Molecular structures of trinitromethane derivatives

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The molecular structures of trinitromethane derivatives $XC(NO_2)_3$ (X = F, Cl, Br, NC, NF_2, N_3) were studied using the density functional approach. The rules for changing the configurations of substituents in these compounds were revealed. Acceptability of the method employed for the calculations of trinitromethane derivatives is discussed.

Key words: trinitromethane, trinitromethane derivatives, nonempirical quantum-chemical calculations, molecular structure.

Mutual influence of atoms and functional groups in molecules is to a great extent responsible for the chemical and physicochemical properties of various compounds. Detailed analysis of this influence is a fundamental problem of chemical science. Numerous studies on various aspects of this problem have been reported. Naturally, the mutual influence of different structural fragments manifests itself to the greatest extent in the case of compounds with the so-called "strong" substituents including the trinitromethyl group. Therefore, considerable attention was previously given to the molecules of these compounds. It has been experimentally found[1,2] that the Hal atoms in the molecules of halo derivatives of trinitromethane, $HC(NO_2)_3$ (**1**), significantly change their "conventional" properties under the action of the $—C(NO_2)_3$ group. The molecular structures of $ClC(NO_2)_3$ and $BrC(NO_2)_3$ were studied by gas-phase electron diffraction[3] and that of $IC(NO_2)_3$ was studied by X-ray diffraction analysis.[4]

Numerous spectroscopic studies of $HalC(NO_2)_3$ compounds have been reported (see Ref. 5 and references cited therein). Unfortunately, experimental data for other types of substituents (*e.g.*, N_3 instead of Hal) are few and fragmentary.[6]

Thus, the physicochemical properties and molecular structures of $RC(NO_2)_3$ compounds have been poorly studied as yet.

In this work, we undertook an attempt to bridge this gap. Since modern quantum-chemical methods allow successful calculations of the molecular geometry of nitro compounds,[7—9] we carried out a theoretical study of the structures of $XC(NO_2)_3$ (X = F, Cl, Br, NC, NF_2, N_3) molecules in order to elucidate the mutual influence of the $—C(NO_2)_3$ group and different types of substituents.

Calculation Procedure

Calculations were carried out using the GAUSSIAN-94 program package.[10] The molecular geometries were optimized with the B3LYP density functional and 6-311+G(d,p) basis set.

Results and Discussion

Halo derivatives of trinitromethane. The calculated geometric parameters of the molecules of halo derivatives of **1** are listed in Table 1. The mutual arrangement of the atoms in these molecules is shown in Fig. 1 taking bromotrinitromethane as an example.

All oxygen atoms in the molecule can be divided into two classes, I and II. It should be noted that all the O atoms lie in the same plane, which is perpendicular to the C_3 molecular axis. As can be seen from the data listed in Table 1, for the trinitromethane derivatives we get $d(N—O_I) \geq d(N—O_{II})$, whereas the reverse holds for molecule **1**. The C—N—O angles also differ for O_I and O_{II}, but this difference is significant only for fluorotrinitromethane.

Table 1. Geometric parameters of the molecules of halo derivatives of trinitromethane, $XC(NO_2)_3$, obtained by gas-phase electron diffraction (I) and from DFT(B3LYP/6-311+G(d,p)) calculations (II)

Parameter	X = H*		X = F	X = Cl		X = Br	
	I	II	II	I	II	I	II
Bond length				*d*/Å			
C—X	1.13	1.085	1.305	1.712	1.721	1.885	1.894
C—N	1.505	1.526	1.554	1.513	1.568	1.514	1.570
$N—O_I$	1.219	1.209	1.208	1.213	1.208	1.214	1.209
$N—O_{II}$	1.219	1.214	1.208	1.213	1.205	1.214	1.206
Bond angle				ω/deg			
X—C—N	108.2	109.2	110.0	—	112.1	—	112.2
$C—N—O_I$	115.7	118.0	116.3	—	115.4	—	115.7
$C—N—O_{II}$	115.7	113.4	114.2	—	115.2	—	115.5
O—N—O	128.6	128.6	129.5	128.3	129.3	132.5	128.8
N—C—N	110.7	109.8	109.0	106.7	106.7	107.9	106.6
Torsion angle				φ/deg			
	26.3	42.0	38.2	49.3	42.9	49.5	44.0

* Given for comparison.[1]

