	231.9	180.0	–
1-Aminophenyl	398.2	370.5	359.5	380.7	353.5	397.4	358.9	–
2-AAminophenyl	395.2	367.1	356.3	377.7	350.5	394.2	355.1	–
3-Aminophenyl	399.9	373.8	362.9	384.3	357.0	400.7	363.6	–
1-Methylphenyl	369.2	343.3	332.7	360.2	334.6	367.2	320.5	–
2-Methylphenyl	367.5	344.0	333.4	360.9	335.3	367.9	320.5	–
3-Methylphenyl	372.3	346.2	335.6	363.3	337.8	370.1	325.3	–
1-Formylphenyl	298.8	256.2	241.8	275.3	246.4	285.7	232.3	–
2-Formylphenyl	298.2	255.6	241.1	274.4	245.6	285.1	233.3	–
3-Formylphenyl	297.4	254.9	240.3	274.1	244.8	284.4	232.5	–
1-Carboxyphenyl	61.9	11.8	–6.2	35.3	–1.7	45.6	–28.6	–
2-Carboxyphenyl	59.9	9.7	–8.2	33.5	–3.3	43.3	–29.7	–
3-Carboxyphenyl	59.1	9.0	–8.9	32.7	–4.0	42.7	–30.5	–
1-Nitrophenyl	407.9	358.2	331.5	380.2	338.4	391.2	333.5	–
2-Nitrophenyl	396.2	350.6	323.9	373.3	331.5	383.5	322.3	–
3-Nitrophenyl	395.6	322.4	323.5	372.7	330.7	383.0	324.0	–

reliable experimental data are available only for the phenyl and NO_2 radicals. For these compounds, the calculation satisfactorily reproduces the experimental values of the formation enthalpy, therewith, for the phenyl radical they are systematically overestimated while for NO_2 underestimated (Table 5).

Of great interest is the theoretical estimation of *D*(C–N) in a series of aromatic nitro compounds using modern quantum-chemical methods. To do this, together with the calculation of formation enthalpy should be calculated the reaction products of the homolytic cleavage of C–NO_2 bond. Calculation of *D*(C–N) is carried out according to Eq. (3).

If the recombination reaction of radicals formed during thermal decomposition is barrierless, the enthalpy of the reaction of homolytic bond cleavage $R–NO_2 \rightarrow R^{\cdot} + NO_2^{\cdot}$ does not differ from the activation enthalpy [2,3]. In this case, the activation energy of radical decomposition coincides with the C–NO_2 bond dissociation energy, and from *D*(C–N) can be estimated also the activation energy of the radical gas-phase decomposition by the Eq. (4):

$$E = D(\text{C–N}) + RT. \quad (4)$$

Table 6 shows the dependence of the hemolytic cleavage of the C–NO_2 bond in nitrobenzene, *D*(C–N), on the temperature, based on the data of quantum-chemical calculations.

As one can see, the activation energy for this reaction only slightly dependent on temperature

(within 5 kJ mol^{-1}). The slight decrease in D(C–N) with increasing temperature is compensated by an increase in RT [see Eq. (2)]. Consequently, we can evaluate the activation energy of radical decomposition of aromatic nitro compounds at standard temperature and thereby obtain rough estimates of energy changes in this process. Therefore, all further calculations carried out for the temperature 298.15 K.

If using Eq. (4) to recalculate the calculated activation energies of gas-phase decomposition to the experimental temperature (700 K), is possible to observe very good agreement with experimental estimates of activation energies (Table 7). To some extent this owes to the fact that at the calculation of dissociation energy with Eq. (1) the errors in the

Table 6. Temperature dependence of the C–NO_2 bond dissociation energy in nitrobenzene according to the method B3LYP/6-31G(d,p)

Temperature, K	D(C–N), kJ mol^{-1}	Temperature, K	D(C–N), kJ mol^{-1}
298.15	292.6	600	291.0
300	292.6	650	290.5
350	292.6	700	290.0
400	292.4	750	289.4
450	292.1	800	288.9
500	291.8	850	288.3
550	291.4	900	287.7

Table 7. Comparison of the calculated activation energies for gas-phase decomposition at the temperature of the experiment (700 K) with the experimental estimates of activation energies [2, 6] (kJ mol^{-1})

