SYNTHESIS AND STRUCTURE OF NITRO DERIVATIVES OF PENTANE. COMMUNICATION 2. 1,1,1,3,5,5,5-HEPTANITROPENTANE AND ITS 3-FLUORO AND 3-CHLORO DERIVATIVES

UDC 542.91+541.6:547.414.8

L. O. Atovmyan, N. I. Golovina

L. T. Eremenko, N. G. Zhitomirskaya,

G. V. Oreshko, and M. A. Fadeev

Molecules of polynitro compounds containing a large number of NO_2 groups are highly polarized; therefore, the packing of such molecules in the crystal must obviously be influenced to a great degree by electrostatic intermolecular interaction [1, 2]. The present work has been aimed at obtaining a series of nitro derivatives of pentane and subsequently studying these compounds by means of x-ray structure analysis and quantum-chemical calculations.

In a series of molecules differing in the structure of the central fragment, the charge distribution in the molecule will depend on the electron-donor characteristics of the central fragment. As a result of the syntheses we have carried out, it became possible to compare the donor-acceptor capabilities of the following central groups of molecules:



We have investigated the compounds 1,1,1,3,5,5,5-heptanitropentane (I), 3-fluoro-1,1,1,3,5,5,-5-heptanitropentane (II), and 3-chloro-1,1,1,3,5,5,5-heptanitropentane (III).

EXPERIMENTAL

The synthesis of (I) was accomplished by interaction of the K salt of trinitromethane with the Na salt of 2-nitro-1,3-propanediol.

To a 300-ml three-neck reactor equipped with a stirrer and thermometer, 80 ml of water and 40 ml of concentrated HCl were added; at 5-10°C, 20 g of the K salt of trinitromethane was added in portions. At 0-5°C with vigorous stirring, a suspension of 13 g of the Na salt of 2-nitro-1,3-propanediol in 35 ml of water was added over the course of 10 min. The reaction mixture was held at this temperature for 30 min until the odor of trinitromethane disappeared. The crystalline product was filtered off and washed thoroughly with water until the washwater was colorless. The product, precompressed on the filter, was dried in air and finally in vacuum over P_2O_5 . Yield 15 g (73% on K salt of trinitromethane). Single crystals of (I) with mp 103-104°C were obtained by recrystallization from CCl4.

The synthesis of (II) was accomplished by fluorination. A solution of 3 g of the NH₄ salt of 1,1,1,3,5,5,5-heptanitropentane in 30 ml of CCl₄ was added to a mixture of 200 ml H₂O and 20 g of CaCO₃ at 0-2°C, and a fluorine/nitrogen mixture ($F_2/N_2 = 1/10$) was passed through rapidly for 15 min. The (II) was extracted with CH₂Cl₂, and the resulting product was washed with concentrated H₂SO₄. Single crystals of (II) with mp 101-101.5°C were obtained by recrystallization from CCl₄. The (III) was obtained by chlorination of (I) in aqueous CH₃OH in the presence of NaNO₂ [3].

The lattice cell constants of the crystals of the three compounds were refined in a DRON-1 diffractometer with a single-crystal attachment. $C_5H_5N_7O_{14}$ (I)· M = 387.13, α = 10.176(1), b = 21.082(3), c = 6.2929(5) Å, β = 93.28(3), V = 1347.54 Å³, dmeas = 1.90, dcalc = 1.919 g/cm³, Z = 4, space group P2₁/n.

 $C_{sH_{4}N_{7}O_{14}F}$ (11): M = 405.12, α = 9.975(1), b = 6.3003(5), c = 11.647(1) Å, γ = 102.63(2)°, V = 702.98 Å³, d_{meas} = 1.91, d_{calc} = 1.925 g/cm³, Z = 2, space group P2₁.

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 549-555, March, 1984. Original article submitted November 10, 1982.

