Tetryl, Pentyl, Hexyl, and Nonyl

Preparation and Explosive Properties

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Synthesis of new analogs of tetryl and the determination of explosive properties are given. The correlation between the explosive properties assigned by the explosive sensitivity to impact, to friction, the explosive power and brisance, and the molecular structure represented by modified oxygen balance is graphically shown. Graphical illustration clearly proves the detoted explosive properties to be directly related to modified oxygen balance. The following series of compounds are examined: 2,4,6,-trinitrophenyl-*n*-alkylnitramines (tetryls), 2,4,6-trinitro-1,3-bis(alkylnitramino)-benzenes(pentyls), and 2,4,6-trinitro-1,3,5-tris(alkylnitramino)-benzenes(hexyls). Nonyl(2,4,6-trinitrophenyl-1,3,5-triethanoltrinitraminetrinitrate) and pentryl (2,4,6-trinitrophenylnitraminoethylnitrate) are also investigated.

THE AUTHORS studied the preparation of tetryl, pentyl, hexyl, nonyl, and some related analogs with the aim of investigating the explosive properties; the explosive characteristics, determined under similar conditions of testing, were then compared.

TETRYL

Tetryl has long been used both as a high explosive and as an initiator or primer for high explosives. It was first prepared by Mertens (*27*); a little later its constitution was established by van Romburgh (*40*). Patent literature provides much information on the methods of preparation of tetryl. Most methods involve the addition of a solution of dimethylaniline in concentrated sulfuric acid to nitric acid or to a mixture of nitric and sulfuric acids (*9*, *45*). Recently Urbanski and Semenczuk (*39*) have safely prepard tetryl by treatment of dimethylaniline with a great excess of nitric acid (specific gravity, 1.40) and/or with fuming nitric acid in presence of inert organic solvents (*35*).

There seems every reason to believe that tetryl in the future will be prepared chiefly or wholly from dinitrochlorobenzene (*4*, *12*, *34*) by condensation with methylamine followed by nitration of the resulting 2,4-dinitro-N-methylaniline. Boyer, Spencer, and Wright (*7*) obtained tetryl in a good yield by the nitration of N-methylpicramide, obtained via the interaction of picryl chloride with methylamine, with nitric acid.

Ethyl tetryl was first prepared by van Romburgh (*43*) and later by Blanksma (*1*) via the nitration of ethylaniline and diethylaniline. Recently Desseigne (*13*) studied the preparation of ethyl tetryl by nitration of 2,4-dinitro-N-ethylaniline.

The propyl analog of tetryl was prepared by van Romburgh (*41*) by the nitration of either 2,4-dinitrophenyl-*n*-propylamine or 2,4,6-trinitrophenyl-*n*-propylamine with fuming nitric acid.

The butyl analog of tetryl was prepared by the direct nitration of 2,4-dinitrophenyl-*n*-butylamine (*11*, *16*). Later Reilly and Hickinbottom (*31*) described a method for the preparation of the butyl analog by the nitration of a solution of N-dibutylaniline in acetic acid by fuming nitric acid.

EXPERIMENTAL

Preparation of Tetryl and Analogs. Two main procedures were adopted.

PROCEDURE A. 2,4-Dinitrochlorobenzene was condensed with the appropriate normal alkylamine by heating the reaction mixture, followed by neutralization of the liberated hydrochloric acid with aqueous sodium hydroxide. A mixture of sulfuric and nitric acids was used for the nitration of the resulting 2,4-dinitrophenyl-*n*-alkylamine (*13*).

In a 2-liter, 4-necked, round-bottomed flask (fitted with a reflux condenser, mechanical stirrer, and thermometer) was introduced 2,4-dinitrochlorobenzene (202.5 grams; 1 mole, m.p. 50.5° C.) and 200 ml. of water. The reaction mixture was heated (water bath, temp. 60-5°) under continuous stirring until dinitrochlorobenzene completely fused. A 34% aqueous solution of the appropriate lower *n*-alkylamine, or 34% aqueous-alcoholic solution (1 to 3) in the case of the higher *n*-alkylamine (C_8-C_{18}) was added dropwise, while stirring and keeping the temperature of the reaction mixture at 60–5°. The reaction mixture was then neutralized by the slow addition of the calculated amount of aqueous sodium hydroxide solution (30%) while the reaction mixture was maintained at 60–5°. Stirring was then continued for half an hour at 60–5°, and for an additional half hour at 80–90°. The solid reaction was collected, washed with cold distilled water until the washings gave negative test for the chlorine ion then crystallized from 95% ethanol, and kept over sulfuric acid.

In separation of oily products, the oil was decanted from the reaction mixture, washed thoroughly with water, and directly treated with the nitration mixture.

The analytical figures for the new 2,4-dinitrophenyl-*n*-alkylamines, as well as their solubilities in common solvents, are reported in Table I.

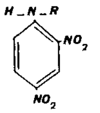
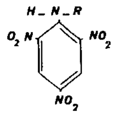
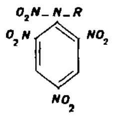
Nitration of 2,4-Dinitrophenyl-n-alkylamines. Into a 1-liter, 3-necked, round-bottomed flask, fitted with a mechanical stirrer and thermometer, was introduced 255.2 grams (2.5 moles) of sulfuric acid (96%, specific gravity, 1.835). The acid was then heated to 45° and 0.5 mole of the dried 2,4-dinitrophenyl-*n*-alkylamine was added portionwise with stirring. The resulting solution was cooled to room temperature and was added dropwise, with stirring, to cooled 80.3 grams (1.25 moles) of nitric acid (98%, specific gravity, 1.5) contained in a 1-liter, 3-necked, round-bottomed flask fitted with a mechanical stirrer and thermometer. The amount of nitric acid used was calculated so as to attain the final molecular ratio of dinitrophenyl-*n*-alkylamine to nitric acid to sulfuric acid as 1 to 2.5 to 5.

The temperature during nitration was maintained not to exceed 40° by controlling the rate of the addition. A blue violet tint was imparted to the reaction mixture during the start of addition, but disappeared with the separation of the formed yellow reaction product (*9*). The reaction mixture was further stirred for 15 minutes at 50°, cooled to room temperature, and filtered. The solid product was transferred to a beaker containing 500 ml. of cold water, stirred, and filtered, and the solid was washed thoroughly with water, then with distilled water until free from contaminated acids. It was crystallized from 95% ethanol and kept in a desiccator over sulfuric acid.

The analytical figures for the new 2,4,6-trinitrophenyl-*n*-alkylnitramines as well as their solubilities are reported in Table I.

PROCEDURE B. Picryl chloride was used for 2,4-dinitro-

Table I. List of New Synthesized Compounds

Compd.	Calcd. For	Analysis, %						M.P., ° C.	Color[a]	Yield,[b] %	Solubility[c]													
		Found			Calcd.																			
		C	H	N	C	H	N				A	B	C	D	E	F	G	H	I	J	K	L	M	N
																								
C_8H_{17}	$C_{14}H_{21}N_3O_4$	56.82	7.07	14.20	56.93	7.16	14.22	Oil[d]	...	91	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
C_9H_{19}	$C_{15}H_{23}N_3O_4$	57.96	7.31	13.43	58.23	7.49	13.58	46	L.Y.	92.5	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{16}H_{25}N_3O_4$	58.91	7.63	12.80	59.42	7.79	12.99	37.5	L.Y.	94	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{18}H_{29}N_3O_4$	61.40	8.23	11.87	61.51	8.31	11.95	38	L.Y.	93.5	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{20}H_{33}N_3O_4$	62.94	8.71	11.34	63.29	8.76	11.07	53	L.Y.	92.5	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{22}H_{37}N_3O_4$	64.76	9.20	10.60	64.83	9.15	10.31	51.5	Y.	94	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{24}H_{41}N_3O_4$	66.69	9.39	9.49	66.17	9.48	9.64	61.3	Y.	93	−	±*	±	+	+	+	±	+	±	+	+	+	+	+
																								
C_5H_{11}	$C_{11}H_{14}N_4O_6$	44.20	4.57	18.58	44.29	4.73	18.78	67	Y.	82	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
C_6H_{13}	$C_{12}H_{16}N_4O_6$	46.23	5.21	18.04	46.15	5.16	17.94	67.5	Y.	85	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
C_7H_{15}	$C_{13}H_{18}N_4O_6$	48.00	5.82	16.96	47.85	5.56	17.17	59	Y.	82	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
C_8H_{17}	$C_{14}H_{20}N_4O_6$	49.54	5.74	16.51	49.40	5.92	16.46	58.2	Y.	78	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
C_9H_{19}	$C_{15}H_{22}N_4O_6$	50.72	6.19	15.91	50.84	6.23	15.81	34.4	Y.	77.5	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{16}H_{24}N_4O_6$	52.23	6.55	15.20	52.16	6.56	15.21	68	Y.	78	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{18}H_{28}N_4O_6$	54.32	7.25	13.97	54.53	7.12	14.13	63	Y.	79	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{20}H_{32}N_4O_6$	56.35	7.38	13.29	56.58	7.59	13.20	80.5	Y.	82	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{22}H_{36}N_4O_6$	57.97	8.18	12.31	58.38	8.01	13.38	82.2	Y.	85	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{24}H_{40}N_4O_6$	59.55	8.19	11.68	59.97	8.39	11.65	86	Y.	79.5	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
																								
C_3H_5	$C_9H_7N_5O_8$	34.38	2.22	22.45	34.51	2.25	22.36	98.2	L.Y.	12 9.5	−	+*	±	+	±	±	−	±	±	+	+	+	+	+
C_5H_{11}	$C_{11}H_{13}N_5O_8$	38.39	3.73	20.36	38.48	3.81	20.40	85	L.Y.	92.5 91	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
C_6H_{13}	$C_{12}H_{15}N_5O_8$	40.50	4.44	19.72	40.34	4.23	19.60	86	L.Y.	92 90.5	−	±*	±	+	±	±	−	+	±	+	+	+	+	+
C_7H_{15}	$C_{13}H_{17}N_5O_8$	42.21	4.77	19.33	42.05	4.61	18.86	91.2	L.Y.	90.5 90	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
C_8H_{17}	$C_{14}H_{19}N_5O_8$	43.59	4.93	18.44	43.63	4.97	18.17	88.3	L.Y.	92 91	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
C_9H_{19}	$C_{15}H_{21}N_5O_8$	45.27	5.34	17.70	45.11	5.30	17.53	90.5	L.Y.	91.5 93	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{16}H_{23}N_5O_8$	46.20	5.52	16.86	46.48	5.60	16.94	93.8	L.Y.	90 92	−	±*	+	+	±	±	−	±	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{18}H_{27}N_5O_8$	49.37	6.21	15.83	48.97	6.16	15.85	88.2	L.Y.	89 92	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{20}H_{31}N_5O_8$	50.94	6.78	14.68	51.16	6.65	14.91	94.2	L.Y.	93 90	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{22}H_{35}N_5O_8$	52.84	7.19	13.88	53.10	7.09	14.07	98	L.Y.	90.5 88.5	−	±*	±	+	±	±	−	±	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{24}H_{39}N_5O_8$	55.04	7.57	13.44	54.84	7.48	13.32	95	L.Y.	91 90.5	−	±*	±	+	±	±	−	±	±	+	+	+	+	+

[a] Color symbols: Y yellow, L.Y. light yellow.

[b] Yields in center of table by procedures A and B.