Comp. no.	B3LYP/6-31G(d)	B3LYP/6-31G(d,p)	B3LYP/6-31G(df,p)	B3LYP/6-31G(d',p')	B3LYP/6-31G(d'f,p')	B3LYP/6-31+G(d,p)
X	298.7	298.7	298.6	296.5	296.5	291.1
XI	281.1	281.2	281.5	278.4	279.2	269.3
XII	293.4	293.5	293.5	291.3	291.4	285.1
XIII	301.1	301.3	301.5	299.0	299.4	292.8
XIV	267.3	267.3	268.0	265.4	266.1	260.9
XV	291.3	291.5	291.5	289.2	289.3	284.2
XVI	297.3	297.4	297.5	295.2	295.3	290.6
XVII	269.5	269.5	271.5	266.5	267.8	266.2
XVIII	291.2	291.4	291.9	289.4	289.9	289.4
XIX	296.9	297.1	297.7	295.3	295.7	295.2
XX	332.3	333.0	332.3	329.5	329.1	320.4
XXI	296.3	296.3	296.2	294.2	294.3	288.4
XXII	309.2	309.3	309.3	307.0	307.1	301.5
XXIII	316.8	317.9	318.2	314.4	315.0	308.4
XXIV	300.7	300.8	300.8	298.6	298.7	293.0
XXV	316.6	317.0	317.4	314.2	314.5	308.4
XXVI	288.0	288.4	288.4	286.4	286.5	279.4
XXVII	299.4	299.5	299.5	297.3	297.2	289.6
XXVIII	302.9	303.1	303.1	300.8	300.8	296.1
XXIX	270.8	271.2	271.4	269.2	269.5	261.9
XXX	292.7	292.9	292.9	290.7	290.8	285.2
XXXI	289.8	290.0	290.0	287.9	287.9	282.1
XXXII	261.5	261.6	262.7	259.4	260.5	254.2
XXXIII	293.6	293.8	293.8	291.6	291.7	285.8
XXXIV	291.3	291.5	291.6	289.4	289.5	283.5
XXXV	250.8	255.2	251.9	248.7	249.7	248.8
XXXVI	286.9	283.8	287.0	284.7	284.9	275.8
XXXVII	285.8	286.0	286.1	283.9	284.0	278.1

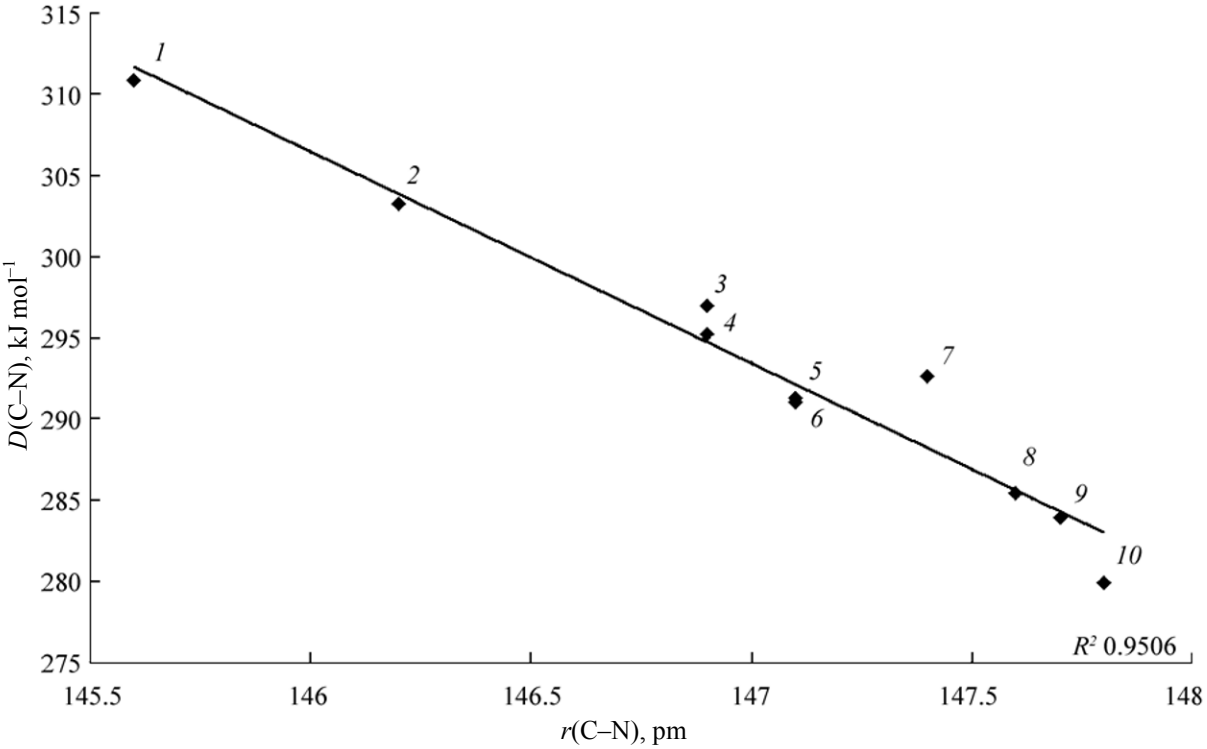
Table 7. (Contd.)

