

Synthesis and Structure of 1,1,1,3,3,5,5,5-Octanitropentane

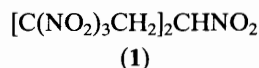
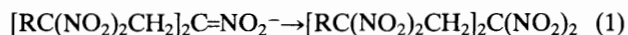
Leonid T. Eremenko,* Lev O. Atovmyan, Nina I. Golovina, Galina V. Oreshko, and Mikhail A. Fadeev

Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, Moscow Region, 142432, USSR

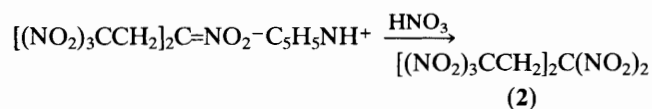
1,1,1,3,3,5,5,5-Octanitropentane is prepared by nitration of the pyridine salt of 1,1,1,3,5,5,5-heptanitropentane, the conformation of the molecules of the new substance not being optimal for packing in the crystal.

The investigation of crystalline polynitropentanes has shown them to have high density¹ and their n.m.r. chemical shifts show a complicated dependence² on the electronegativity of substituents owing to the effect of electrostatic interactions of closely located charged fragments in the molecule.

Although Frankel described the synthesis of 1,1,1,3,5,5,5-heptanitropentane (1) twenty years ago,³ its 3-halogenoderivatives of general formula $[C(NO_2)_3CH_2]_2CXNO_2$, where X is F, Cl, Br, have been obtained only recently.^{4,5} However, the nitration of a salt of (1) to give a 3-*gem*-dinitro substituted compound under Klager and Frankel's conditions,⁶ used for compounds of the type shown in equation (1), was unsuccessful.



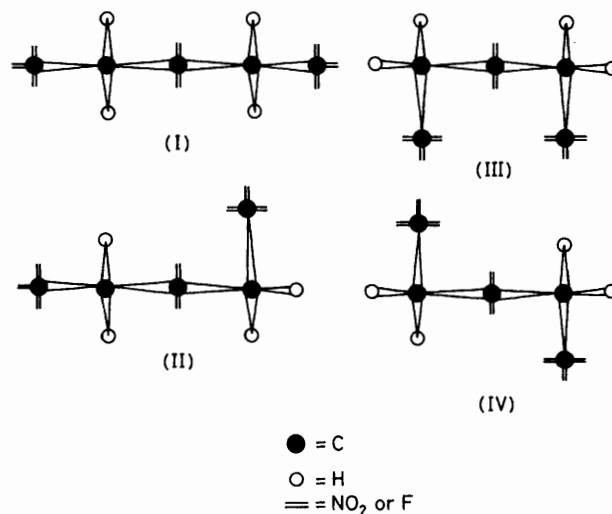
The nitration of the pyridine salt of (1) with 100% nitric acid has been found to give 1,1,1,3,3,5,5,5-octanitropentane (2) in 45% yield. The reaction was carried out under mild conditions (0 °C, presence of CCl_4) and compound (2) was obtained as colourless crystals, m.p. 47.5–48.5 °C (after crystallization from CF_3CO_2H). The crystals were unstable, and so the X-ray crystallographic study was carried out at 100 K.



Crystal data for (2); monoclinic, space group $P2_1/a$, $a = 18.555(5)$, $b = 6.3675(5)$, $c = 12.673(2)$ Å, $\beta = 98.87(2)^\circ$, $U = 1479.49$ Å³, $D_c = 1.940$ g cm⁻³, $T = 100$ K,

$\mu(Cu-K\alpha) = 18.22$ cm⁻¹, $\lambda = 1.5418$ Å. A total of 1798 intensities of non-zero independent reflections [$I \geq 2\sigma(I)$] were measured on a DAR-UM diffractometer within the range of $0.048 \leq \sin\theta/\lambda \leq 0.61$.†

The structure was solved by a direct method with the 'RENTGEN-75' program and refined by the least-squares technique in the block-diagonal approximation to give $R = 0.054$. For non-hydrogen atoms thermal parameters were refined anisotropically and for hydrogen atoms isotropically.



† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

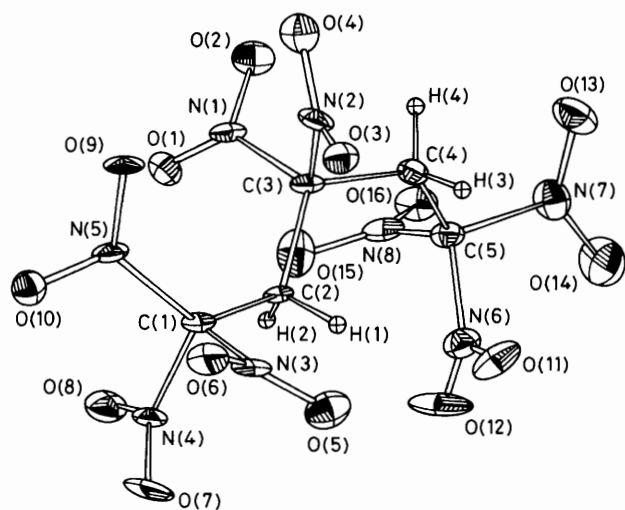


Figure 1. The molecule of 1,1,1,3,3,5,5,5-octanitropentane, (2).

There are four possible conformers for this derivative of n-pentane [(I)–(IV)]: the molecule of (2) is found to have conformation (II). The bond lengths of (2) are standard for such molecules (Figure 1); torsion angles C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) are 161.3 and 46.9°, respectively. Molecules of 1,5-difluoro-1,1,3,3,5,5-hexanitropentane also adopt conformation (II) while molecules of 1,1,1,3,5,5,5-heptanitropentane, 3-fluoro-, and 3-chloro-1,1,1,3,5,5,5-heptanitropentanes have conformation (I).⁷

The presence of a large number of nitro groups in such compounds leads to high polarization of the molecule and, hence, to the appearance of a significant electrostatic component⁸ in the energy of the crystal lattice which is dependent on the distribution of charge density over the molecule.

Conformation (I) involves the shortest contacts between the terminal and central nitro groups. As a rule, these contacts

occur between differently charged atoms of the O ··· N and O ··· C types, which means that an electrostatic 'latch' operates stabilizing and additionally polarizing the molecule. The crystal lattice with the largest electrostatic contribution to its energy must be that consisting of molecules of form (I) and the van der Waals energy in this structure must be the least among the forms compared.

The most favourable case for molecule packing is form (IV) when the terminal nitro groups are at the greatest possible distance from the central ones and from each other. This is the case where the least polarization of the molecules and the highest density of the crystals would occur. The forms (III) and (IV) have been found in two crystallographically independent molecules in the structure of bis(2-fluoro-2,2-dinitroethyl)nitramine.⁹

Our conclusions on the character of the energy variations in the crystal lattice were confirmed by analysing the distribution of intermolecular contacts of the O⁻ ··· O⁻, O⁻ ··· N⁺, and O⁻ ··· C⁺ types in the structures of the crystals. The results will be fully described elsewhere.

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