Crystallography of 2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl and Its Relation to Initiation Reactivity

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X-ray crystallographic study of 2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl (HNBP, $C_{12}H_4N_6O_{12}$, $M_r = 424.21$) has been carried out with the following results: triclinic, $a = 8.1860(7)$, $b = 12.1370(8)$, $c = 16.2040(12)$ Å, $\alpha = 98.728(6)°$, $\beta = 93.101(6)°$, $\gamma = 104.688(6)°$, $V = 1532.05$ Å^3, $Z = 4$, $D_x = 1.839$ g·cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.169$ cm^{-1}, $F(000) = 856$, temperature of 150 K, final $R = 0.0765$ for 4415 independent observed reflections. The interplanar angles between benzene rings are 85.38 and 86.82° for two independent molecules. A possibility of intermolecular hydrogen bonds was indicated, and atypically short distances between oxygen atoms of nitro groups in the 2,6-positions of one molecule and nitro groups in the 4-position of adjacent molecules were found. These interactions might be a reason for the primary reaction of nitro group in the position 4(4′), compared to nitro groups in positions 2,6(2′,6′), in the HNBP molecule during its initiation. In this respect, HNBP differs from the other members of polynitro polyphenylene series containing trinitrophenyl building blocks in their molecules.

Introduction

Several polynitro polyphenylene energetic materials, which are “genuine” polynitro arenes of high thermal stability, are still very attractive from the point of view of their use as an active part of perforators or detonators in downhole well applications,[1–3] and some of them are registered also for use in spacecraft applications.[4,5] Primarily, the following polynitro arenes should be mentioned:[1,3] 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), 1,4,5,8-tetranitronaphthalene (TENN), 2,2″,4,4′,4″,6,6′,6″-octanitro-1,1′:3′,1″-terphenyl (ONT), 2,2′,2″,4,4′,4″,6,6′,6″-nonanitro-1,1′:3′,1″-terphenyl (NONA), 2,4,6-*tris*(2,4,6-trinitrophenyl)-1,3,5-triazine (TPT), *N*,*N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA), 2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-dodecanitro-1,1′:3′1″:3″,1‴-quaterphenyl (DODECA), and 1,3,7,9-tetranitro[1,2,3]benzotriazolo[2,1-*a*][1,2,3]benzotriazole-5,11-diium-6,12-diide (TACOT-Z).

Not only from the standpoint of thermal stability of these compounds[6] but also from the standpoint of initiation reactivity of energetic materials in general[7,8] does the intensity of intermolecular interactions in their crystals play a significant part. For better understanding of the said interactions it is useful to know the respective crystal structures. However, this is an aspect that has not yet been studied in the case of “genuine” polynitroarenes with trinitrophenyl and trinitrophenylene groups in their molecules, except for 1,3,5-trinitrobenzene (TNB),[9] which can be regarded as a notional building unit of the mentioned molecules. Therefore, in the present paper we have focused our attention on the second member of the series of polynitro polyphenylenes, namely, 2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl (HNBP), which can be viewed as a “dimer” of TNB.

Experimental Section

2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl. 2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl was obtained by the Ullmann condensation of 2-chloro-1,3,5-trinitrobenzene in nitrobenzene, catalyzed by activated copper.[10] It was purified by fourfold crystallization from acetone-methanol mixture; mp 242–243 °C.

X-ray Crystallographic Study. The details of the crystal structure determination and refinement for the compound studied are given bellow. The suitable single crystal of HNBP was mounted on glass fiber with a perfluorinated silicone oil and measured on four-circle diffractometer Kappa CCD with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(1) K and the φ and ω scan mode. Data reductions were performed with DENZO-SMN.[11] Structures were solved by direct methods (Sir92)[12]