 $C_{5H_4N_7O_14C1}$ (III): M = 421.57, α = 13.271(1), b = 21.792(2), c = 6.2962(5) Å, γ = 53.03 (3)°, V = 1454.66 Å³, d_{meas} = 1.92, d_{calc} = 1.936 g/cm³, Z = 4, space group P2₁b. The intensities of 1914 nonzero reflections of (I) (0.083 < sin θ/λ < 0.599) with I > 2 σ , 1221 nonzero reflections of (II) (0.051 < sin θ/λ < 0.603) with I > 2 σ , and 1972 nonzero reflections of (III) (0.048 < sin θ/λ < 0.628) with I > 2 σ were measured in a DAR-UM automatic diffractometer on CuK_{α} radiation; absorption was not taken into account [μ (I) = 17.68, μ (II) = 18.4, μ (III) = 33.45 cm⁻¹]. The structures were determined by the direct method, using the Rentgen-75 program in the automatic regime.

Least-squares refinement in the block diagonal anisotropic approximation, using a weight scheme, led to final values R (I) = 0.068, R (II) = 0.057, and R (III) = 0.043. The coordinates of the atoms of the three structures are given in Tables 1-3.

DISCUSSION OF RESULTS

The molecules of all three structures can be represented as a closed chain: The bulky substituents are located on the same side of the chain of carbon atoms (Figs. 1-3).

Despite the fact that all three molecules (I)-(III) take on the same conformation of a closed chain in the crystal, there are certain differences in the values of the intramolecular nonvalence contacts. Thus, the intramolecular contact between the terminal oxygen atom of the trinitroethyl fragment and the nitrogen atom of the central NO2 group takes on the following values in the series of molecules: 2.773 (I); 2.595 (II); and 2.574 Å (III).

The specific features of the conformation of the chain of carbon atoms are such that different closure of the ends of the molecules on its center leads to different distances between the terminal oxygen atoms of the trinitroethyl fragments. These distances are as follows: 2.971 (I); 2.854 (II); and 3.272 Å (III). Consequently, from (I) to (III), the ends

Atom	x	Y	Z	Atom	X	Y Y	Z
$\begin{array}{c} C^{1} \\ C^{2} \\ C^{3} \\ C^{4} \\ C^{5} \\ N^{1} \\ N^{2} \\ N^{3} \\ N^{4} \\ N^{5} \\ N^{6} \\ N^{7} \\ O^{1} \\ O^{2} \\ O^{3} \\ O^{4} \end{array}$	2921 (2) 3855 (2) 3242 (2) 3990 (2) 3323 (2) 4280 (2) 2904 (2) 2124 (2) 3370 (2) 2492 (2) 3591 (2) 1657 (2) 4973 (2) 4248 (2) 1763 (2) 3778 (2)	4444 (1) 3889 (1) 32706 (1) 2067 (1) 1587 (1) 1772 (1) 2059 (1) 3211 (1) 4748 (1) 4966 (1) 4278 (1) 1800 (1) 1615 (1) 1730 (1)	$\begin{array}{c} 6525 (3) \\ 6350 (3) \\ 5466 (3) \\ 6576 (3) \\ 6672 (3) \\ 4542 (3) \\ 4542 (3) \\ 3080 (3) \\ 4398 (3) \\ 7876 (3) \\ 7876 (3) \\ 7576 (3) \\ 9239 (3) \\ 7146 (4) \\ 4245 (3) \\ 3329 (3) \end{array}$	$\begin{array}{c} O^{5} \\ O^{6} \\ O^{7} \\ O^{8} \\ O^{9} \\ O^{10} \\ O^{11} \\ O^{12} \\ O^{13} \\ O^{14} \\ H^{1} \\ H^{2} \\ H^{3} \\ H^{4} \\ H^{5} \end{array}$	1382 (2) 1982 (2) 4254 (2) 2565 (2) 2974 (2) 4714 (2) 674 (2) 1760 (2) 47160 (2) 4760 4240 4600 2240	2507 (1) 1620 (1) 3481 (1) 2872 (1) 4375 (1) 5318 (1) 5207 (1) 5086 (1) 2880 2640 3830 4600 3830 4000 3230	7778 (3) 9199 (3) 2241 (3) 3056 (3) 4229 (3) 9225 (3) 7458 (3) 7005 (4) 8912 (3) 8150 6010 7950 5360 5720