±* Especially suitable for recrystallization. + Very soluble. ± Fairly soluble. Solubility qualitatively determined at 25° C. following arbitrary standards employed by Vogel (*44*)

[c] Solubility symbols: A water, B ethanol (95%), C methanol, D acetone, E ether, F chloroform, G carbon tetrachloride, H carbon disulfide, I petroleum ether, J benzene, K chlorobenzene, L nitrobenzene, M acetic acid, N acetic anhydride.

[d] B.p. 263/760 mm.

[e] Tetryl analogs starting from allyl to octadecyl analog.

chlorobenzene, in the condensation reaction, followed by treatment of the resulting 2,4,6-trinitrophenyl-*n*-alkylamine with a mixture of sulfuric and nitric acids.

Picryl chloride used in the condensation reaction (m.p. 83°) was emulsified with stirring with an equal quantity of aqueous-alcoholic solution (3 to 1) at 85° in a 4-necked round-bottomed flask fitted with a reflux condenser, mechanical stirrer, and thermometer.

A 34% solution of the *n*-alkylamine prepared as previously described (Procedure A) was then dropwise added while stirring and keeping the temperature of the reaction mixture at 85-7°. The reaction mixture was then neutralized by the slow addition of the calculated amount of aqueous sodium hydroxide solution (30%) to keep the temperature maintained at 85-7°, and stirring was further continued for an additional half hour at the same temperature. The reaction mixture was then allowed to cool under continual stirring to room temperature; the solid product that separated was thoroughly washed with cold distilled water until the washings gave a negative test for chlorine. Solid product was crystallized from 95% ethanol and kept over sulfuric acid for desiccation. 2,4,6-Trinitrophenyl-*n*-alkylamines are reported in Table I.

Nitration of 2,4,6-Trinitrophenyl-*n*-Alkylamines. A procedure similar to procedure A for the nitration of the dinitro derivative has been adopted. 2,4,6-Trinitrophenyl-*n*-alkylamine was first dissolved in sulfuric acid (96%, specific gravity, 1.835) at 45°, 2.5 moles of sulfuric acid used was for each mole of the trinitrophenyl-*n*-alkylamine.

The resulting solution after being cooled to room temperature was added dropwise to cooled nitric acid (98%, specific gravity, 1.5). The nitric acid used was 25% in excess of that theoretically required to achieve complete nitration (for each mole of trinitrophenyl-*n*-alkylamine, 1.25 moles of nitric acid was used to get the final molecular ratio of trinitrophenyl-*n*-alkylamine to nitric acid to sulfuric acid as 1 to 1.25 to 2.5).

The nitration temperature was controlled not to exceed 40°, by external cooling of the nitration flask and by controlling the rate of the addition. At the end of nitration, a yellow product was dispersed in the medium. The reaction mixture was further stirred for 15 minutes at 50°, cooled to room temperature, and filtered. The product obtained was freed from contaminated acids as the first procedure, crystallized from 95% ethanol, and finally dried by desiccation over sulfuric acid.

Explosive Characteristics of Tetryl and Analogs. SENSITIVITY TO HEAT. The sensitivity of the explosive to heat is measured by determination of its ignition temperature or the temperature at which the explosive burns, explodes, or "puffs" spontaeously (*10*). Though the method adopted differs from the earlier techniques of Marshall (*25*), Kostevitch (*23*), and the recent methods of Robertson (*32*), and Henkin and McGill (*20*), we would like to mention that the data are comparative only and are based on results on one particular apparatus (*10, 20*). The experiment was carried out by inserting three ingnition test tubes, each containing 0.1 gram of the dry sample of the explosive, in the corresponding holes of an ignition point apparatus (Julius Peters, Berlin) as soon as its temperature attained 100°. The temperature was then raised at a rate of 20° every minute by means of a sliding resistance. The mean value (corrected) of the three temperatures, recorded as soon as the sample exploded in each of the three tubes, was taken as the ignition temperature of the explosive sample.

These results indicate an increase in the sensitivity to heat from tetryl to its pentyl analog; the sensitivity of other higher analogs is, however, more or less similar.

SENSITIVITY TO DIRECT IMPACT. The sensitivity to direct impact was determined using (Oerlikon impact machine No. 26 Model M.F. 54), by subjecting a small quantity of the explosive (0.02 gram) to the transmitted shock from a falling weight and the minimum height of fall causing at least one explosion in ten tests, was determined (*22*). The results of tests on tetryl and its analogs are given in Table II.

Results, recorded in Table II, indicate a gradual increase in the required energy of direct impact from tetryl to its octadecyl analog; hence, a gradual decrease in the explosive sensitiveness. This variation is better illustrated by plotting the data for the sensitivity to direct impact against the oxygen balances (Ω) of tetryl and its analogs calculated according to Martin and Yallop (*26*) (Figure 1.). Oxygen balances (Ω) were calculated using the modified formula:

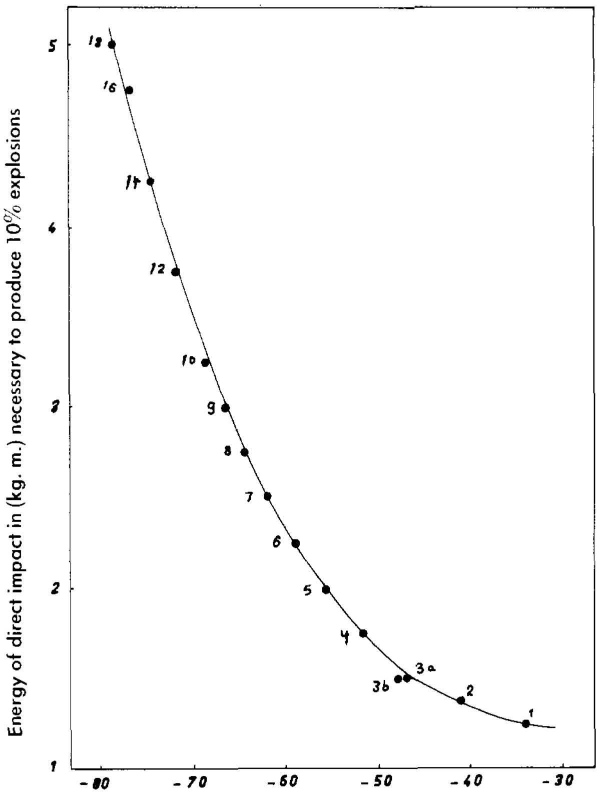


Figure 1. Effect of oxygen balance on the sensitivity to direct impact of tetryl and its analogs

Numbers refer to explosives in Table II

$$\frac{[z - 2x - (y/2)]\,100}{n} \pm \frac{100\omega}{n}$$

where *x*,*y*, and *z* are the respective numbers of atoms of carbon, hydrogen, and oxygen in the molecule; *n* is the number of atoms in the molecule and ω is computed by summing the oxygen atoms according to their linkages.

Figure 1 shows a close direct relationship between the sensitivity of tetryl and its analogs to direct impact and

Table II. Sensitivity to Direct Impact Test

Explosive		Sensitivity to impact			
No.	Name	Kg.	M.	%	Kg. M.[a]
1	Tetryl	5	0.25	10	1.25
2	Ethyl	5	0.275	10	1.375
3a	Allyl	5	0.30	10	1.50
3b	Propyl	5	0.30	10	1.50
4	Butyl	5	0.35	10	1.75
5	Pentyl	5	0.40	10	2.00
6	Hexyl	5	0.45	10	2.25
7	Heptyl	5	0.50	10	2.50
8	Octyl	5	0.55	10	2.75
9	Nonyl	5	0.60	10	3.00
10	Decyl	5	0.65	10	3.25
12	Dodecyl	5	0.75	10	3.75
14	Tetradecyl	5	0.85	10	4.25
16	Hexadecyl	5	0.95	10	4.75
18	Octadecyl	5	1.00	10	5.00

[a] Energy of direct impact to produce 10% explosions.

the oxygen balances. This result agrees with the findings of Lothrop and Handrick (*24*) and Roth (*33*).

Allyl and propyl analogs of tetryl, being closely related to each other, are of similar sensitivity.

SENSITIVITY TO FRICTIONAL IMPACT. This test was carried out by the frictional test machine [Julius Peters N.W. 21, Type S.M. (VI)]. The procedure is based on the principle described by Thorpe and Whiteley (*38*). In carrying out the test 0.05 gram of the dried, ground explosive was placed in an even layer on a nonenameled porcelain disk (25 x 25 mm.). A china porcelain rolling pin 10 mm. in diameter fixed to a rod for pressure lever divided into six divisions, each 5 cm. in length, was allowed to slide on the explosive so as to produce maximum shearing stresses. The rod for pressure lever was driven by a suitable motor mounted on a wooden base. The test was carried out with nine increasing weights 0.212, 0.492, 1.052, 1.612, 2.172, 3.340, 4.412, 6.650, and 10 kg.; fractions of weights represent the weights of loads in Julius Peters frictional test apparatus for high explosives. Five trials were conducted with each weight at every rod division, and the energy of frictional impact (kilograms per meter of arm length) necessary to produce 100% explosions was determined.

The data recorded in Table III show a gradual decrease in the sensitivity to frictional impact from tetryl to its octadecyl analog; Figure 2 shows this by the decrease of the sensitivity to frictional impact with the decrease of the oxygen balance. This agrees with sensitivity of the explosives to direct impact. Both results are in confirmation with the findings of Lothrop and Handrick (*24*) and Roth (*33*).

SENSITIVITY TO DETONATION BY INITIATING AGENTS. The sensitivity of an explosive to detonation by a certain initiating agent is determined by the lead plate test (*10*, p.421) by which the least amount of the initiating agent which causes complete detonation is ascertained. Details of the test are given in the patent literature (*18*, *19*).

In this test 0.50 gram of base charge of the explosive was weighed into a No. 8 detonator shell, in two 0.25 gram increments, and each was pressed at 98 kg. per sq. cm. Priming charges constituting varying weights of initiating compositions (either a 80-20 lead azide-lead styphnate mixture or 80-20 mercury fulminate-potassium chlorate mixture), in 0.025 gram increments, were then inserted, each as a single charge on top of the base charge and pressed at 49 kg. per sq. cm. A reinforcing capsule was then inserted, and a pressure of 49 kg. per sq. cm. was applied for 1 minute so as to enclose the priming charge. The detonator was fired in an upright position resting upon the center of 5 x 5 x 0.4. cm. lead plate, which in turn rested upon a suitable base opened beneath the position of the detonator. On firing the detonator, the lead plate was dented or punctured and marked variously. Six trials were made for each weight of the priming charge to the nearest 0.025 gram. The weight which produced three complete detonations without partial or imcomplete detonations, was taken as the minimum initiating charge. Complete detonation was manifested by a clean-cut hole through the lead plate with divergent ray marks radiating to the edges of the plate; moreover, the diameter of the hole produced was taken as the criterion of the detonator strength or the explosive brisance (*18*, *28*). Table IV shows the results of tests on tetryl and its analogs.