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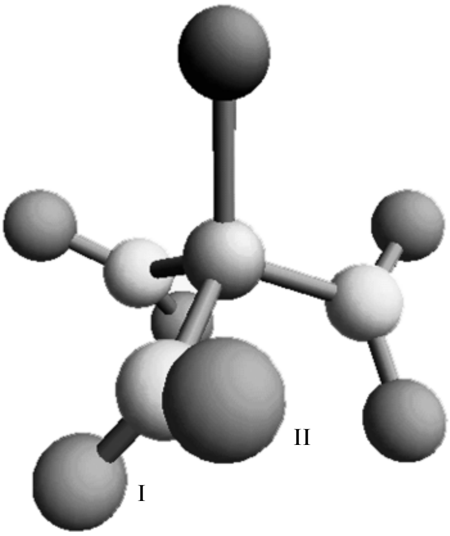

Fig. 1. Molecular geometry of $BrC(NO_2)_3$.

The CNO_2 groups can be considered planar. For all the molecules, the sum of the C—N—O_I, C—N—O_{II}, and O—N—O angles is 360° with an accuracy of 0.1°.

Let us consider the dihedral angle φ(X—C—N—O). As can be seen, the calculated φ values for $ClC(NO_2)_3$ and $BrC(NO_2)_3$ are in fairly good agreement with the results of gas-phase electron diffraction study. This is not observed for trinitromethane. We may only mention that currently it is impossible to find a correct way of studying the dependence of the angle φ on the nature of substituent X.

The method employed reproduced the C—X bond lengths in the chloro and bromo derivatives of **1** correctly. It should be noted that the calculated *d*(C—X) values for the molecules $XC(NO_2)_3$ are systematically underestimated as compared to XCH_3 [11] (Fig. 2).

As for molecule **1**, the calculated C—N bond lengths in the $ClC(NO_2)_3$ and $BrC(NO_2)_3$ molecules are overestimated. Despite this fact, lengthening of the C—N bonds as compared to the *d*(C—N) values in mononitro compounds XCH_2NO_2[12] (Fig. 3) was also reproduced correctly (on the qualitative level). Therefore, introduction of nitro groups into a molecule causes lengthening of the C—N rather than C—X bonds, though the reverse could be expected taking into account an increase in the atomic charge of substituent X (it should be noted that the H atom in the $HC(NO_2)_3$ molecule possesses acidic properties).

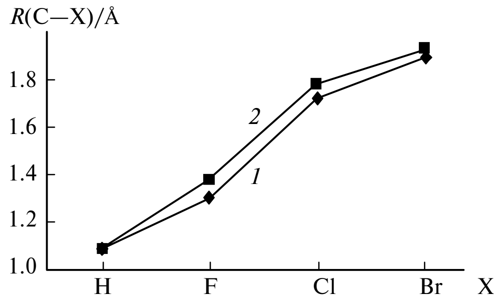

Fig. 2. Dependence of the C—X bond length in the $XC(NO_2)_3$ (*1*) and XCH_3 molecules (*2*) on the type of substituent X.

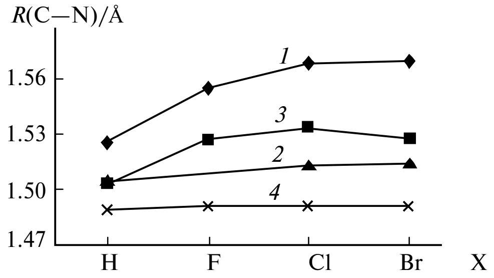

Fig. 3. Dependence of the C—N bond length in the $XC(NO_2)_3$ (*1*, *2*) and XCH_2NO_2 molecules (*3*, *4*) on the type of substituent X: calculated (*1*, *3*) and experimental data (*2*, *4*).

Since the C—N bond lengths obtained from DFT(B3LYP) calculations are overestimated, we also carried out a theoretical study of $ClC(NO_2)_3$ by the MP2/6-31G** method. The calculated values are *d*(C—Cl) = 1.708 Å, *d*(C—N) = 1.532 Å, *d*(N—O_I) = 1.236 Å, and *d*(N—O_{II}) = 1.232 Å; other parameters changed insignificantly as compared to those found using the density functional approach. As can be seen, the C—N bond length is much closer to the experimental value, though the error remains rather large. On the other hand, the MP2 method overestimates the N—O bond length. By and large the MP2 perturbation theory seems to be inappropriate for calculations of these compounds since the computational cost of the results obtained is too high as compared to that of density functional calculations.