TABLE 1. Coordinates of Atoms in Structure of (I) ($\cdot 10^4$)

TABLE 2. Coordinates of Atoms in Structures of (II) $(\bullet 10^4)$

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Atom	X	Y	z	Atom	x	Ý Ý	z
0° 04/8(4) 11013(7) $2040(4)$	F ¹ C ² C ³ C ⁴ C ⁵ N ² N ⁵ N ⁶ N ⁷ O ² O ³	2790 (2) 417 (4) 1048 (4) 2445 (3) 3597 (4) 5074 (4) 0034 (4) 5480 (4) 5480 (4) 5457 (4) 2163 (4) -1047 (3) 258 (4) 1183 (4) 5674 (5) 7089 (4) 6478 (4)	9653 (4) 6512 (6) 7064 (6) 8754 (6) 7798 (6) 8997 (6) 7742 (7) 11344 (6) 9014 (8) 10651 (5) 5073 (6) 8559 (4) 5156 (5) 7039 (8) 7658 (9) 11813 (7)	1250 (0) 1105 (3) 2263 (3) 2294 (3) 2823 (4) 2604 (3) 3231 (4) 3066 (4) 1349 (4) 3062 (3) 1225 (4) 422 (3) 350 (3) 4164 (4) 2743 (5) 3625 (4)	04 05 06 07 08 09 010 011 012 013 014 H1 H2 H3 H4	4727 (4) 5164 (4) 6031 (5) 1874 (4) 2195 (4) -118 (4) -1895 (4) -325 (4) -252 (4) 523 (5) 2332 (3) 3652 (49) 3539 (75) 308 (46) 963 (57)	12530 (6) 7266 (8) 10785 (9) 12216 (6) 10373 (7) 3742 (6) 5366 (7) 8745 (6) 9809 (6) 4169 (7) 5183 (6) 7692 (79) 6274 (123) 7397 (73) 5695 (92)	2741 (5) 859 (4) 922 (4) 2576 (5) 4064 (4) 1982 (3) 543 (5) -553 (3) 994 (4) -439 (4) 601 (3) 3787 (49) 2363 (78) 2738 (47) 2663 (58)



Fig. 1. Molecule of 1,1,1,3,5,5,5-heptanitropentane (I).

TABLE	3.	Coordinates	of	Atoms	in	Structure	of	(III)	(•104)
			_	n		1		1	· · · · ·

Atom	x	Y	Z	Atom	x	¥	Z
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	628 (1) 630 (2) 898 (2) 7074 (2) 229 (2) 316 (2) 229 (2) 316 (2) 2256 (2) 2256 (2) 2256 (2) 0255 (2) 0027 (2) 819 (2) 819 (2) 844 (2)	$\begin{array}{c} 4773(0)\\ 3884(1)\\ 4739(1)\\ 5243(1)\\ 6017(1)\\ 6332(1)\\ 7161(1)\\ 6378(1)\\ 5935(1)\\ 5480(1)\\ 3617(1)\\ 3582(1)\\ 3647(1)\\ 3582(1)\\ 3434(1)\\ 7220(1)\\ 7674(1)\\ 6209(1)\\ \end{array}$	$\begin{array}{c} 1070(1)\\ 2987(1)\\ 3348(3)\\ 1935(3)\\ 3112(3)\\ 3367(3)\\ 4163(3)\\ 1315(3)\\ 5050(3)\\ -89(3)\\ 798(3)\\ 4470(3)\\ 3634(4)\\ 5828(3)\\ 3096(4)\\ 1368(4) \end{array}$	$ \begin{array}{c} 0^4 \\ 0^5 \\ 0^6 \\ 0^7 \\ 0^8 \\ 0^9 \\ 0^{10} \\ 0^{11} \\ 0^{12} \\ 0^{13} \\ 0^{14} \\ H^1 \\ H^2 \\ H^3 \\ H^4 \end{array} $	2093 (2) 3611 (2) 3605 (2) 176 (2) 1597 (2) 2419 (2) 2716 (2) 962 (2) 4789 (2) 4195 (2) 1190 750 2240 970	6583 (1) 5300 (1) 5655 (1) 5655 (1) 5519 (1) 4027 (1) 3022 (1) 2954 (1) 3985 (1) 2952 (1) 3613 (1) 6010 6410 4740 4960	-188 (3) 5569 (3) 251 (3) -1768 (3) -666 (3) 667 (4) 5240 (4) 4668 (3) 2425 (4) 5323 (3) 4630 2430 4770 3410