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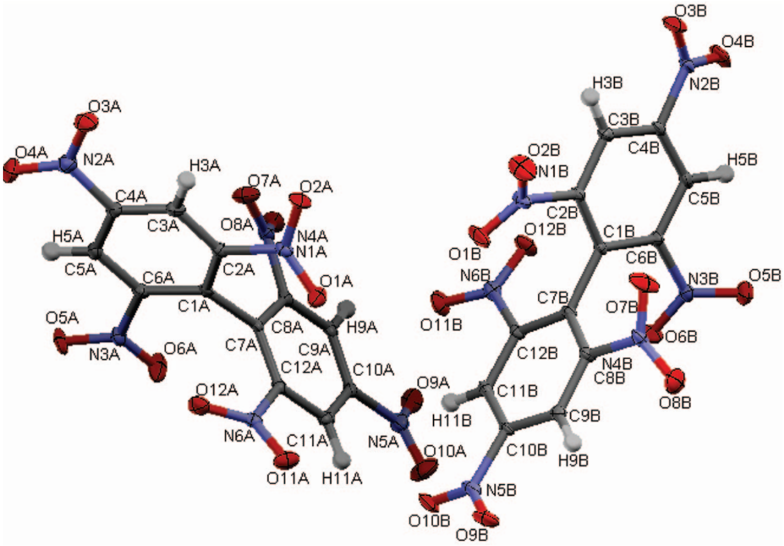

Figure 1. Drawing of the A and B molecules in order to define the atoms numbering that is used.

and refined by full matrix least-squares based on F^2 (SHELXL97).[13] All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with C−H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$.

The numerical absorption corrections from crystal shape by Gaussian integration were applied.[14] Crystallographic data for HNBP: $C_{12}H_4N_6O_{12}$, $M = 424.11$, triclinic, $P\bar{1}$, $a = 8.1860(7)$, $b = 12.1370(8)$, $c = 16.2040(12)$ Å, $\alpha = 98.728(6)$, $\beta = 93.101(6)$, $\gamma = 104.688(6)°$, $Z = 4$, $V = 1532.0(2)$ Å^3, $D_c = 1.839$ g·cm^{-3}, $\mu = 0.169$ mm^{-1}, $T_{\min} = 0.907$, $T_{\max} = 0.965$; 19065 reflections measured ($\theta_{\max} = 27.5°$), 5835 independent ($R_{\mathrm{int}} = 0.093$), 4415 with $I > 2\sigma(I)$, 541 parameters, $S = 1.133$, $R1$(obs. data) = 0.0765, $wR2$(all data) = 0.1900; max., min. residual electron density = 0.452, –0.531 e Å^{-3}.

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre.[15]

Results and Discussion

The numbering scheme for both the A and the B molecules is shown in Figure 1. Bond lengths for the two independent molecules are given in Table 1 and the corresponding bond angles in Table 2. Table 3 presents interplanar angles in the HNBP molecule.

The results of the structure determination show the crystal to be an array of molecular units with connectivity and geometry consistent with those expected. A drawing of the four molecules in the unit cell is shown in Figure 2.

Table 1. Interatomic Distances (Å) (standard uncertainties) in the HNBP Molecules

molecule A			molecule B		
C1A	C2A	1.390(5)	C1B	C2B	1.381(6)
C1A	C6A	1.404(5)	C1B	C6B	1.393(5)
C3A	C2A	1.377(6)	C3B	C2B	1.384(5)
C3A	C4A	1.372(6)	C3B	C4B	1.378(6)
C5A	C4A	1.377(6)	C5B	C4B	1.370(6)
C5A	C6A	1.378(6)	C5B	C6B	1.384(5)
C7A	C1A	1.502(5)	C7B	C1B	1.507(5)
C7A	C8A	1.394(5)	C7B	C8B	1.388(5)
C7A	C12A	1.388(5)	C7B	C12B	1.390(5)
C8A	C9A	1.385(6)	C8B	C9B	1.374(5)
C10A	C9A	1.366(6)	C10B	C9B	1.372(6)
C11A	C10A	1.371(6)	C11B	C10B	1.366(6)
C11A	C12A	1.383(6)	C11B	C12B	1.377(5)
C2A	N1A	1.468(5)	C2B	N1B	1.471(5)
C4A	N2A	1.473(5)	C4B	N2B	1.467(5)
C6A	N3A	1.479(5)	C6B	N3B	1.463(5)
C8A	N4A	1.478(5)	C8B	N4B	1.472(5)
C10A	N5A	1.477(5)	C10B	N5B	1.472(5)
C12A	N6A	1.472(5)	C12B	N6B	1.466(5)
N1A	O1A	1.220(4)	N1B	O1B	1.220(5)
N1A	O2A	1.218(4)	N1B	O2B	1.210(5)
N2A	O3A	1.221(5)	N2B	O3B	1.213(5)
N2A	O4A	1.222(5)	N2B	O4B	1.222(5)
N3A	O5A	1.219(4)	N3B	O5B	1.217(5)
N3A	O6A	1.200(5)	N3B	O6B	1.220(5)
N4A	O7A	1.219(5)	N4B	O7B	1.218(5)
N4A	O8A	1.224(5)	N4B	O8B	1.208(5)
N5A	O9A	1.213(5)	N5B	O9B	1.216(5)
N5A	O10A	1.206(5)	N5B	O10B	1.218(5)
N6A	O11A	1.209(4)	N6B	O11B	1.214(5)
N6A	O12A	1.220(5)	N6B	O12B	1.228(4)