Unfortunately, the molecules of iodine-containing compounds cannot be calculated with the 6-311G basis set and $IC(NO_2)_3$ was not studied.

Molecular geometry of $NCC(NO_2)_3$. The geometric parameters of the $NCC(NO_2)_3$ molecule are listed in Table 2. The molecule has a C_3 symmetry and the CNO_2

Table 2. Geometric parameters of the $NCC(NO_2)_3$ molecule obtained from DFT(B3LYP/6-311+G(d,p)) calculations

Parameter	Value
Bond length	*d*/Å
C—C	1.438
N—C*	1.152
C—N	1.568
N—O_I	1.207
N—O_{II}	1.205
Bond angle	ω/deg
X—C—N	111.5
C—N—O_I	114.1
C—N—O_{II}	116.4
O—N—O	129.5
N—C—N	107.3
Dihedral angle	φ/deg
	43

* The N—C bond length in the nitrile group.

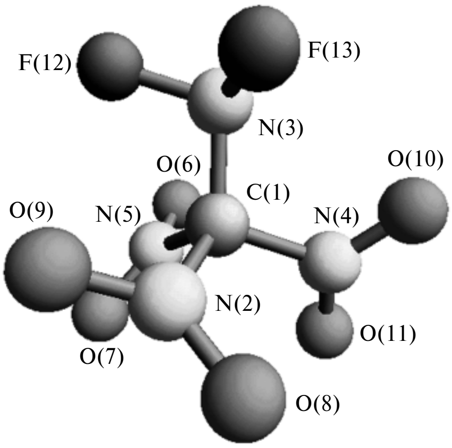

Fig. 4. Molecular geometry of $NF_2C(NO_2)_3$.

groups are planar and rotated by 43° with respect to the upright position. The $NCC(NO_2)_3$ molecule is structurally similar to the molecules of halo derivatives of **1** and the NC group behaves much like the Hal atoms.

Molecular geometry of $NF_2C(NO_2)_3$. Unlike all the above-mentioned compounds, the molecular symmetry of $NF_2C(NO_2)_3$ (Fig. 4) differs from C_3. Nevertheless, the CNO_2 groups were found to be planar, which simplifies the description of the molecular geometry.

Symmetry violation has little effect on the bond lengths and bond angles in the $C(NO_2)_3$ fragment. However, asymmetrization of the molecule due to the presence of the NF_2 group has a pronounced effect on the magnitudes of the dihedral angles φ_1—φ_3, which characterize the deviation of the NO_2 groups from the upright position (Table 3). The most distant (from the NF_2 fragment) nitro group deviates to the smallest extent (by 31.8°), whereas the $N(2)O_2$ group situated below the two F atoms of the NF_2 fragment deviates to the greatest extent (by 55.5°). The $N(5)O_2$ group situated below one F atom makes an intermediate angle of 46° with the vertical axis. This can be explained by mutual repulsion between the atoms of the nitro groups and the NF_2 group, namely, the shorter the distance from the nitro group to the F atoms, the larger the deviation of the nitro group from the upright position.

Thus, introduction of the NF_2 group leads to changes in the positions of nitro groups in the molecule. It was also of interest to reveal changes in the geometric parameters of the NF_2 group introduced into the molecule. To this end, we carried out the B3LYP/6-311+G(d,p) calculations of the NF_2CH_3 molecule, which has a C_s symmetry. The calculated geometric parameters are 1.415 and 1.465 Å for the N—F and C—N bond length, respectively; 104.5° for the C—N—F angle, and 53.4° for the H—C—N—F dihedral angle. The NF_2 group is rotated by 18° about the C—N bond, the N—F bond is shortened by 0.025 Å, and the C—N bond is lengthened by 0.012 Å.

Thus, molecules $NF_2C(NO_2)_3$ and **1** differ mainly in the angles of rotation of the nitro groups and NF_2 group.