of the molecules are more strongly closed on the central NO_2 group, thereby increasing the distance between the terminal oxygen atoms of the trinitroethyl fragments.

The chain becomes more highly convoluted in (III) in comparison with (I). In Table 4 we have listed the characteristics of the mean-square planes passed through the atoms of the molecular fragments. The averaged intermolecular contacts for all three structures were calculated in the interval <3.8 Å, values being calculated for the mean contacts of the types 0...0, 0...N, 0...C, and 0...H, and also the mean contact for all types. These values are given in Table 5. The mean contact 0...0 increases in length from (I) to (III), the averaged contacts of the type of 0...N and 0...C become shorter, and the contact 0...H increases in length symbatically. Such a distribution of values of the averaged contacts, before calculation of the charge distribution, suggests that the oxygen atoms in (III) will carry a larger negative charge in comparison with the oxygen atoms in (I), which explains the longer intermolecular contact 0...0 and the shorter contacts 0...N and 0...C in the structure of (III) with (I). (The N and C atoms are positively charged.) The parameters of the electronic structure of (I)-(III) are given in Tables 6 and 7.

As pointed out in [1], because of the limited dimensions of the program that was used, only a fragment-by-fragment calculation could be carried out. The principal differences in the electronic makeup of the structures under consideration pertain to the central group of atoms. In [1], a detailed examination was made of the possible errors in the proposed method for the calculation of large compounds. With the limitations imposed by the size of the program, in this stage we should eliminate from consideration q and Δp of the atoms and bonds of the core of the molecule, and then the data should be regarded as a first approximation. It should be taken into account that the error in the fragment-by-fragment calculation will be identical for all three compounds. With such an approach, the net charges of the terminal and central groups are distributed as shown in Table 8.

0,342 0,342 9,150 9,150 4,509

TABLE 4. Equations of Planes Passed through Atoms of $\rm NO_2$ Croups in Molecules of (I)-(III), and Angles between Planes



Fig. 2. Molecule of 3-fluoro-1,1,1,3,5,5,5-heptanitropentane (II).



Fig. 3. Molecule of 3-chloro-1,1,1,3,5,5,5-heptanitropentane (III).

TABLE 5.	Averaged	Intermol	Lecular	Contacts	in
Structures	; (I)-(III	:), Å			

Compound	00	0N and 0C	ОН	From O, for all types
(I)	3,259	3,565	2,960	3,315
(II)	3,327	3,527	2,963	3,341
(III)	3,331	3,496	3,059	3,349

Thus, the structures of (I) and (II) are nearly symmetrical, which is further confirmed by the closeness of values of q and Δp of the terminal and intermediate groups; but the terminal fragments of (III) are more strongly polarized, and the structure of (III) proves to be, in effect, more highly charged.

Summation of Δp of both fragments in (1)-(III) led to the results presented in Table 9.

The structure of (III) occupies the greatest volume, and that of (11) is intermediate between (1) and (III). Consequently, according to the distribution of q and ΔP , the best packing in the crystal will be that of the molecules of (I), then (II), and (III). These data are in complete agreement with the distribution of average contacts of different types in all three compounds (see Table 7).