The dihedral interplanar angle in gaseous nonsubstituted biphenyl is 42°, while in its crystal it is equal to zero.[16] In the molecular crystal of 2,2′,4,4′,6,6′-hexanitrobiphenyl-3,3′,5,5′-tetramine (DIDATB) this angle is 83.8°, its C_6 skeletal atoms of each of its aromatic rings defining reasonable but not exact planes with connecting carbon−carbon distance of 1.518(5) Å.[17] For one, from the two aromatic rings in DIDATB the planes of 2,4,2′-nitro substituents respectively lie at the dihedral angles of 39.3°, 10.5°, and 49.3° to the ring plane, and for the other ring the corresponding angles are 59.0°, 11.7°, and 6.7° (the first ring mentioned is highly distorted, some of its overall stabilization being retained by the conjugation between its amino and nitro groups).[17] In contrast to DIDATB, the HNBP molecule is

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Table 2. Bond Angles (deg) (standard uncertainties) in the HNBP Molecules

molecule A				molecule B			
C2A	C1A	C6A	114.9(3)	C2B	C1B	C6B	115.8(3)
C2A	C1A	C7A	122.7(3)	C2B	C1B	C7B	121.6(3)
C6A	C1A	C7A	122.1(3)	C6B	C1B	C7B	122.5(3)
C3A	C2A	C1A	123.9(4)	C1B	C2B	C3B	124.1(4)
C3A	C2A	N1A	115.4(3)	C1B	C2B	N1B	119.9(3)
C1A	C2A	N1A	120.7(3)	C3B	C2B	N1B	115.9(4)
C4A	C3A	C2A	117.3(4)	C4B	C3B	C2B	116.3(4)
C3A	C4A	C5A	122.9(4)	C5B	C4B	C3B	123.5(4)
C3A	C4A	N2A	118.6(4)	C5B	C4B	N2B	119.1(4)
C5A	C4A	N2A	118.5(4)	C3B	C4B	N2B	117.4(4)
C4A	C5A	C6A	117.3(4)	C4B	C5B	C6B	117.1(4)
C5A	C6A	C1A	123.5(4)	C5B	C6B	C1B	123.1(4)
C5A	C6A	N3A	116.4(3)	C5B	C6B	N3B	116.5(3)
C1A	C6A	N3A	120.1(3)	C1B	C6B	N3B	120.4(3)
C12A	C7A	C8A	114.9(4)	C8B	C7B	C12B	115.8(3)
C12A	C7A	C1A	123.9(3)	C8B	C7B	C1B	121.1(3)
C8A	C7A	C1A	121.2(3)	C12B	C7B	C1B	122.9(3)
C9A	C8A	C7A	123.6(4)	C9B	C8B	C7B	123.4(4)
C9A	C8A	N4A	115.5(3)	C9B	C8B	N4B	116.1(3)
C7A	C8A	N4A	120.8(3)	C7B	C8B	N4B	120.5(3)
C10A	C9A	C8A	117.3(4)	C10B	C9B	C8B	117.5(4)
C9A	C10A	C11A	123.0(4)	C11B	C10B	C9B	122.4(3)
C9A	C10A	N5A	118.3(4)	C11B	C10B	N5B	119.3(4)
C11A	C10A	N5A	118.7(4)	C9B	C10B	N5B	118.4(4)
C10A	C11A	C12A	117.2(4)	C10B	C11B	C12B	118.2(4)
C11A	C12A	C7A	123.9(4)	C11B	C12B	C7B	122.6(4)
C11A	C12A	N6A	116.1(3)	C11B	C12B	N6B	116.2(3)
C7A	C12A	N6A	120.0(3)	C7B	C12B	N6B	121.2(3)
O1A	N1A	O2A	124.3(3)	O2B	N1B	O1B	125.1(4)
O1A	N1A	C2A	118.5(3)	O2B	N1B	C2B	117.3(4)
O2A	N1A	C2A	117.1(3)	O1B	N1B	C2B	117.6(4)
O3A	N2A	O4A	124.3(4)	O3B	N2B	O4B	125.5(4)
O3A	N2A	C4A	118.1(4)	O3B	N2B	C4B	118.0(4)
O4A	N2A	C4A	117.6(4)	O4B	N2B	C4B	116.5(4)
O6A	N3A	O5A	124.1(4)	O5B	N3B	O6B	124.7(4)
O6A	N3A	C6A	119.4(3)	O5B	N3B	C6B	117.6(3)
O5A	N3A	C6A	116.5(3)	O6B	N3B	C6B	117.7(3)
O7A	N4A	O8A	124.0(3)	O8B	N4B	O7B	124.5(4)
O7A	N4A	C8A	118.8(3)	O8B	N4B	C8B	118.2(3)
O8A	N4A	C8A	117.1(3)	O7B	N4B	C8B	117.2(3)
O10A	N5A	O9A	125.1(4)	O10B	N5B	O9B	125.4(4)
O10A	N5A	C10A	117.5(4)	O10B	N5B	C10B	116.6(4)
O9A	N5A	C10A	117.4(4)	O9B	N5B	C10B	117.9(4)
O11A	N6A	O12A	125.3(4)	O11B	N6B	O12B	123.6(4)
O11A	N6A	C12A	117.4(3)	O11B	N6B	C12B	118.8(3)
O12A	N6A	C12A	117.3(3)	O12B	N6B	C12B	117.6(3)