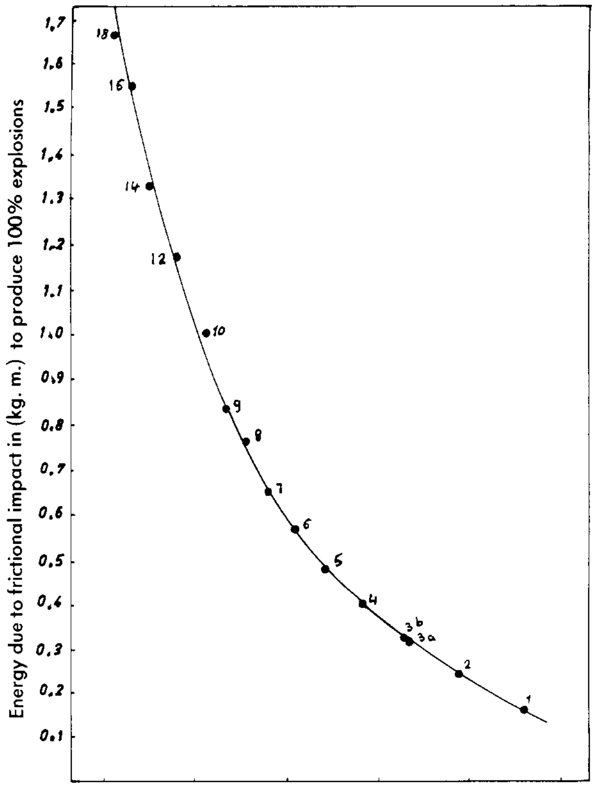


Figure 2. Effect of oxygen balance on the sensitivity to frictional impact of tetryl and its analogs

Numbers refer to explosives in Table III

The sensitivity to detonation by either (80-20 lead azide-lead styphante) or (80-20 mercury fulminate-potassium chlorate) compositions decreases from tetryl to its octyl analog. The sensitivity to detonation of other tetryl analogs, higher than the octyl analog, exceeds the limit possible to determine practically.

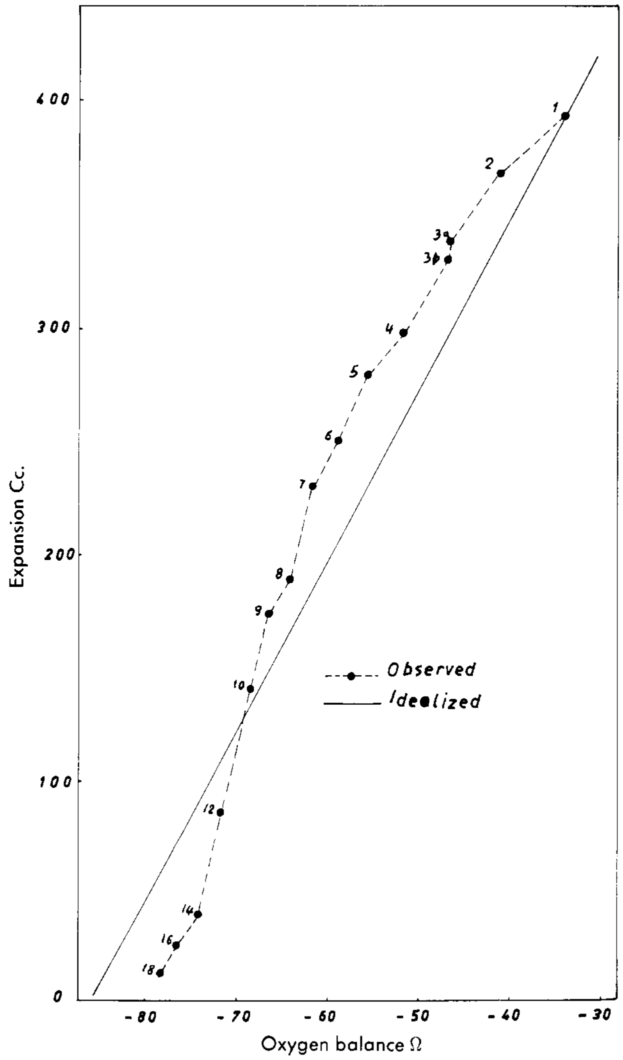


Figure 3. Effect of oxygen balance on power and brisance of tetryl and its analogs determined by the Trauzl test

Numbers refer to explosives in Table V.

Brisance. The brisance or the shattering effect of investigated explosives was compared by detonating them, filled in detonators, on plates or disks of lead or steel and comparing the cavities formed (*25*, *28*). The lead plate test was used. The results obtained give an instructive idea of the relative brisance of the explosives concerned (*25*). Thorough comparison of figures of hole diameters produced with the lead plate test (Table IV) for tetryl and its analogs shows a decrease from tetryl to its octyl analog. The brisance of other tetryl analogs higher than the octyl analog stands, however, beyond the lowest limit attained.

Power. The Trauzl lead block test offers a means of ascertaining the comparative disruptive power of explosives (*29*, *37*). The test is based on measuring the volume of the cavity produced when a 10 gram weight of an explosive is fired in a bore hole in a lead block of specified dimensions. The test was carried out according the standard conditions recommended by the 5th International Congress of Applied Chemistry, Berline (1903). Results of this test can be taken as expressive of a combination of power and brisance, since both qualities appear to vary concomitantly (*24*). A comparison of the power of tetryl and its analogs is given in Table V.

Results of the Trauzl lead block test indicate a decrease in power from tetryl to its octadecyl analog. Figure 3

Table III. Sensitivity to Frictional Impact Test

Explosive		Sensitivity to Friction Arm Length			
No.	Name	Kg.	M.	%	Kg. M.[a]
1	Tetryl	1.052	0.15	100	0.157
2	Ethyl	1.612	0.15	100	0.242
3a	Allyl	1.052	0.30	100	0.315
3b	Propyl	1.612	0.20	100	0.322
4	Butyl	1.612	0.25	100	0.403
5	Pentyl	1.612	0.30	100	0.483
6	Hexyl	1.612	0.35	100	0.564
7	Heptyl	2.172	0.30	100	0.651
8	Octyl	2.172	0.35	100	0.760
9	Nonyl	3.340	0.25	100	0.835
10	Decyl	3.340	0.30	100	1.002
12	Dodecyl	3.340	0.35	100	1.169
14	Tetradecyl	4.412	0.30	100	1.323
16	Hexadecyl	4.412	0.35	100	1.544
18	Octadecyl	6.650	0.25	100	1.662

[a] Energy due to frictional impact to produce 100% explosions.

Table IV. Lead Plate Test

Explosive (Base charge)	Priming Charge, G.[a]	Diameter, Mm.[b]	Priming Charge, G.[c]	Diameter, Mm.[b]	Initiating Charge, G.	
					Min.[a]	Min.[c]
Tetryl	0.025	9.4	0.175	...	0.025	0.200
	0.050	9.8	0.200	9.5		
	0.075	10.0	0.225	10.0		
	0.100	10.5	0.250	10.2		
Ethyl	0.200	...	0.350	...	0.225	0.375
	0.225	9.2	0.375	8.0		
	0.250	9.7	0.400	8.5		
	0.275	10.1	0.425	8.6		
	0.300	10.3	0.450	8.8		
Allyl	0.225	...	0.375	...	0.250	0.400
	0.250	9.2	0.400	8.2		
	0.275	10.2	0.425	8.5		
	0.300	10.3	0.450	8.7		
Propyl	0.225	...	0.375	...	0.250	0.400
	0.250	9.1	0.400	8.0		
	0.275	10.0	0.425	8.5		
	0.300	10.2	0.450	8.7		
Butyl	0.275	...	0.575	...	0.300	0.600
	0.300	7.5	0.600	6.6		
	0.325	8.0	0.625	7.0		
	0.350	8.1	0.650	7.2		
Pentyl	0.350	...	0.675	...	0.375	0.700
	0.375	5.0	0.700	5.0		
	0.400	5.5	0.725	5.2		
	0.425	5.6	0.750	5.2		
Hexyl	0.375	...	0.725	...	0.400	0.750
	0.400	5.0	0.750	4.8		
	0.425	5.5	0.775	4.9		
	0.450	5.6	0.800	5.0		
Heptyl	0.425	...	0.775	...	0.450	0.800
	0.450	4.8	0.800	4.5		
	0.475	5.0	0.825	4.6		
	0.500	5.2	0.850	4.6		
Octyl	0.625	...	2.0	...	0.650	>2
	0.650	4.8				
	0.675	5.1				
	0.700	5.2				
Nonyl	2.0	...	2.0	...	>2	>2
Decyl	2.0	...	2.0	...	>2	>2
Dodecyl	2.0	...	2.0	...	>2	>2
Tetradecyl	2.0	...	2.0	...	>2	>2
Hexadecyl	2.0	...	2.0	...	>2	>2
Octadecyl	2.0	...	2.0	...	>2	>2

[a] Composition: 80 lead azide–20 lead styphnate. [b] Size of hole produced in lead plate. [c] Composition: 80 mercury fulminate–20 potassium chlorate.

reports the effect of oxygen balance on power and brisance of explosives. In Figure 3 the data have been conveniently summarized by drawing an idealized straight line curve, which can be considered a useful generalization of no great accuracy. The conclusion, to be drawn from the curve, that the power and brisance of tetryl and its analogs vary directly with oxygen balance, finds analogy with the theoretical considerations laid down by Lothrop and Handrick (*24*).

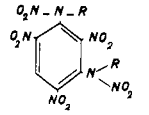
STABILITY. Explosives were subjected for 48 hours to the international heat test at 75° (*36*). To ascertain the effect of higher temperatures, the material used for the International heat test was subjected to a temperature of 100°, for 48 hours, and for an additional 48 hours (*22*). At the expiration of every mentioned period, the loss in weight was determined. Table VI shows results of these tests on tetryl and its analogs.

These results indicate a variable degree of decomposition from one tetryl analog to the other on exposure to the 75° test. The same is true when analogs of tetryl are heated at 100° for 48 and 96 hours, respectively. Tetryl is the only member in this series that shows no marked decomposition when subjected to the moderately high temperature stability test. Tetryl analogs starting from the ethyl to the butyl analog show moderate decomposition. Higher analogs than butyl tetryl show higher but still variable decomposition.

PENTYL

2,4,6-Trinitro-1,3,-bis(alkylnitramino)-benzenes

2,4,6 - Trinitro - 1,3 - bis(methylnitramino) - benzene(Ia) (pentyl) was first prepared by van Romburgh (*42*), and later Blanksma and Terwogt (*6*) by nitration of 4,6-dinitro-1,3-bis(methylamino)-benzene obtained by the condensation of 1,3-dichloro-4,6-dinitrobenzene with *n*-methylamine.



Blanksma (*2*) prepared (Ia) by the nitration of 2,4,6-trinitro-1,3-bis(methylamino)-benzene, readily obtained by the condensation of 2,4,6-trinitro-3-chloroanisol with *n*-methylamine.

The ethyl analog of pentyl, ethyl pentyl (Ib), was obtained by Blanksma (*3*) through the nitration of 2,4,6-trinitro-1,3-bis(ethylamino)-benzene, prepared by the interaction of an alcoholic solution of 2,4,6-trinitro-5-chlorophenetole with *n*-ethylamine.

EXPERIMENTAL

Preparation of Pentyl and Analogs. The procedure was principally the condensation of 1,3-dichloro-4,6-dinitrobenzene (1 mole) with the appropriate normal alkylamine (4 moles) followed by nitration of the resulting product (*6, 42*).