TABLE 6. Charge Distribution in Molecules of (I)-(III)

Atom		q, e		Atom		q, ē	
	(1)	(11)	(111)		(1)	(11)	(111)
$ \begin{array}{c} & C \\ & N \\ & O \\ & N \\ & O \\ & N \\ & O \\ & C \\ & H \\ & H \\ & C^{*} \\ & H^{*}_{(I)}, F^{*}_{(II)}, Cl^{*}_{(III)} \\ & N^{*} \end{array} $		$ \begin{array}{c} 0.031\\ 0.500\\ -0.209\\ -0.295\\ 0.512\\ -0.264\\ -0.224\\ -0.224\\ -0.266\\ -0.053\\ 0.168\\ 0.146\\ 0.432\\ -0.032\\ 0.540\\ \end{array} $	0,042 0,497 -0,216 -0,290 0,509 -0,257 -0,225 0,487 -0,234 -0,271 -0,234 -0,274 0,164 0,109 0,284 0,254	O* CHHCN ON ON ON	$ \begin{array}{c} -0,124\\ -0,172\\ -0,024\\ 0,116\\ 0,168\\ 0,059\\ 0,503\\ -0,290\\ -0,204\\ 0,506\\ -0,212\\ -0,262\\ 0,487\\ -0,280\\ -0,217\\ \end{array} $	$ \begin{vmatrix} -0,123\\ -0,143\\ -0,055\\ 0,132\\ 0,157\\ 0,056\\ 0,509\\ -0,327\\ -0,179\\ 0,508\\ -0,227\\ -0,254\\ 0,486\\ -0,249\\ -0,240 \end{vmatrix} $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

*Here and in Table 7, for the atoms and bonds of the central fragment, averaged values are listed; for the H, F, and Cl atoms in (I), (II), and (III), the data are listed in the columns corresponding to the structures.

Dand		Δp		Dami		Δp	
DOIIG	(I)	(11)	(111)	DIIG	(I)	(11)	(111)
$ \begin{array}{c} C-N \\ N-0 \\ C-N \\ N-0 \\ C-N \\ C-C \\ C-H \\ C-H \\ C-C \\ C-H \\ C-C \\ C-F(II) \\ C-Cl_{(III)} \end{array} $	$\begin{array}{c} 0,958\\ 1,237\\ 1,183\\ 0,958\\ 1,202\\ 1,216\\ 0,943\\ 1,224\\ 1,203\\ 0,970\\ 0,938\\ 0,979\\ 1,060\\ 0,969\\ \end{array}$	0,951 1,223 1,203 0,952 1,184 1,238 0,943 1,220 1,210 1,011 0,932 0,945 1,046	0.960 1.226 1.194 0.952 1.207 1.211 0.944 1.218 1.208 0.990 0.938 0.968 1.038	C-N N-O C-C C-H C-C C-N N-O C-N N-O C-N N-O	$\begin{array}{c} 0.967\\ 1.263\\ 1.151\\ 1.075\\ 0.975\\ 0.934\\ 0.966\\ 0.953\\ 1.195\\ 1.226\\ 0.948\\ 1.230\\ 1.222\\ 0.958\\ 1.196\\ 1.222\\ \end{array}$	$\begin{array}{c} 0,921\\ 1,251\\ 1,191\\ 1,053\\ 0,970\\ 0,941\\ 0,961\\ 1,199\\ 1.216\\ 0,963\\ 1,214\\ 1,215\\ 0,955\\ 1,159\\ 1,263\end{array}$	$\begin{array}{c} 0,934\\ 1,210\\ 1,218\\ 1,053\\ 0,967\\ 0,943\\ 0,977\\ 0,960\\ 1,181\\ 1,214\\ 1,214\\ 1,214\\ 1,214\\ 1,216\\ 0,949\\ 1,203\\ 1,223\\ 1\end{array}$

TABLE 7. Bond Population Distribution in (I)-(III)

TABLE 8. Net Charges of Terminal and Central Groups in (1)-(III)

Compound	Σqkıe	Σqh ₂ e	Σq _C ^a	
(I) (II) (III) (III)	0,033 0,028 0,018	0,031 0,027 0,028	0,355 0,242 0,451	

TABLE 9. Total Populations of First and Second Fragments of Compounds (I)-(III)

.