Table 3. Interplanar Angles (deg) in the HNBP Molecules

molecule A		molecule B	
ring–ring	85.38	ring–ring	86.82
parent ring–N1A–O_2	25.24	parent ring–N1B–O_2	36.95
parent ring–N2A–O_2	9.64	parent ring–N2B–O_2	21.23
parent ring–N3A–O_2	11.97	parent ring–N3B–O_2	34.33
parent ring–N4A–O_2	26.35	parent ring–N4B–O_2	37.60
parent ring–N5A–O_2	13.03	parent ring–N5B–O_2	8.30
parent ring–N6A–O_2	25.65	parent ring–N6B–O_2	13.87

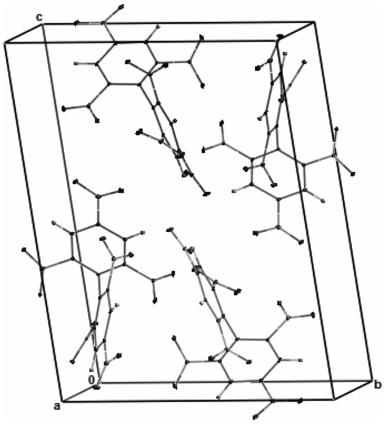

Figure 2. Drawing showing the packing of the four HNBP molecules in the unit cell.

not so deformed in its molecular crystal. The dihedral angles of its benzene rings are 85.38 and 86.82° for two independent molecules, and the dihedral angles of 2,2′,6,6′-nitro groups do not exceed 38° (see Table 3). It should be pointed out that there is a small difference between the bond lengths C6A−N3A and C8A−N4A (at 2-positions) and the bond length C10A−N5A (at 4-position); the bond lengths C8B−N4B (at 2-positions) and C10B−N5B (at 4-positon) are almost equal in the case of the B molecule (see Tables 1 and 4). This very low difference corresponds also with the tiny difference in the ^{13}C NMR chemical shifts[7] and low difference in the ^{15}N NMR chemical shifts[13] of the key atoms in the corresponding C−N bonds (see Table 4), even if these shifts were specified in solution.

Analysis of the data obtained revealed that four different intermolecular C−H···O−N (*ortho*-nitro group) distances are shorter (2.336, 2.415, 2.568, and 2.646 Å) than the corresponding van der Waals distances. This fact can indicate existence of intermolecular hydrogen bonds in the molecular crystal of HNBP (Figure 3). Intermolecular interaction distances between N−H···O−N of adjacent molecules in the molecular crystals of 2,3,4,6-tetranitroaniline, for example, lie in the 2.39−2.41 Å interval.[18] Also atypically short distances were found between oxygen atoms of nitro groups at the 2,6-positions of one molecule and nitrogen atoms of nitro groups at the 4-position of adjacent molecules (2.742, 2.896, 2.903, and 2.991 Å). There are two more contacts between the 2 and the 6 position with the same position of adjacent molecule 2.786 and 2.819 Å. An interesting feature is that molecule B does not reveal this type of contact through its para positions. For comparison, analogous distances in the crystals of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) lie in the 2.927−2.991 Å interval;[19] the TATB molecules are bound here in the planar nets by hydrogen bonds.[19]