Preparation of 4,6-Dinitro–1,3-bis(alkylamino)-benzene. A quantity (237 grams) of 1,3-dichloro-4,6-dinitrobenzene (1 mole; m.p. 103° C.) prepared by the method of Nietzki and Schedler (*30*) was dissolved in 200 ml. of 95% ethyl alcohol (bath temperature 60–5°). A 34% aqueous solution of the appropriate lower *n*-alkylamine, or 34% aqueous-alcoholic solution (1 to 3) in the case of the higher *n*-alkylamine (C_8-C_{18}) (4 moles in each case) was added dropwise to the agitated alcoholic solution, temperature being maintained at 60–5°. A 25% sodium carbonate solution was then slowly added to neutralize the liberated hydrochloric acid reaction temperature was always kept, during addition, at 60–5°, and for half an hour after addition of the sodium carbonate was completed. At the end of the second period of heating, the temperature was raised to 85–90° and maintained constant for half hour. The reaction mixture was then cooled and filtered free of the precipitated sodium chloride. The yield, after washing, was several times crystallized from 95% ethanol and kept over sulfuric acid to dry.

The new 4,6-dinitro-1,3-bis(alkylamino)-benzenes are reported in Table VII; the yield ranges from 90 to 95%.

Nitration of 4,6-Dinitro–1,3-bis(alkylamino)-benzene. Many procedures have been followed to obtain pentyl and its *n*-alkyl analogs in good yield. Excess of nitric acid (13 times the theory) has been used in every procedure (*17*) to obtain an acid mixture gently agitated until complete nitration and to effect regular precipitation of the nitrated product. When sulfuric acid was used in a mixture with nitric acid, the ratio of the two acids was always maintained 2 to 1, a ratio found common in nitration procedures described in the patent literature to produce nitramines or nitramine nitrates (*13, 14, 17*).

PROCEDURE C. The nitration of 4,6-dinitro-1,3-bis (alkylamino)-benzene was effected by sing fuming nitric acid (*3, 6*).

Dried 4,6-dinitro-1,3-bis(alkylamino)–benzene (0.5 mole) was added portionwise to cooled rapidly agitated 1228.5 grams (19.5 moles) of fuming nitric acid (specific gravity, 1.52), the temperature being maintained below 25°. Then, the temperature of the reaction mixture was raised slowly, while stirring, to 40–50°, during which time the color of the solution changed from brown to green to violet to blue. accompanied with separation of the nitrated product. It was further stirred for 30 minutes at 50°, then cooled to room temperature. The acid mixture was poured, with stirring, into ice-cold water. Crude product was collected after thorough washing with water and distilled water, crystallized from 95% ethanol, and kept in a desiccator over sulfuric acid.

Data on the new 2,4,6-trinitro-1,3-bis(alkylnitramino)-benzenes (analogs of pentyl) are reported in Table VII. The yield ranges from 86 to 90%.

Table V. Comparative Tests

Explosive		Ignition	Expansion,
No.	Name	Temp., ° C.[a]	Cc.[b]
1	Tetryl	192	395
2	Ethyl	179	368
3a	Allyl	180.5	338
3b	Propyl	175	330
4	Butyl	167	297
5	Pentyl	165	280
6	Hexyl	160	250
7	Heptyl	162	230
8	Octyl	160	190
9	Nonyl	161	174
10	Decyl	159	140
12	Dodecyl	158	86
14	Tetradecyl	160	40
16	Hexadecyl	159	26
18	Octadecyl	157	14

[a] Mean value, 20° C./min. [b] Mean value of 3 trials corrected to 18° C.

Table VI. Stability Tests

	Weight Loss, %[a]		
Explosive	48 Hr.[b]	48 Hr.[c]	96 Hr.[c]
Tetryl	0.125	0.125	0.125
Ethyl	0.173	2.826	5.020
Allyl	0.160	2.510	6.340
Propyl	0.158	2.308	7.950
Butyl	0.134	1.387	6.480
Pentyl	0.192	5.830	11.960
Hexyl	0.153	5.016	11.990
Heptyl	0.144	6.064	11.800
Octyl	0.342	6.880	12.480
Nonyl	0.277	6.635	12.440
Decyl	0.228	5.388	11.720
Dodecyl	0.225	6.808	13.730
Tetradecyl	0.444	5.697	12.770
Hexadecyl	0.331	8.467	10.340
Octadecyl	0.561	8.662	10.940

[a] Weight losses are corrected for the moisture content of different explosives. [b] After 48 hours, using international test, 75° C. [c] After 48 and 96 hours, using heat test, 100° C.

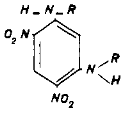
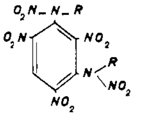
PROCEDURE D. Nitration was carried out by portionwise addition, under continual stirring, of dried 4,6-dinitro-1,3-bis(alkylamino)-benzene (0.1 mole) to sulfuric-nitric acid mixture (796.2 grams; specific gravity, 1.835 and 245.7 grams; specific gravity, 1.52, respectively). The temperature of the reaction mixture was not allowed to exceed 15-20° during the addition. It was then raised to 40-50° and kept at 50° for an additional half hour. The solid product that separated out was filtered, and washed as described in Procedure C. The yield ranges from 82 to 85% for pentyl and its *n*-alkyl analogs.

PROCEDURE E. Pentyl and its analogs were obtained in 84 to 87% yield when a sulfuric acid solution (7.8 moles; specific gravity, 1.835) of 0.1 mole of dried 4,6-dinitro-1,3-bis(alkylamino)-benzene was added to fuming nitric acid (3.9 moles; specific gravity, 1.52); temperature of the reaction mixture was maintained at 20-30° during addition. The nitration reaction was brought to completion by raising the temperature of the reaction mixture to 50° under stirring, and keeping it for an additional half hour at that temperature.

Explosive Properties of Pentyl and Analogs. Pentyl and its analogs were subjected to sensitivity tests as indicated by: ignition temperature (an indication of sensitivity to heat), full hammer impact, frictional impact, and sensitivity to detonation as well as brisance (lead plate test), power (Trauzl test), and stability (international 75° and 100° tests).

SENSITIVITY TO HEAT. The sensitivity of pentyl and its analogs to heat varies from one analog to the other but

Table VII. List of New Synthesized Compounds

Compd.	Calcd. For	C	H	N	C	H	N	M.P., ° C.	Color[a]	A	B	C	D	E	F	G	H	I	J	K	L	M	N
																							
C_2H_5	$C_{10}H_{14}N_4O_4$	47.35	5.50	22.00	47.24	5.55	22.04	173.5	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_3H_7	$C_{12}H_{18}N_4O_4$	51.21	6.33	19.72	51.05	6.43	19.85	148.2	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_4H_9	$C_{14}H_{22}N_4O_4$	54.10	7.22	18.16	54.18	7.14	18.05	105.6	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_5H_{11}	$C_{16}H_{26}N_4O_4$	56.86	7.70	16.38	56.79	7.74	16.56	63.5	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_6H_{13}	$C_{18}H_{30}N_4O_4$	58.77	8.17	15.31	58.99	8.25	15.29	80.8	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_7H_{15}	$C_{20}H_{34}N_4O_4$	60.93	8.75	14.13	60.89	8.69	14.20	70.3	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_8H_{17}	$C_{22}H_{38}N_4O_4$	62.31	9.21	13.19	62.53	9.06	13.26	73.7	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
C_9H_{19}	$C_{24}H_{42}N_4O_4$	63.82	9.35	12.40	63.97	9.39	12.43	85.0	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
$C_{10}H_{21}$	$C_{26}H_{46}N_4O_4$	65.20	9.75	11.59	65.24	9.69	11.70	83.5	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
$C_{12}H_{25}$	$C_{30}H_{54}N_4O_4$	67.49	10.16	10.52	67.38	10.18	10.48	89.6	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
$C_{14}H_{29}$	$C_{34}H_{62}N_4O_4$	69.19	10.60	9.55	69.11	10.58	9.48	96.9	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
$C_{16}H_{33}$	$C_{38}H_{70}N_4O_4$	70.43	10.97	8.58	70.54	10.90	8.66	91.7	Y.	–	±*	±	+	–	+	±	±	±	+	+	+	±	±
$C_{18}H_{37}$	$C_{42}H_{78}N_4O_4$	71.62	11.22	7.90	71.75	11.18	7.97	97.3	Y.	–	±*	±	+	–		±	±	±	+	+	+	±	±
																							
C_3H_7	$C_{12}H_{15}N_7O_{10}$	34.67	3.59	23.43	34.54	3.62	23.50	174.3	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_4H_9	$C_{14}H_{19}N_7O_{10}$	37.65	4.34	22.19	37.76	4.30	22.02	158.2	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_5H_{11}	$C_{16}H_{23}N_7O_{10}$	40.67	4.82	20.73	40.59	4.90	20.71	152.3	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_6H_{13}	$C_{18}H_{27}N_7O_{10}$	43.19	5.40	19.50	43.11	5.43	19.55	120.6	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_7H_{15}	$C_{20}H_{31}N_7O_{10}$	45.28	5.93	18.43	45.36	5.90	18.52	112.2	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_8H_{17}	$C_{22}H_{35}N_7O_{10}$	47.33	6.30	15.51	47.40	6.33	15.59	110.0	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
C_9H_{19}	$C_{24}H_{39}N_7O_{10}$	49.31	6.67	16.72	49.22	6.71	16.74	151.8	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
$C_{10}H_{21}$	$C_{26}H_{43}N_7O_{10}$	50.95	7.01	15.94	50.89	7.06	15.98	108.5	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
$C_{12}H_{25}$	$C_{30}H_{51}N_7O_{10}$	53.71	7.69	14.60	53.80	7.67	14.64	102.9	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
$C_{14}H_{29}$	$C_{34}H_{59}N_7O_{10}$	56.20	8.16	13.52	56.26	8.19	13.51	92.4	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
$C_{16}H_{33}$	$C_{38}H_{67}N_7O_{10}$	58.38	8.61	12.50	58.36	8.64	12.54	91.5	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+
$C_{18}H_{37}$	$C_{42}H_{75}N_7O_{10}$	60.09	9.00	11.65	60.19	9.02	11.70	88.2	L.Y.	–	±*	±	+	–	±	–	±	–	+	+	+	+	+

Solubility[b] (columns A–N)

[a] Color symbols: Y yellow, L.Y. light yellow.

[b] Solubility symbols: A water, B ethanol (95%), C methanol, D acetone, E ether, F chloroform, G carbon tetrachloride, H carbon disulfide, I petroleum ether, J benzene, K chlorobenzene, L Nitrobenzene. M acetic acid, N acetic anhydride. ±* Especially suitable for recrystallization. + very soluble. ± Fairly soluble. – slightly soluble. Solubility is qualitatively determined at 25° C. following arbitrary standards employed by Vogel (*44*).

[c] Pentyl analogs from propyl to octadecyl analog.

[d] (d.), Decomposes at melting point.