Comp. no.	B3LYP/6-311G (df,p)	B3LYP/6-311G(2df,p)	B3LYP/6-311++G(df,p)	B3LYP/6-311++G(3df,3pd)	B3LYP/CBSB7	CBS-QB3	Experiment
X	287.4	289.6	285.4	285.8	287.3	331.7	291
XI	268.5	270.6	264.1	265.2	267.5	312.0	–
XII	282.6	284.8	279.7	280.5	282.2	327.4	–
XIII	290.2	292.6	287.6	288.6	289.6	332.9	–
XIV	257.4	260.4	–	257.8	257.4	311.1	281
XV	280.6	282.9	–	279.4	280.4	327.2	293
XVI	286.6	288.9	285.3	286.2	286.3	331.7	300
XVII	255.2	258.0	–	254.5	–	–	–
XVIII	280.4	282.6	–	278.7	–	–	–
XIX	286.3	288.4	–	285.1	–	–	–
XX	318.4	320.5	312.1	313.2	318.3	350.2	–
XXI	285.4	287.5	282.9	283.2	285.1	327.0	298
XXII	298.2	300.5	295.9	296.6	297.9	338.3	–
XXIII	305.2	306.0	301.1	301.1	304.5	338.2	–
XXIV	289.9	291.6	287.2	287.4	289.5	329.8	301
XXV	306.4	307.8	304.3	304.3	305.5	343.0	308
XXVI	276.7	278.2	273.7	273.8	276.4	321.4	–
XXVII	288.4	290.4	286.3	286.6	288.2	330.2	284
XXVIII	292.0	294.1	290.5	290.7	291.8	335.3	275
XXIX	260.4	262.4	256.9	257.8	260.0	308.5	–
XXX	282.5	284.7	–	280.4	282.2	327.6	–
XXXI	279.7	281.8	–	277.4	279.5	325.8	–
XXXII	252.3	254.2	–	250.7	251.0	304.0	–
XXXIII	283.4	285.5	–	281.0	283.1	328.2	–
XXXIV	281.3	283.4	–	278.8	281.0	326.7	–
XXXV	243.6	246.6	241.7	241.9	242.3	298.8	–
XXXVI	277.1	279.6	274.0	274.7	276.7	320.3	284
XXXVII	248.7	278.9	272.7	274.3	276.1	323.5	286

enthalpies of nitro compounds and their degradation products are partially compensated.

It is important to emphasize that the calculated activation energies of gas-phase decomposition of nitroarenes, for which the most probable radical mechanism of the primary reaction act, are in good agreement with experimental results. The average error in a series of nine studied compounds, except nitrotoluene, in the bases B3LYP/6-31G(d), B3LYP/6-31G(d,p), B3LYP/6-31G (df,p), B3LYP/6-31G(d',p'), and B3LYP/6-31G (d'f,p') does not exceed ±5 kJ mol^{-1}. This value is even somewhat lower than the error in the activation energy given in the best experimental work (an average of 10 kJ mol^{-1}) [2, 4]. For a more powerful bases, the agreement is slightly worse, of the order ±8 to ±13 kJ mol^{-1}. However, the composite CBS–QB3 method used by us gives the results which rather disagree with the experimental data (±33.7 kJ mol^{-1}), apparently due to the overestimation in the calculation of enthalpies of the radicals formed by homolytic cleavage of C–NO_2 bond. Reasonably good agreement between experiment and calculation allows to use the quantum-chemical estimates for the adjustments when necessary of experimental data.