Table 3. Geometric parameters of the $NF_2C(NO_2)_3$ molecule obtained from DFT(B3LYP/6-311+G(d,p)) calculations

Parameter	Value
Bond length	d/Å
C(1)—N(3)	1.477
C(1)—N(2)	1.556
C(1)—N(4)	1.556
C(1)—N(5)	1.550
N(2)—O(8)	1.209
N(2)—O(9)	1.206
N(4)—O(10)	1.206
N(4)—O(11)	1.208
N(5)—O(6)	1.209
N(5)—O(7)	1.205
N(3)—F(12)	1.391
N(3)—F(13)	1.389
Bond angle	ω/deg
N(3)—C(1)—N(2)	114.4
N(3)—C(1)—N(4)	107.8
N(3)—C(1)—N(5)	108.8
N(2)—C(1)—N(4)	108.4
N(2)—C(1)—N(5)	110.2
N(4)—C(1)—N(5)	106.8
C(1)—N(5)—O(6)	113.9
C(1)—N(5)—O(7)	116.6
C(1)—N(2)—O(8)	116.2
C(1)—N(2)—O(9)	114.6
C(1)—N(4)—O(10)	115.8
C(1)—N(4)—O(11)	114.9
O(8)—N(2)—O(9)	129.2
O(10)—N(4)—O(11)	129.3
O(6)—N(5)—O(7)	129.4
C(1)—N(3)—F(12)	106.1
C(1)—N(3)—F(13)	105.5
F(12)—N(3)—F(13)	103.3
Dihedral angle	φ/deg
N(3)—C(1)—N(2)—O(9) (φ_1)	55.5
N(3)—C(1)—N(4)—O(10) (φ_2)	31.8
N(3)—C(1)—N(5)—O(6) (φ_3)	46.0
N(2)—C(1)—N(3)—F(12)	−73.6
N(2)—C(1)—N(3)—F(13)	35.7

Molecular geometry of $N_3C(NO_2)_3$. Let us consider the molecule $N_3C(NO_2)_3$ as yet another representative of asymmetrical molecules. The molecular structure of $N_3C(NO_2)_3$ is shown in Fig. 5 and the geometric parameters obtained from B3LYP/6-311+G(d,p) calculations are listed in Table 4.

Similarly to all the molecules considered above, the CNO_2 groups were found to be planar. However, unlike the $NF_2C(NO_2)_3$ molecule, asymmetrical N_3 fragment causes significant changes in the C—N bond lengths in the $C(NO_2)_3$ fragment. The C—N distance in the C(2)N(3) group, which is the most distant from the N_3 fragment, was found to be 1.552 Å. Much longer, 1.589 and 1.580 Å, are these distances in other CN groups. The N(13)N(12)N(1)C(2) fragment is nearly planar.

The largest differences were found for the φ_1—φ_3 angles. One of the nitro groups situated near the N_3 group is in nearly upright position (φ_2 = 19.9°) while

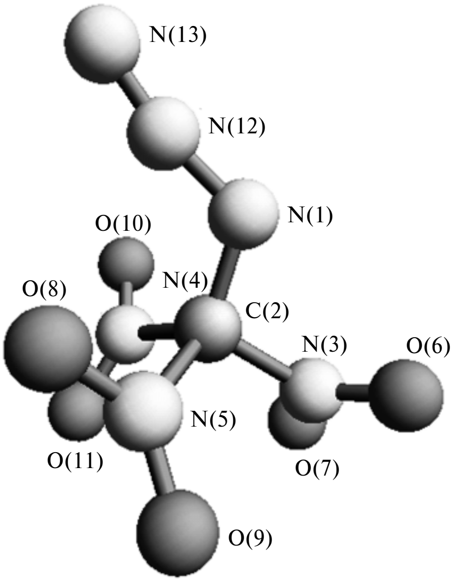

Fig. 5. Molecular geometry of $N_3C(NO_2)_3$.

Table 4. Geometric parameters of the $N_3C(NO_2)_3$ molecule obtained from DFT(B3LYP/6-311+G(d,p)) calculations

Parameter	Value
Bond length	d/Å
C(2)—N(1)	1.381
C(2)—N(3)	1.552
C(2)—N(4)	1.589
C(2)—N(5)	1.580
N(3)—O(6)	1.207
N(3)—O(7)	1.210
N(4)—O(10)	1.210
N(4)—O(11)	1.207
N(5)—O(8)	1.215
N(5)—O(9)	1.203
N(1)—N(12)	1.251
N(12)—N(13)	1.121
Bond angle	ω/deg
N(1)—C(2)—N(3)	106.8
N(1)—C(2)—N(4)	115.2
N(1)—C(2)—N(5)	114.4
N(3)—C(2)—N(4)	108.3
N(3)—C(2)—N(5)	107.9
N(4)—C(2)—N(5)	104.0
C(2)—N(3)—O(6)	114.6
C(2)—N(3)—O(7)	116.5
C(2)—N(4)—O(10)	115.0
C(2)—N(4)—O(11)	116.2
C(2)—N(5)—O(8)	113.1
C(2)—N(5)—O(9)	118.1
O(6)—N(3)—O(7)	128.8
O(10)—N(4)—O(11)	128.8
O(8)—N(5)—O(9)	128.9
C(2)—N(1)—N(12)	118.5
Dihedral angle	φ/deg
N(1)—C(2)—N(3)—O(6) (φ_1)	54.0
N(1)—C(2)—N(4)—O(10) (φ_2)	19.9
N(1)—C(2)—N(5)—O(8) (φ_3)	45.5
N(12)—N(1)—C(2)—N(3)	172.9