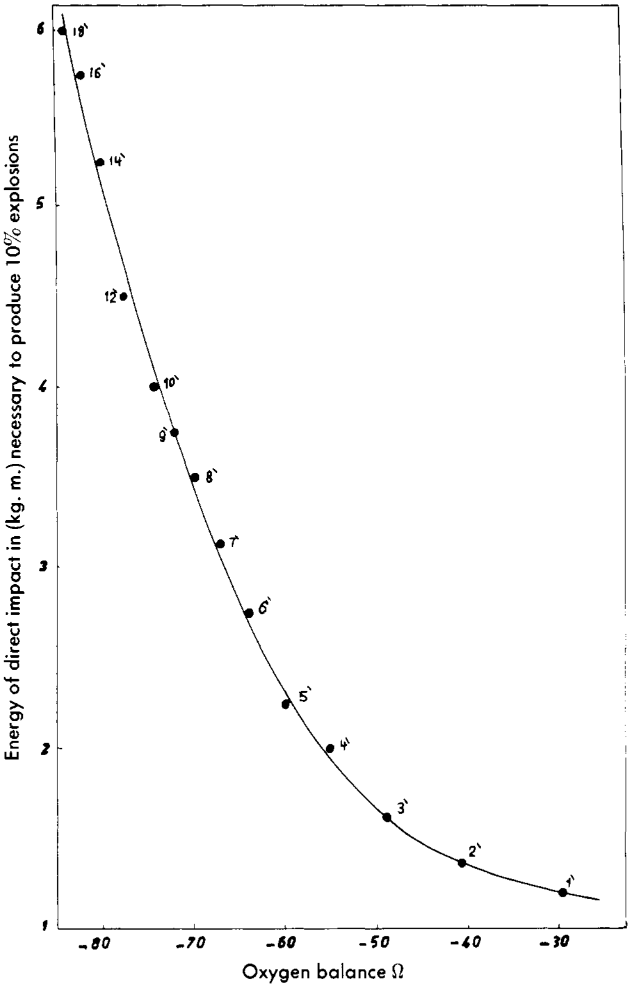


Figure 4. Effect of oxygen balance on the sensitivity to direct impact of pentyl and its analogs
Numbers refer to explosives in Table VIII

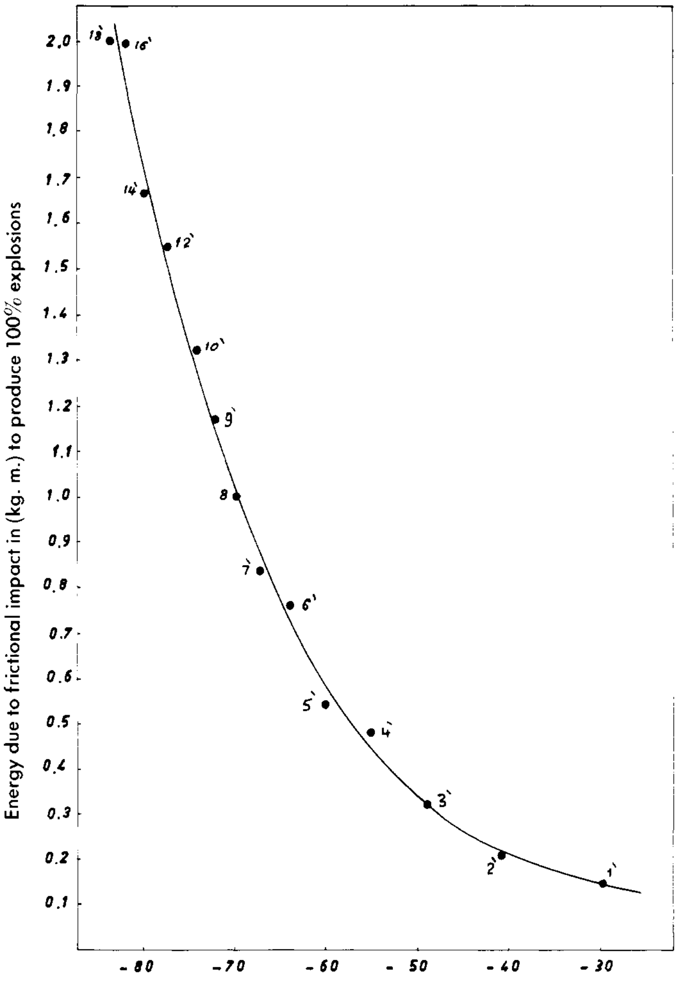


Figure 5. Effect of oxygen balance on the sensitivity to frictional impact of pentyl and its analogs
Numbers refer to explosives in Table IX

generally the sensitivity of pentyl and its ethyl and propyl analogs is somewhat lower than that of other higher analogs.

Sensitivity to Direct Impact. Table VIII shows a gradual increase in the required energy of direct impact from pentyl to its octadecyl analog; hence a gradual decrease in the explosive sensitivity. Sensitivity to direct impact decreases from pentyl to its octadecyl analog in an order similar to that observed in the case of tetryl and its *n*-alkyl analogs. Plotting the data for the sensitivity to direct impact against the oxygen balances of the explosives concerned (Ω, Figure 4.) illustrates that the sensitivity to direct impact of pentyl and its analogs is directly related to their oxygen balances.

Sensitivity to Frictional Impact. Results of the sensitivity to frictional impact tests (Table IX) indicate a gradual decrease in the sensitivity to frictional impact from pentyl to its octadecyl analog. Figure 5 shows the close direct relationship between the sensitivity to frictional impact and the oxygen balances of the concerned explosives. This conclusion agrees with the determination of the sensitivity to direct impact; both findings concur with the theories of Lothrop and Handrick (*24*) and Roth (*33*).

Sensitivity to Detonation by Initiating Agents. Results of lead plate test (Table X), show that the sensitivity to detonation by either initiating compositions (80-20 lead azide–lead styphanate mixture or 80-20 mercury fulminate–potassium chlorate mixture) decreases from pentyl to its hexyl analog; the sensitivity to detonation of other analogs higher than the "hexyl pentyl", however, exceeds the extreme limit practically possible to determine.

Brisance. Thorough comparison of measurements of hole diameters produced with the lead plate test (Table X) for pentyl and its analogs shows a decrease from pentyl to its hexyl analog. The brisance of other pentyl analogs higher than the hexyl analog stands, however, beyond the lowest limit attained.

Power. The data obtained by the Trauzl lead block test for pentyl and its analogs (Table XI) indicate a decrease in power from pentyl to its tetradecyl analog. The power of the tetradecyl, hexadecyl, and octadecyl analogs is more or less simiar. Figure 6 shows the variation of the explosive power from pentyl to its higher *n*-alkyl analogs and represents the effect of oxygen balance on power and brisance of explosive. The data in Figure 6, summarized by an idealized straight-ling curve, show that the power and birsance of this series of analogs vary directly with the oxygen balance. This is analogus with the findings of Lothrop and Handrik (*24*).

Stability. The decomposition of pentyl and its analogs, whether subjected to the 75° or 100° heat tests, varies from one explosive to the other (Table XII). Pentyl and its analogs withstand the exposure to the international 75° heat test. Pentyl shows marked stability towards the elevated 100° heat test, other analogs starting from the ethyl to the hexyl analog are less stable than pentyl, though still of good stability; higher analogs than hexyl pentyl to the octadecyl analog are of much lower stability.

HEXYL

2,4,6-Trinitro-1,3,5-tris(alkylnitramino)-benzenes

2,4,6-Trinitro-1,3,5-tris(methylnitramino)-benzene (hexyl) was prepared first by Blanksma (*4*) by the interaction of 1,3,5-tribromo-2,6-dinitrobenzene with *n*-methylamine followed by nitration of the resulting 2,6-dinitro-1,3,5-tris(methylamino)-benzene with nitric acid (sp. gr.

Table VIII. Sensitivity to Direct Impact test

Explosive		Sensitivity to Impact			
No.	Name	Kg.	M.	%	Kg. M.
1′	Pentyl	5	0.24	10	1.20
2′	Ethyl	5	0.275	10	1.375
3′	Propyl	5	0.325	10	1.625
4′	Butyl	5	0.40	10	2.00
5′	Pentyl	5	0.45	10	2.25
6′	Hexyl	5	0.25	10	2.75
7′	Heptyl	5	0.625	10	3.125
8′	Octyl	5	0.70	10	3.50
9′	Nonyl	5	0.75	10	3.75
10′	Decyl	5	0.80	10	4.00
12′	Dodecyl	5	0.90	10	4.50
14′	Tetradecyl	5	1.05	10	45.25
16′	Hexadecyl	5	1.15	10	5.75
18′	Octadecyl	5	1.20	10	6.00

[a] Energy of direct impact to produce 10% explosions.

Table IX. Sensitivity to Frictional Impact Test

Explosive		Sensitivity to Friction, Arm Length			
No.	Name	Kg.	M.	%	Kg. M.[a]
1′	Pentyl	0.492	0.30	100	0.147
2′	Ethyl	1.052	0.20	100	0.210
3′	Propyl	1.612	0.20	100	0.322
4′	Butyl	1.612	0.30	100	0.483
5′	Pentyl	2.172	0.25	100	0.543
6′	Hexyl	2.172	0.35	100	0.760
7′	Heptyl	3.340	0.25	100	0.835
8′	Octyl	3.340	0.30	100	1.002
9′	Nonyl	3.340	0.35	100	1.169
10′	Decyl	4.412	0.30	100	1.323
12′	Dodecyl	4.412	0.35	100	1.544
14′	Tetradecyl	6.650	0.25	100	1.662
16′	Hexadecyl	6.650	0.30	100	1.995
18′	Octadecyl	10.000	0.20	100	2.000

[a] Energy due to frictional impact to produce 100% explosions.

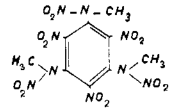
Table X. Lead Plate Test.

(Minimum charges of priming compositions (to nearest 0.025 g.) required)
(to detonate 0.5 g. of base charge)

Initiating Charge, G.		Explosive (Base charge)	Priming Charge, G.[a]	Diameter, Mm.[b]	Priming Charge, G.[c]	Diameter, Mm.[b]
Min.[a]	Min.[c]					
Pentyl	0.025	9.5	0.175	...	0.025	0.200
	0.050	10.0	0.200	9.6		
	0.075	10.3	0.225	10.2		
	0.100	10.6	0.250	10.5		
Ethyl	0.175	...	0.325	...	0.200	0.350
	0.200	9.4	0.350	8.4		
	0.225	10.1	0.375	8.8		
	0.250	10.2	0.400	8.9		
Propyl	0.250	...	0.450	...	0.275	0.475
	0.275	9.0	0.475	8.1		
	0.300	9.3	0.500	8.3		
	0.325	9.5	0.525	8.3		
Butyl	0.350	...	0.625	...	0.375	0.650
	0.375	5.5	0.650	6.0		
	0.400	5.9	0.675	6.8		
	0.425	6.1	0.700	6.9		
Pentyl	0.400	...	0.725	...	0.425	0.750
	0.425	4.9	0.750	5.0		
	0.450	5.3	0.775	5.2		
	0.475	5.4	0.800	5.3		
Hexyl	0.575	...	2.0	...	0.600	>2
	0.600	4.9				
	0.625	5.0				
	0.650	5.0				
Heptyl	2.0	...	2.0	...	>2	>2
Octyl	2.0	...	2.0	...	>2	>2
Nonyl	2.0	...	2.0	...	>2	>2
Decyl	2.0	...	2.0	...	>2	>2
Dodecyl	2.0	...	2.0	...	>2	>2
Tetradecyl	2.0	...	2.0	...	>2	>2
Hexadecyl	2.0	...	2.0	...	>2	>2
Octadecyl	2.0	...	2.0	...	>2	>2

[a] Composition: 80 lead azide-20 lead styphnate. [b] Size of hole produced in lead plate. [c] Composition: 80 mercury fulminate-20 potassium chlorate.

1.52). Later he (*5*) obtained it via the nitration of 2,4,6-trinitro-1,3,5-tris(methylamino)-benzene prepared by the action of 3,5-dichloro-2,4,6-trinitroanisol on *n*-methylamine at 165°.