Thus, for example, has long been doubtful given in the literature values of activation energies of gas-phase decomposition of *meta*- and *para*-nitrotoluene, equal to 284 and 275 kJ mol^{-1} respectively, that is lower than that for nitrobenzene [2, 12]. To explain these data assuming radical mechanism of the primary act of the



The correlation between the C–NO_2 bond length and dissociation energy in a series of aromatic nitro compounds.

reaction is very difficult. In literature has already been suggested that the experimental values of activation energy of nitrotoluenes are not consistent with the radical mechanism. We calculated the activation energy of the radical gas-phase decomposition of *meta*- and *para*-nitrotoluenes using the B3LYP/6-31G(d,p) method. The values of 299.5 kJ mol^{-1} and 303.1 kJ mol^{-1} are slightly higher than the experimental ones and the calculated values of activation energy for nitrobenzene, which is consistent with the basic regularities of the influence of donor substituents on the strength of the C–NO_2 bond in a number of aromatic nitro compounds.

The most significant increase in activation energy among the monofunctional derivatives of nitrobenzene is observed for *para*-nitroaniline and *para*-nitrophenol. This is a result of direct polar conjugation of the donor substituents with the acceptor NO_2 group. In *meta*-isomers, the direct polar conjugation is absent, therefore for these compounds the calculation, in agreement with experiment, predicts the greatest decrease in *D*(C–N) and *E* compared with the *para*-isomers. Direct polar conjugation may also occur in the *ortho*-isomers, for example, in *ortho*-nitroaniline, and especially in the *ortho*-nitrophenol. For these compounds, the calculation predicts a maximum in the range of the values of *D*(C–N), equal to 317.9 and 333 kJ mol^{-1} respectively [according to the B3LYP/6-31G(d,p) method]. However, the decay of these molecules in the gaseous state passes through the non-radical mechanism, but through isomerization to aci-nitro form and its subsequent decay. Therefore, for these compounds the experimental estimates of activation energy of radical decay are absent. The above calculated values of *D*(C–N) can be used to consider the competition of various mechanisms of gas-phase decomposition of *ortho*-nitroaniline and *ortho*-nitrophenol, as know that at the increase in temperature should increase the decay along the radical mechanism, since to this process corresponds substantially higher value of the preexponential factor.

The estimated values of *D*(C–N) and the activation energy of radical decomposition for compounds decompose under the experimental conditions along various non-radical mechanisms apparently are enough precise. This assumption can be made because in the case of the compounds for which the radical mechanism is most likely, the experimental and calculated values of activation energy are in very good agreement. For example, if we use the calculated activation energies of gas-phase decomposition obtained by 6-31G(d,p) calculation, the average

absolute error $|E_{calc} - E_{exp}|$ for 9 of the studied compounds (**X, XIV-XVI, XXI, XXIV, XXV, XXXVI,** and **XXXVII**) is 4.1 kJ mol^{-1}. These data convincingly demonstrate the capability of quantum-chemical methods to estimate D(C–N) and the activation energy of the radical gas-phase decomposition.

Analyzing the changes in a series of values of r(C–N) and D(C–N), we noted that according to the calculation the most significant decrease in the C–NO_2 bond length and an increase in its strength is observed for the nitrobenzene derivatives with donor substituents in *para*-position. Acceptor substituents in the *para*-position, on the contrary, lead to an increase in the length of the C–NO_2. One might assume that the changes in r(C–N) and D(C–N) correlate. The data in th figure indicate the existence of such a relationship (correlation coefficient 0.975).

The study carried out shows that using the hybrid method of density functional theory gives the values of the C–NO_2 bond dissociation energy and the activation energy of gas-phase radical decomposition in good agreement with the kinetic data. At the usie of the bases 6-31G(d), 6-31G(d,p), 6-31G(df,p), 6-31G(d',p'), and 6-31G (d'f,p') the average error of the calculated and experimental values does not exceed ±5 kJ mol^{-1}. As noted, the most significant increase of the bond dissociation energy of C–NO_2 and the activation energy of the radical gas-phase decomposition in the series of compounds relate to the direct polar conjugation of the donor substituent (NH_3, OH, CH_3, F, Cl) with the acceptor NO_2 group. Acceptor substituents (NO_2, CHO, COOH) cause a decrease in the bond strength. Such trend is the most pronounced for *para*-substituted derivatives of nitrobenzene. For these derivatives is found a correlation between the change in length and strength of C–NO_2 bond.

All calculations were performed in the Kazan Branch of the Interdepartmental Supercomputer Center of Russian Academy of Sciences (http://wt.knc.ru).

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