Compound	$\Sigma \Delta p_1$	$\Sigma \Delta p_2$
(I)	16,39	16,43
(II)	16,45	16,49
(III)	16,54	16,51

In the first approximation, these compounds have an appreciable uncompensated charge, in contrast, for example, to 1,5-difluoro-1,1,1,3,3,5,5-hexanitropentane, which was calculated in the same approximation and which has the symmetry of an open carbon chain (approximately local symmetry C_2) [1].

CONCLUSIONS

1. The compound 1,1,1,3,5,5,5-heptanitropentane has been prepared, and from this, 3-fluoro-1,1,1,3,5,5,5-heptanitropentane has been synthesized.

2. By means of x-ray structure analysis, a closed-chain conformation of the carbon atoms has been established for 1,1,1,3,5,5,5-heptanitropentane, 3-fluoro-1,1,1,3,5,5,5-heptanitropentane.

3. Calculations of the electronic structure of all three compounds showed that the 3chloro-1,1,1,3,5,5,5-heptanitropentane is more strongly polarized, and this should lead to an increase in the electrostatic intermolecular interaction in the crystal. The distribution of averaged contacts of different types in the crystals of these compounds corresponds to their electronic structure.

LITERATURE CITED

- L. O. Atovmyan, N. I. Golovina, L. T. Eremenko, N. G. Zhitomirskaya, F. V. Oreshko, and M. A. Fadeev, Izv. Akad. Nauk SSSR, Ser. Khim., 543 (1983).
 N. I. Golovina and L. O. Atovmyan, "Intermolecular interactions and density of polynitro
- N. I. Golovina and L. O. Atovmyan, "Intermolecular interactions and density of polynitro compounds," Summaries of Papers from 3rd All-Union Conference on Organic Crystal Chemistry [in Russian], Gor'kii (1981).
- 3. L. T. Eremenko, G. V. Oreshko, M. A. Fadeev, and N. G. Zhitomirskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2163 (1982).

IR SPECTROSCOPIC STUDY OF MATRIX-ISOLATED FREE ALLYL RADICALS

AND ANALYSIS OF VIBRATIONAL SPECTRA AND STRUCTURE OF *π*-ALLYL

ORGANOMETALLIC COMPOUNDS

A. K. Mal'tsev, V. A. Korolev, and O. M. Nefedov UDC 543.422.4:541.515:547.1'13

The matrix isolation method [1] offers the unique possibility of stabilization and direct IR spectroscopic study of highly reactive free radicals, carbenes, and other species with the aim of determining their structures [2, 3] and the mechanisms of reactions in which they take part [2]. The IR spectrum of the free allyl radical (AR), which is the simplest delocalized π -system with equalized carbon-carbon bonds [4, 5], is of particular importance because of the existence of a broad class of organometallic compounds (substances of practical importance) with compositions including the π -allyl ligand C₃H₅.

The character of the chemical bond and the changes in structure of the allyl system when a π -complex is formed can be evaluated by comparing the physicochemical characteristics of the free AR and the π -allyl ligand. A good experimental base for such an analysis might be found in vibrational spectroscopy, since the known ESR [6-8], photoelectron [9], and mass spectra (see [10] and literature cited therein) of the free AR are difficult to compare with the properties of the stable complexes. It is specifically the change in vibrational frequencies of the ligand, including a decrease of 100-200 cm⁻¹ in ν (C=C), that are characteristic for the formation of π -complexes of unsaturated compounds [11]. However, spectral data for a variety of π -allyl complexes have not been subjected to such an analysis, since the IR spectrum of the free AR had not been obtained up until quite recently.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 555-568, March, 1984. Original article submitted September 28, 1983.