EXPERIMENTAL

Preparation of Hexyl and Analogs. Hexyl and its analogs were prepared by the condensation of 1,3,5-tribromo-2,6-dinitrobenzene (1 mole) with the appropriate *n*-alkylamine (6 moles) followed by nitration of the condensation product (*4*). In another procedure for preparation, sym-tribromotrinitrobenzene or sym-trichlorotrinitrobenzene was replaced for 1,3,5-tribromo-2,6-dinitrobenzene.

Procedure F. PREPARATION OF 2,6-DINITRO-1,3,5-TRIS (ALKYLAMINO)-BENZENES. A quantity (202.4 grams) of 1,3,5-tribromo-2,6-dinitrobenzene (0.5 mole, m.p. 192°) prepared by the method of Hill and Taylor (*21*) was dissolved in a solvent mixture of 200 ml. of 95% ethyl alcohol and 50 ml. of benzene (bath temperature 60-5°). A 34% aqueous

Table XI. Comparative Tests

Explosive		Ignition	Expansion,
No.	Name	Temp., ° C.[a]	Cc.[b]
1′	Pentyl	190	410
2′	Ethyl	168	357
3′	Propyl	174	305
4′	Butyl	153	266
5′	Pentyl	161.5	238
6′	Hexyl	158	195
7′	Heptyl	147	157
8′	Octyl	154.5	116
9′	Nonyl	156	83
10′	Decyl	153	46
12′	Dodecyl	149	23
14′	Tetradecyl	147.5	14
16′	Hexadecyl	150	12
18′	Octadecyl	146	10

[a] Mean value, 20° C./min. [b] Mean value of three trials corrected to 18° C.

Table XII. Stability Tests

	Weight Loss, %[a]		
Explosive	48 Hr.[b]	48 Hr.[c]	96 Hr.[c]
Pentyl	0.019	0.039	0.039
Ethyl	0.050	0.089	0.130
Propyl	0.079	0.079	0.089
Butyl	0.019	0.049	0.079
Pentyl	0.029	0.049	0.099
Hexyl	0.049	0.439	1.809
Heptyl	0.039	0.919	20.827
Octyl	0.049	9.523	20.725
Nonyl	0.049	0.069	0.109
Decyl	0.029	15.691	20.063
Dodecyl	0.109	10.392	14.721
Tetradecyl	0.219	12.665	13.935
Hexadecyl	0.389	9.665	11.467
Octadecyl	0.299	8.909	10.987

[a] Weight losses are corrected for the moisture content of different explosives. [b] After 48 hours, using international test, 75° C. [c] After 48 and 96 hours, using heat test, 100° C.

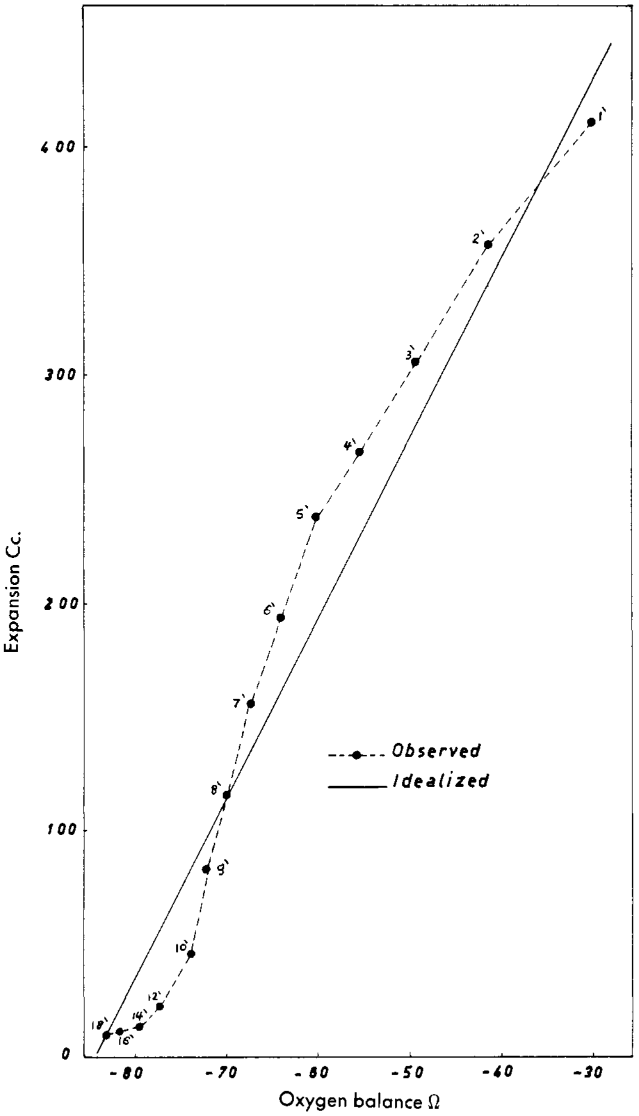


Figure 6. Effect of oxygen balance on power and brisance of pentyl and its analogs determined by the Trauzl test

Numbers refer to explosives in Table XI

solution of the appropriate lower n-alkylamine, or 34% aqueous-alcoholic solution (1 to 3) in the higher n-alkylamine (C_8-C_{18}) (6 moles in every case), was slowly added to the rapidly stirred solution, the temperature of the mixture being maintained at 60–5°. The reaction mixture was then neutralized dropwise by a 25% sodium carbonate solution; reaction temperature was limited to 60–5° during addition and for 30 minutes after the complete addition of the sodium carbonate. Temperature was then raised to 85–90° and kept constant for 30 minutes more. The reaction mixture was put aside to cool with stirring. The reaction product which separated out, whether solid or oily, was freed of sodium bromide by thorough washing with water. Solid crude was crystallized several times from 95% ethanol and was kept over sulfuric acid to dry. Crude oily product after thorough drying over sulfuric acid, was directly nitrated.

The new 2,6-dinitro-1,3,5-tris(alkylamino)-benzenes are reported in Table XIII; the yield ranges from 95 to 98%.

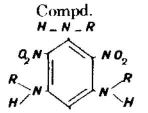
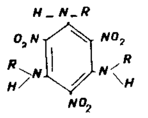
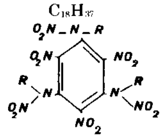
NITRATION OF 2,6-DINITRO-1,3,5-TRIS(ALKYLAMINO)-BENZENES. The nitration of 2,6-dinitro-1,3,5-tris(alkylamino)-benzenes to produce 2,4,6-trinitro-1,3,5-tris(alkylnitramino-)-benzenes (hexyl and its n-alkyl analogs) was carried out using nitric acid 13 times the theory and a molecular ratio of sulfuric acid to nitric acid of 2 to 1; similar nitration conditions were used to prepare pentyl and its analogs.

Procedure F_1. A 0.1 mole of the dried 2,6-dinitro-1,3,5-tris(alkylamino)-benzene was dissolved in 1061.6 grams (10.4 moles) of sulfuric acid (96%; sp. gr., 1.835) at a temperature not exceeding 30°. This solution was then slowly added to an agitated cooled 327.6 grams (5.2 moles) of fuming nitric acid (sp. gr. 1.52). During the addition of the sulfuric acid solution the temperature was not allowed to exceed 18° to avoid the decreased yield in the case of lower analogs of hexyl and the danger of fuming off in the case of higher analogs (C_5-C_{18}). When the addition was completed, the mixed acids solution was stirred for 1 more hour at a temperature below 18°. The reaction mixture was poured into ice water, and the product was filtered and washed with water until free from contaminated acids. Crude was crystallized several times from 95% ethanol; the crystalline yield was dried over sulfuric acid.

The new 2,4,6-trinitro-1,3,5-tris(alkylnitramino)-benzenes (analogs of hexyl) are reported in Table XIII; the yield ranges frpm 30 to 38%.

Procedure F_2. Nitration was carried out by portionwise addition of the dried 2,6-dinitro-1,3,5-tris(alkylamino)-benzene (0.1 mole) to a cooled agitated mixture of sulfuric and nitric acids (1061.6 gram, sp. gr. 1.835, 327.6 grams, sp. gravity, 1.52, respectively); temperature was kept below 25°. After the complete addition of the solid substance, the temperature was raised gradually to 45–50° and kept at 50° for an hour. The reaction mixture was cooled and

Table XIII. List of New Synthesized Compounds

Compd.	Calcd. for	Analysis, %						M.P., °C.	Solubility[b]														
		Found			Calcd.																		
		C	H	N	C	H	N		Color[a]	A	B	C	D	E	F	G	H	I	J	K	L	M	N
																							
C_2H_5	$C_{12}H_{19}N_5O_4$	48.39	6.42	23.34	48.47	6.44	23.55	121.0	O.Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_3H_7	$C_{15}H_{25}N_5O_4$	52.93	7.33	20.52	53.08	7.42	20.63	68.3	O.Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_4H_9	$C_{18}H_{31}N_5O_4$	56.22	8.10	18.40	56.67	8.19	18.36	60.0	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_5H_{11}	$C_{21}H_{37}N_5O_4$	59.60	8.77	16.44	59.55	8.80	16.53	53.6	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_6H_{13}	$C_{24}H_{43}N_5O_4$	61.73	9.21	15.13	61.90	9.30	15.04	57.0	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_7H_{15}	$C_{27}H_{49}N_5O_4$	63.91	9.71	13.65	63.87	9.72	13.79	Oil[c]	...	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_8H_{17}	$C_{30}H_{55}N_5O_4$	65.32	10.12	12.43	65.53	10.08	12.73	Oil[d]	...	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
C_9H_{19}	$C_{33}H_{61}N_5O_4$	66.75	10.21	11.82	66.96	10.38	11.83	66.0	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{36}H_{67}N_5O_4$	68.01	10.49	11.20	68.20	10.65	11.04	43.5	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{42}H_{79}N_5O_4$	70.13	11.20	9.74	70.24	11.08	9.75	51.0	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{48}H_{91}N_5O_4$	71.54	11.29	8.81	70.86	11.43	8.73	60.5	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{54}H_{103}N_5O_4$	73.20	11.65	7.88	73.16	11.71	7.90	62.0	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{60}H_{115}N_5O_4$	74.30	11.82	7.13	74.24	11.94	7.21	79.3	Y.	–	±*	±	+	±	+	+	+	±	+	+	+	+	+
																							
C_2H_5	$C_{12}H_{18}N_6O_6$	41.98	5.21	24.31	42.10	5.30	24.55	206.0	L.Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_3H_7	$C_{15}H_{24}N_6O_6$	46.53	6.19	21.73	46.86	6.29	21.86	149.0	L.Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_4H_9	$C_{18}H_{30}N_6O_6$	50.61	6.96	19.63	50.69	7.09	19.70	86.5	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_5H_{11}	$C_{21}H_{36}N_6O_6$	53.71	7.62	17.81	53.83	7.74	17.93	126.3	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_6H_{13}	$C_{24}H_{42}N_6O_6$	56.23	8.18	16.32	56.45	8.29	16.45	Oil[e]	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_7H_{15}	$C_{27}H_{48}N_6O_6$	58.41	8.72	15.31	58.67	8.75	15.20	Oil[f]	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_8H_{17}	$C_{30}H_{54}N_6O_6$	60.40	9.20	14.08	60.57	9.15	14.13	Oil[g]	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
C_9H_{19}	$C_{33}H_{60}N_6O_6$	61.95	9.40	13.05	62.23	9.49	13.19	Oil[h]	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{36}H_{66}N_6O_6$	63.65	9.73	12.30	63.68	9.79	12.37	59.0	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{42}H_{78}N_6O_6$	66.21	10.21	11.19	66.10	10.30	11.01	62.4	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{48}H_{90}N_6O_6$	68.20	10.63	9.85	68.04	10.70	9.91	74.5	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{54}H_{102}N_6O_6$	69.55	11.07	8.97	69.63	11.03	9.02	63.0	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{60}H_{114}N_6O_6$	70.89	11.29	8.31	70.95	11.31	8.27	61.2	Y.	–	±*	±	+	±	+	±	+	±	+	+	+	+	+
																							