Initiation Reactivity.[8] What is the type of connection between the specified crystallography of HNBP and its initiation reactivity? Generally, this reactivity depends on[7,8] (a) steric conditions and (b) electron configuration in the ground-state of the reaction center of the molecule. Both the electron configuration and the steric situation in the reaction center of the molecule can be characterized[7,8] from the standpoint of organic chemistry on the basis of the NMR chemical shifts of key atoms of the reaction center of the molecule or by direct correlation of reaction characteristics

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Table 4. Characteristics of the C−N Bonds and Atoms Relating to Them

position in molecule	^{13}C NMR (ppm)[7]	^{15}N NMR (ppm)[20]	net charges on NO_2 (e)[3]	charges at the nitrogen atoms (e)[3]	lengths of C−N bonds (Å)	
					molecule A	molecule B
2-	148.2	−20.21	−0.3432	0.4046	1.468	1.463
2′	148.2	−20.21	−0.3432	0.4046	1.478	1.472
4-	148.7	−21.76	−0.3384	0.4115	1.473	1.467
4′	148.7	−21.76	−0.3384	0.4115	1.477	1.472
6-	148.2	−20.21	−0.3432	0.4046	1.478	1.471
6′	148.2	−20.21	−0.3432	0.4046	1.472	1.466

with electron charges at the nitrogen atoms of these first-reacting nitro groups or with net charges of these nitro groups. Both these approaches are documented by Figures 4−8. Primary fission of the polynitro polyphenylenes (i.e., “genuine” polynitro arenes) during initiation lies in the C−N bond homolysis.[7,8,23]

The calculation of electronic charges, q^N, at nitrogen atoms and net charges, Q_{NO2}, of nitro groups of the individual EMs investigated was carried out by means of the Mulliken population analysis of electron densities obtained by the ab initio DFT B3LYP/6-31G** method, under total geometry optimization and without subsequent frequency analysis;[8] these values correspond to isolated molecules at 0 K. Figure 4, taken from ref 3, presents a specification of the reaction centers in the studied polynitro arenes in their thermal decomposition (i.e., initiation by heat) by means of the q^N values. Figure 5[3] specifies these centers for initiation by impact and Figure 7[3] for initiation by shock and detonation development, both using the Q_{NO2} values. Analogously, reaction centers in the initiation by both these impulses are represented by Figures 6 and 8 with the application of ^{13}C NMR chemical shifts of the carbon atoms bearing of the

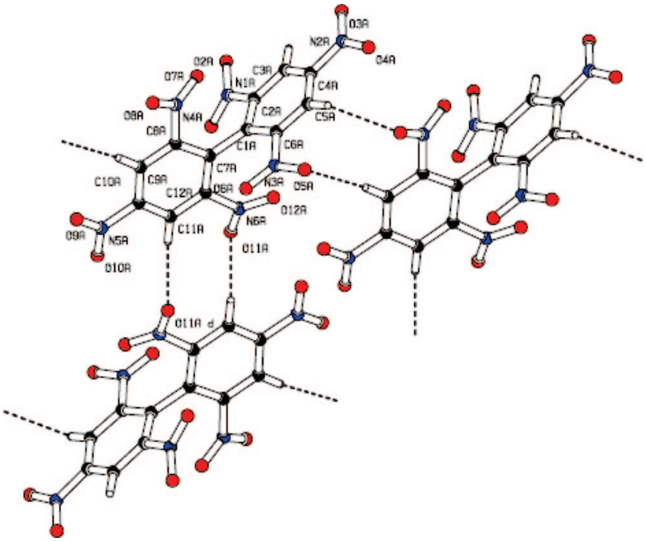

Figure 3. Drawing showing the potential intermolecular H-bonds in the HNBP crystal.