other nitro groups deviate from the upright position by ~50°.

Thus, the nitro groups in this molecule are much more inequivalent than in the $NF_2C(NO_2)_3$ molecule. Hence one can also expect significant changes in the geometric parameters of the N_3 group. For comparison, we performed the B3LYP/6-311+G(d,p) calculations of the N_3CH_3 molecule, which has a C_1 symmetry. According to calculations, the N(1)—N(2), N(2)—N(3), and C—N(1) bond lengths are 1.228, 1.136, and 1.474 Å, respectively, and the C—N(1)—N(2) and N(1)—N(2)—N(3) bond angles are 116.16° and 173.18°, respectively.

The greatest changes were found for the C—N bond length (a decrease by 0.09 Å). The N_3 fragment rotated by 7° with respect to the symmetric position. Changes in the other parameters are less significant.

Summing up, the C—N bond in the $NF_2C(NO_2)_3$ molecule is longer than in the NF_2CH_3 molecule, while that in the $N_3C(NO_2)_3$ molecule is shorter than in the N_3CH_3 molecule. Thus, the interactions of different functional groups with the trinitromethyl group lead to significant changes in the molecular structure.

The results obtained in this work show that DFT(B3LYP) calculations with the 6-311+G(d,p) basis set can be used for studying the structure of this type of polynitro compounds. The C—N bond length is the only parameter, which is systematically overestimated as compared to the experimental results. Qualitatively, all molecular structures were reproduced correctly.

The molecular geometries of the compounds studied in this work can be characterized as follows. All the molecules are of the "propeller" type, which can be either symmetric or asymmetric depending on the type of substituent. The type of substituent affects first of all the mutual arrangement of the nitro groups in the molecule, the C—N bond lengths also change, while all other parameters of the $C(NO_2)_3$ fragment change insignificantly. In all cases, the CNO_2 groups are planar. The substituent configuration in the molecules of halo derivatives and $NCC(NO_2)_3$ changes insignificantly, especially taking into account the fact that the substituent is introduced into highly nitrated molecule. Introduction of the NF_2 and N_3 groups causes changes of their own configurations; however, this mainly affects the first bond of the substituent. Other geometric parameters remain virtually unchanged; however, introduction of these groups affects the configurations of the NO_2 groups.

To elucidate how the type of substituent affects the C—X bond length in the $XC(NO_2)_3$ and XCH_3 molecules, we calculated the corresponding structures using the same computational method, B3LYP/6-311+G(d,p). The results of calculations are listed in Table 5.

The C—X bond lengths in the molecules of halo derivatives of **1** are shortened by nearly the same value (~0.08 Å), the shortening being the smallest for $NCC(NO_2)_3$ and the greatest for $N_3C(NO_2)_3$. The C—X

Table 5. C—X bond lengths (d/Å) in the $XC(NO_2)_3$ and XCH_3 molecules

X	d		Δd
	$XC(NO_2)_3$	XCH_3	
F	1.3048	1.3953	−0.091
Cl	1.7214	1.8053	−0.084
Br	1.8936	1.9446	−0.071
I*	2.1411	2.2127	−0.072
NC	1.4378	1.4568	−0.019
NF_2	1.4769	1.4645	0.012
N_3	1.3813	1.4739	−0.093

* The results of the B3LYP/3-21G calculations are given for comparison. Other geometric parameters of the $IC(NO_2)_3$ molecule obtained from calculations with this basis set are in rather poor agreement with experimental data.

bond in the $NF_2C(NO_2)_3$ molecule is lengthened by 0.012 Å.

These properties can of course be specific to this type of compounds and can not be observed for other nitro compounds because of the specific arrangement of the nitro groups in the $XC(NO_2)_3$ molecules.

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