C_2H_5	$C_{12}H_{15}N_9O_{12}$	30.21	3.12	26.38	30.19	3.16	26.41	190.0	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_3H_7	$C_{15}H_{21}N_9O_{12}$	34.50	4.02	24.31	34.68	4.07	24.27	182.3[d]	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_4H_9	$C_{18}H_{27}N_9O_{12}$	38.56	4.81	22.38	38.50	4.84	22.45	159.0[d]	Y.O.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_5H_{11}	$C_{21}H_{33}N_9O_{12}$	41.68	5.53	20.80	41.79	5.51	20.88	151.4[d]	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_6H_{13}	$C_{24}H_{39}N_9O_{12}$	44.51	6.07	19.46	44.64	6.08	19.52	146.0[d]	...	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_7H_{15}	$C_{27}H_{45}N_9O_{12}$	47.12	6.51	-8.29	47.15	6.59	18.33	149.0[d]	...	–	+*	±	+	±	+	±	±	±	+	+	+	+	+
C_8H_{17}	$C_{30}H_{51}N_9O_{12}$	49.29	7.10	17.21	49.37	7.04	17.27	141.5[d]	...	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
C_9H_{19}	$C_{33}H_{57}N_9O_{12}$	51.38	7.41	16.29	51.35	7.44	16.33	116.8	...	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
$C_{10}H_{21}$	$C_{36}H_{63}N_9O_{12}$	53.09	7.73	15.41	53.12	7.80	15.48	150.0	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
$C_{12}H_{25}$	$C_{42}H_{75}N_9O_{12}$	56.07	8.39	14.21	56.16	8.41	14.03	134.2	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
$C_{14}H_{29}$	$C_{48}H_{87}N_9O_{12}$	58.71	8.88	12.90	58.69	8.92	12.83	132.6	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
$C_{16}H_{33}$	$C_{54}H_{99}N_9O_{12}$	60.87	9.31	11.80	60.81	9.35	11.82	127.5	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+
$C_{18}H_{37}$	$C_{60}H_{111}N_9O_{12}$	62.71	9.66	10.90	62.63	9.72	10.95	142.0	Y.	–	±*	±	+	±	+	±	±	±	+	+	+	+	+

[a] Color symbols: O.Y. orange yellow, Y yellow L.Y. light yellow.

[b] Solubility symbols: A water, B ethanol (95%), C methanol, D acetone, E ether, F chloroform, G carbon tetrachloride, H carbon disulfide, I petroleum ether, J benzene, K chlorobenzene, L nitrohenzene, M acetic acid, N acetic anhydride. ±* Expecially suitable for recrystallization. + very soluble. ± fairly soluble. – slightly soluble. Solubility qualitatively determined at 25° C. following arbitrary standards employed by Vogel (*44*).

Hexyl analogs starting from ethyl to octadecyl analog.

Decomposes at melting point.

Decomposes a little bit above melting point.

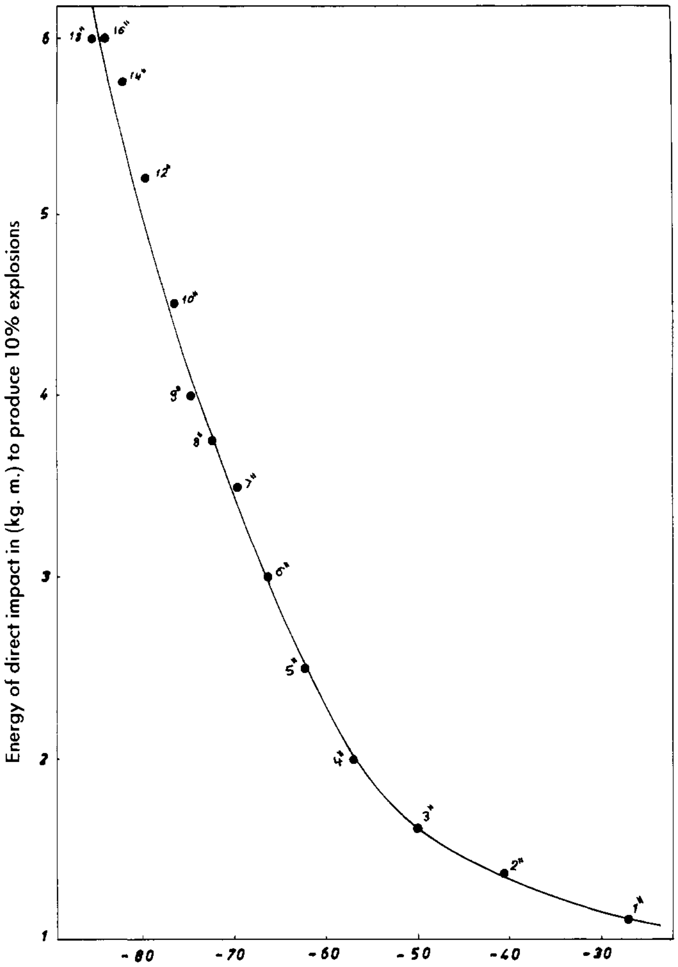


Figure 7. Effect of oxygen balance on the sensitivity to direct impact of hexyl and its analogs

Numbers refer to explosives in Table XIV

poured into ice water; the product that separated out was filtered, washed free from acids, and crystallized from 95% ethanol.

This procedure gives higher yields (72 to 79%) under smooth nitration conditions that are easier to control and safer than those encountered with Procedure F_1.

Procedure G. PREPARATION OF 2,4,6-TRINITRO-1,3,5-TRIS (ALKYLAMINO)-BENZENES. A solution of either *sym*-tribromotrinitrobenzene (*21*) or *sym*-trichlorotrinitrobenzene (*15*) in 95% ethanol-benzene mixture was first prepared. A 34% solution of the appropriate *n*-alkylamine prepared as in Procedure F, was added dropwise to the rapidly stirred solution. The reaction mixture was neutralized by the slow addition of sodium carbonate solution (25%). Temperature was maintained at 60-5° throughout the additions and for 30 minutes after last addition. Then it was raised to 85–90° and held constant for another 30 minutes. The crude product that separated out on cooling was treated as Procedure F.

The new 2,4,6-trinitro-1,3,5-tris(alkylamino)-benzenes are reported in Table XIII; the yield ranges from 78 to 83%.

NITRATION OF 2,4,6-TRINITRO-1,3,5-TRIS(ALKYLAMINO)-BENZENES. Nitrated 2,4,6-trinitro-1,3,5-tris(alkylamino)-benzenes (hexyl and its analogs) were obtained via two main procedures identical with procedures $F_1$and F_2.

In procedure G_1, a solution of 2,4,6-trinitro-1,3,5-tris (alkylamino)-benzene in sulfuric acid (sp. gr. 1.835) was added dropwise, while stirring, to fuming nitric acid (sp. gr. 1.52), keeping the temperature below 18°. The yield ranges from 35 to 42%.

In Procedure G_2, the dried 2,4,6-trinitro-1,3,5-tris(alkylamino)-benzene was nitrated by its portionwise addition, with stirring, to a nitrating mixture of sulfuric acid (sp. gr. 1.835) and fuming nitric acid (sp. gr. 1.52). The yield ranges from 74 to 78%.

Explosive Properties of Hexyl and Analogs. Hexyl and its analogs were tested for the explosive sensitivity to: heat; impact; frictional impact; and detonation by initating agents as well as brisance (lead plate test), power (Trauzl test), and stability (international 75° and 100° tests).

SENSITIVITY TO HEAT. Results of tests given in Table XVII show an increase in the sensitivity to heat from hexyl to its propyl analog; the sensitivity of other higher analogs stands then however, more or less unchanged.

SENSITIVITY TO DIRECT IMPACT. The data given by Table XIV indicate a gradual increase in the required energy of direct impact from hexyl to the hexadecyl and octadecyl analogs; hence, a gradual decrease in the explosive sensitivity. Figure 7 by showing the relation between the explosive sensitivity to direct impact and the oxygen balances (Ω) better illustrates the variation of the sensitivity to impact from hexyl to the higher *n*-alkyl analogs. Sensitivity to direct impact varies directly with oxygen balance. This conclusion agrees with the findings of Lothrop and Handrick (*24*) and Roth (*33*). Hexadecyl and octadecyl analogs of hexyl, being of extreme insensitivity, develop similar magnitudes for the sensitivity to impact.

SENSITIVITY TO FRICTIONAL IMPACT. Tabulated results (Table XV) indicate a gradual decrease in the sensitivity to frictional impact from hexyl to its octadecyl analog. Figure 8 shows the decrease of the sensitivity to frictional impact with decrease of the oxygen balance of the explosives

Table XIV. Sensitivity to Direct Impact Test

Explosive		Sensitivity to impact			
No.	Name	Kg.	M.	%	Kg. M.[a]
1"	Hexyl	5	0.225	10	1.125
2"	Ethyl	5	0.275	10	1.375
3"	Propyl	5	0.325	10	1.625
4"	Butyl	5	0.40	10	2.00
5"	Pentyl	5	0.50	10	2.50
6"	Hexyl	5	0.60	10	3.00
7"	Heptyl	5	0.70	10	3.50
8"	Octyl	5	0.75	10	3.75
9"	Nonyl	5	0.80	10	4.00
10"	Decyl	5	0.90	10	4.50
12"	Dodecyl	5	1.04	10	5.20
14"	Tetradecyl	5	1.15	10	5.75
16"	Hexadecyl	5	1.20	10	6.00
18"	Octadecyl	5	1.20	10	6.00

[a] Energy of direct impact to produce 10% explosions.

Table XV. Sensitivity to Frictional Impact Test

Explosive		Sensitivity to Friction, Arm Length			
No.	Name	Kg.	M.	%	Kg. M.[a]
1"	Hexyl	0.492	0.20	100	0.098
2"	Ethyl	1.052	0.20	100	0.210
3"	Propyl	1.052	0.35	100	0.369
4"	Butyl	1.612	0.30	100	0.483
5"	Pentyl	2.172	0.30	100	0.651
6"	Hexyl	3.340	0.25	100	0.835
7"	Heptyl	3.340	0.30	100	1.002
8"	Octyl	3.340	0.35	100	1.169
9"	Nonyl	4.412	0.30	100	1.323
10"	Decyl	4.412	0.35	100	1.544
12"	Dodecyl	6.650	0.25	100	1.662
14"	Tetradecyl	6.650	0.30	100	1.995
16"	Hexadecyl	10.000	0.20	100	2.060
18"	Octadecyl	6.650	0.35	100	2.327

[a] Energy due to frictional impact to produce 100% explosions.