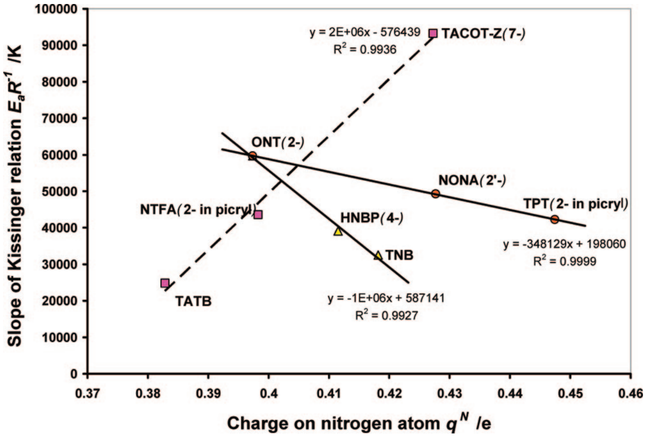

Figure 4. Relationship between the characteristics of thermal reactivity from differential thermal analysis (slopes E_aR^{-1} of the Kissinger relation) and charges on nitrogen atoms of the primarily reacting nitro groups in initiation: here an influence of the stabilizing effect of the crystal lattice manifests itself in the cases of TATB, NTFA, and TACOT-Z (in parentheses are given the respective positions in molecule). Reproduced with permission from ref 3. Copyright 2006 Elsevier Limited.

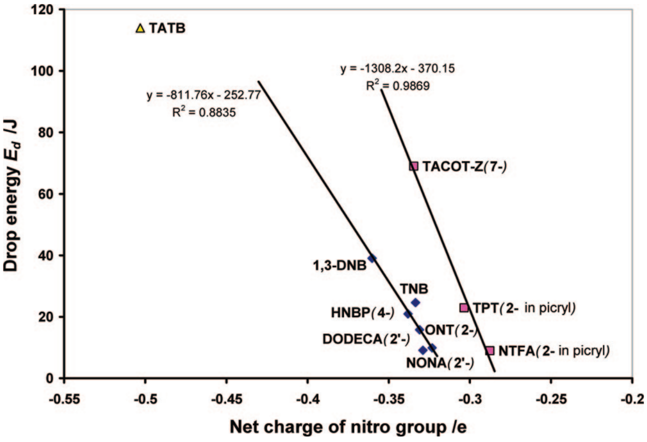

Figure 5. Relationship between drop energies (impact sensitivity) and net charges of nitrogen atoms of the primarily reacting nitro groups in initiation (in parentheses are given the positions in molecule). Reproduced with permission from ref 3. Copyright 2006 Elsevier Limited. Here 1,3-DNB means 1,3-dinitrobenzene.

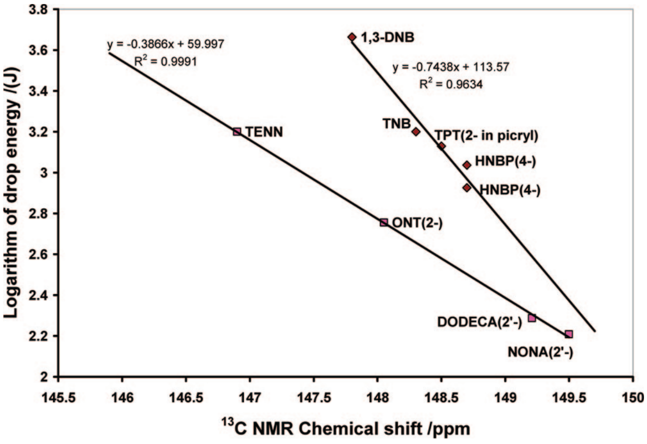

Figure 6. Relationship between the impact sensitivity (drop energy) and ^{13}C NMR chemical shifts of “the bearers” of the primarily leaving nitro groups of the studied polynitro arenes (in parentheses are given the respective positions in molecule), data from ref 21. Here, 1,3-DNB means 1,3-dinitrobenzene.

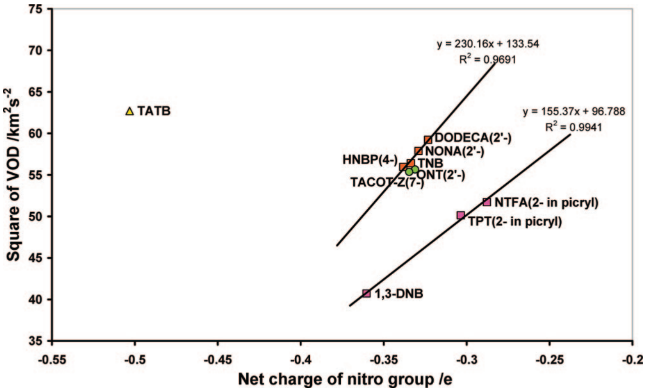

Figure 7. Relationship between the square of detonation velocity (VOD) and net charges of nitrogen atoms of the primarily reacting nitro groups in initiation (in parentheses are given the respective positions in molecule). Reproduced with permission from ref 3. Copyright 2006 Elsevier Limited. Here 1,3-DNB means 1,3-dinitrobenzene.

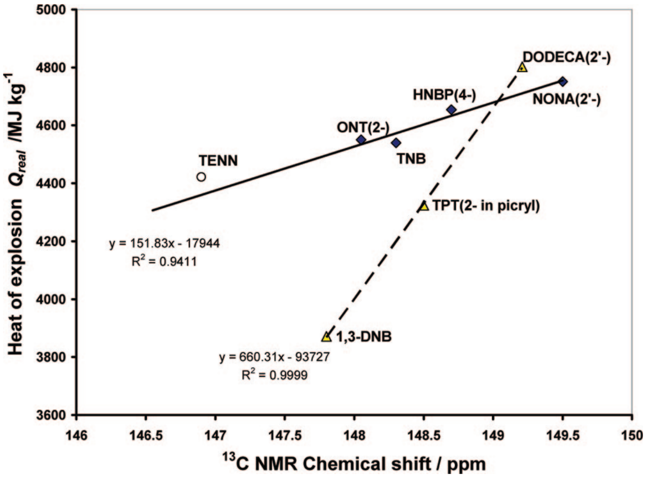

Figure 8. Relationship between the heat of explosion and ^{13}C NMR chemical shifts of "the bearers" of the primarily leaving nitro groups of the studied polynitro arenes (in parentheses are given the respective positions in molecule), data from ref 21. Here 1,3-DNB means 1,3-dinitrobenzene.

primarily leaving nitro groups (both the figures were taken from ref 21); these figures can remind us of the modified Evans−Polanyi−Semenov equation for energetic materials.[8] This relationship is valid for narrow sets of substance structures, and it documents that the strength of bond being split is a decisive factor in the given reaction.[7,8]

In Figures 4−8 the HNBP molecule behaves in corresponding correlations by characteristics of its position 4(4′). However, the expected correlations should cover the data of the positions 2,6(2′,6′), because most structural deformations are in these parts of HNBP molecule (see the crystallographic data). It is well-known that deformations due to steric hindrance in polynitro compounds increase the reactivity of these compounds.[6,22,23] Also the longest C−N bond is here (C8B−N4B), which should be the weakest bond in the molecule. Nevertheless, the closeness of the C8B−N4B (position 2) and C10B−N5B (position 4) bond lengths (see also Table 4), together with the already mentioned possibility of hydrogen bond and also the above-mentioned possibility of intermolecular interactions of nitro groups, might have a causal relationship to findings from the study of the HNBP initiation reactivity (see Figures 4−8). In this respect, HNBP differs from the other members of the polynitro polyphenylene series containing trinitrophenyl building blocks in their molecules and presented in Figures 4−8. Recent papers[6,20] deal with the characteristics of the *ortho*-groupings in HNBP molecule; no mathematical mistake was made there, but the relationships found[6,20] could have been slightly better if the findings from this present study had been available at that time.

Conclusions

The crystallographic study on HNBP shows that the largest dihedral angles are exhibited by nitro groups at *ortho*-positions, as expected. However, this result of steric hindrance is not in full accordance with the bond lengths at these positions. Intermolecular distances in molecular crystal signal a possibility of participation of *ortho*-nitro groups in intermolecular hydrogen bonds. Also it was found that there are atypically short distances between oxygen atoms of nitro groups at the 2,6-positions of one molecule and nitro groups at the 4-position of adjacent molecules. In some cases, the C−N bond lengths at *para*-positions are almost identical with the longest C−N bonds at the *ortho*-position. The given facts could represent a reason of preferable splitting of *para*-standing C−N bond, in contrast to the logically expected elimination of *ortho*-standing nitro groups of the HNPB molecule during the process of its initiation. In this respect, HNBP differs from the other members of polynitro polyphenylene series containing trinitrophenyl building blocks in their molecules.

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