Table XVI. Lead Plate Test

Explosive (Base charge)	Priming Charge, G.[a]	Diameter, Mm.[b]	Priming Charge, G.[c]	Diameter, Mm.[b]	Initiating Charge, G. Min.[a]	Initiating Charge, G. Min.[c]
Hexyl	0.025	10.0	0.175	...	0.025	0.200
	0.050	10.5	0.200	10.2		
	0.075	10.8	0.225	10.5		
	0.100	10.9	0.250	10.8		
Ethyl	0.175	...	0.325	...	0.200	0.350
	0.200	9.5	0.350	8.5		
	0.225	10.0	0.375	8.8		
	0.250	10.2	0.400	8.9		
Propyl	0.275	...	0.525	...	0.300	0.550
	0.300	7.6	0.550	6.8		
	0.325	7.9	0.575	7.2		
	0.350	8.2	0.600	7.5		
Butyl	0.350	...	0.700	...	0.375	0.725
	0.375	5.3	0.725	5.0		
	0.400	5.5	0.750	5.1		
	0.425	5.7	0.775	5.2		
Pentyl	0.425	...	0.775	...	0.450	0.800
	0.450	4.9	0.800	4.0		
	0.475	5.2	0.825	4.3		
	0.500	5.3	0.850	4.3		
Hexyl	0.700	...	2.0	...	0.725	>2
	0.725	4.5		...		
	0.750	4.6		...		
	0.775	4.6		...		
Heptyl	2.0	...	2.0	...	>2	>2
Octyl	2.0	...	2.0	...	>2	>2
Nonyl	2.0	...	2.0	...	>2	>2
Decyl	2.0	...	2.0	...	>2	>2
Dodecyl	2.0	...	2.0	...	>2	>2
Tetradecyl	2.0	...	2.0	...	>2	>2
Hexadecyl	2.0	...	2.0	...	>2	>2
Octadecyl	2.0	...	2.0	...	>2	>2

[a] Composition: 80 lead azide—20 lead styphnate.
[b] Size of hole produced in lead plate.
[c] Composition: 80 mercury fulminate—20 potassium chlorate.

under investigation. This conclusion agrees with that previously attained in the determination of the sensitivity to direct impact; both results are in concordance with the findings of Lothrop and Handrick (*24*) and Roth (*33*).

SENSITIVITY TO DETONATION BY INITIATING AGENTS. The sensitivity to detonation by either azide or fulminate initiating mixtures decreases, from hexyl to its hexyl analog (Table XVI). The sensitivity to detonation of other hexyl analogs, higher than the hexyl analog, however, exceeds the extreme magnitude practically possible to determine.

BRISANCE. Thorough comparison of figures for hole diameters (Table XVI) shows a brisance decrease from hexyl to its hexyl analog. The brisance of other hexyl analogs higher than the hexyl analog stands, however, beyond the lowest limit attained.

POWER. The data show (Table XVII) that the explosive power decreases from hexyl to its dodecyl analog. The power of hexyl analogs from dodecyl to octadecyl stands nearly on same level, the lowest extreme level to be attained. The change of the explosive power from one hexyl analog to another is better illustrated by Figure 9, which shows the effect of oxygen balance on power and brisance of explosives. The straight-line curve, Figure 9, shows that the power and brisance of hexyl and its analogs vary directly with oxygen balance; this agrees with the work of Lothrop and Handrick (*24*).

Table XVII. Comparative Tests

Explosive No.	Explosive Name	Ignition Temp., ° C.[a]	Expansion, Cc.[b]
1″	Hexyl	188	424
2″	Ethyl	163	360
3″	Propyl	157	300
4″	Butyl	151	258
5″	Pentyl	150	225
6″	Hexyl	152	168
7″	Heptyl	148	115
8″	Octyl	150.5	82
9″	Nonyl	146	38
10″	Decyl	151.5	30
12″	Dodecyl	148	14
14″	Tetradecyl	145	10
16″	Hexadecyl	151	7
18″	Octadecyl	148	7

[a] Mean value, 20° C./min. [b] Mean value of 3 trials corrected to 18° C.

Table XVIII. Stability Tests

Explosive	Weight Loss, %[a] 48 Hr.[b]	Weight Loss, %[a] 48 Hr.[c]	Weight Loss, %[a] 96 Hr.[c]
Hexyl	0.069	0.189	0.189
Ethyl	0.109	0.458	0.747
Propyl	0.139	1.527	2.316
Butyl	0.339	1.452	3.216
Pentyl	0.449	5.203	28.405
Hexyl	0.339	8.317	34.210
Heptyl	0.616	4.081	30.179
Octyl	0.519	22.515	27.419
Nonyl	0.498	31.679	33.563
Decyl	0.199	17.441	24.197
Dodecyl	0.159	13.925	17.564
Tetradecyl	0.339	19.505	27.135
Hexadecyl	0.449	29.679	31.550
Octadecyl	0.389	21.710	28.680

[a] Weight losses are corrected for the moisture content of different explosives. [b] After 48 hours, using international test, 70° C. [c] After 48 and 96 hours, using heat test, 100° C.

STABILITY. Excluding hexyl, all hexyl analogs show marked but variable degrees of decomposition when subjected to either 75° or 100° heat tests (Table XVIII). Decomposition is much more pronounced in the case of hexyl analogs higher than the butyl hexyl, expecially in the elevated temperature 100° heat test. In general, lower analogs of hexyl up to butyl hexyl are the most stable members in this series.

Table XIX. Sensitivity to Impact

Explosive	Direct impact Kg.	 Meter	 Explosion, %	 Kg. M.[c]
	Direct Impact			
Nonyl	5	0.22[a]	10	1.10
Pentryl	5	0.24	10	1.20
Tetryl	5	0.25	10	1.25
	Frictional Impact			
Nonyl	0.212	0.35[b]	100	0.074
Pentryl	0.492	0.25	100	0.123
Tetryl	1.052	0.15	100	0.157

[a] Height of fall. [b] Arm length. [c] Energy of direct impact.

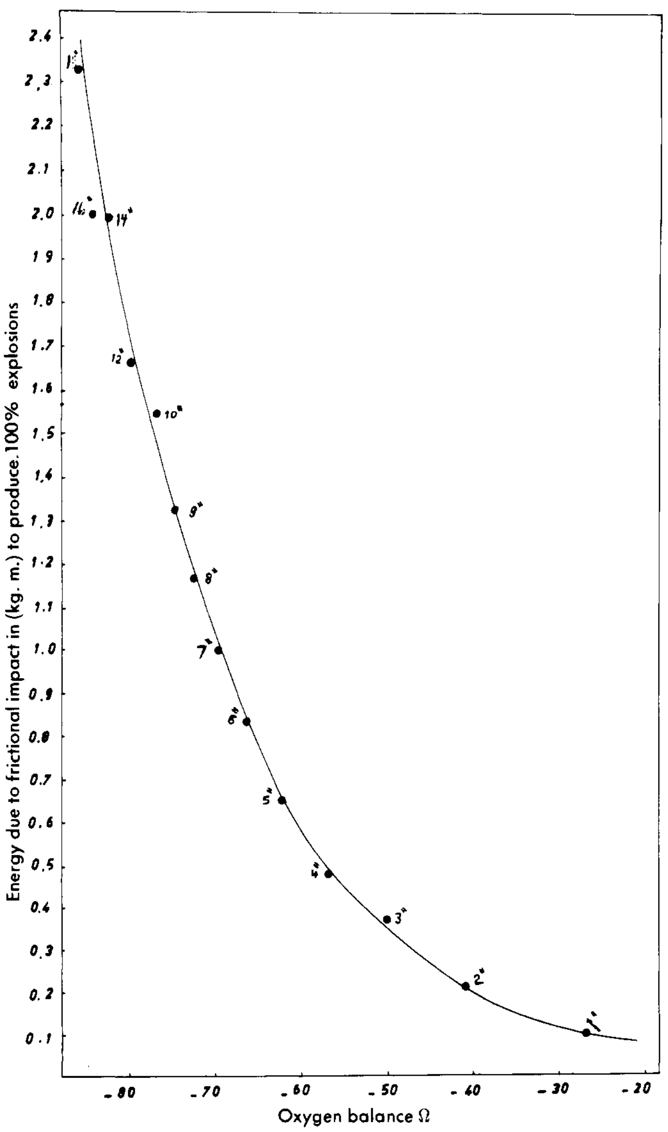


Figure 8. Effect of oxygen balance on the sensitivity to frictional impact of hexyl and its analogs

Numbers refer to explosives in Table XV

NONYL

2,4,6-Trinitrophenyl-1,3,5,-Triethanoltrinitraminetrinitrate

Giua and Pansini (*17*) obtained nonyl by the interaction of 1,3,5-trichloro-2,4,6-trinitrobenzene (1 mole) with monoethanolamine (3 moles) in ethanol solution followed by nitration of the resulting 2,4,6-trinitrophenyl-1,3,5-triethanolamine with mixed sulfuric and nitric acids.

The method now adopted for the preparation of nonyl was not much different from that devised by Blanksma (*4*) for the preparation of 2,4,6-trinitro-1,3,5-tris(methylnitramino)benzene. 1,3,5-Tribromo-2,6-dinitrobenzene (1 mole) was allowed to condense with monoethanolamine (6 moles) under the conditions described by Desseigne (*14*) for the condensation of 2,4-dinitrochlorobenzene with monoethanolamine. Nitration of the resulting intermediate product was after the procedure described by Giua and Pansini (*17*).

EXPERIMENTAL

Preparation of 2,6-dinitrophenyl-1,3,5-triethanolamine. A quantity (202.4 grams) of 1,3,5-tribromo-2,6-dinitrobenzene (0.5 mole; m.p. 192° C.) prepared as directed by Hill and Taylor (*21*) were dissolved in a mixture of 200 ml. of 95% ethanol and 50 ml of benzene at 60–5°. Benzene was added to increase the solubility of sym-tribromodinitrobenzene; a 34% aqueous solution of the appropriate monoethanolamine was added dropwise during stirring. A 25% aqueous sodium carbonate solution was slowly added to the rapidly agitated solution. Stirring was continued for half an hour. Temperature was maintained at 60–5°, then increased, 85–90°, 0.5 for an hour after addition of the sodium carbonate was completed. The reaction mixture was then allowed to cool to room temperature under agitation. The solid, so separated, was filtered and washed with ice-cold, distilled water until the washings gave negative test for the bromine ion. It was then crystallized several times from 95% ethanol A yellow crystalline product melting at 174° was obtained; 80.5% of theoretical. Analysis. Calcd. for $C_{12}H_{19}N_5O_7$: N, 20.28. Found: N, 20.22, 2.6-Dinitrophenyl-1,3,5-triethanolamine is soluble in hot water, 95% ethanol, methanol, acetone, acetic acid, and acetic anhydride; and is slightly soluble in ether, chloroform, carbon tetrachloride, benzene, chlorobenzene, and petroleum ether.

Nitration of 2,6-dinitrophenyl-1,3,5-triethanolamine. A 0.1 mole of the dried 2,6-dinitrophenyl-1,3,5-triethanolamine was dissolved in 1857.9 grams (18.2 moles) of sulfuric acid (96%; sp. gr. 1.835), between 20° and 30°. The sulfuric acid solution was then added dropwise to a stirred 573.3 grams (9.1 moles) of fuming nitric acid (sp. gr. 1.52) at a temperature not exceeding 40°; this was effected by external cooling and the control of rate of addition. Tne addition completed, the temperature was raised to 50°, where it was maintained constant for 0.5 hour. The reaction mixture was cooled to room temperature and poured into ice water. The crude obtained was recrystallized from methanol in light yellow, needly-like crystals melting at 160°; the yield was 52% of theoretical.

Analysis. Calcd. for $C_{12}H_{12}N_{12}O_{21}$: N, 25.45. Found: N, 25.40.

Nonyl is easily soluble in 95% ethanol, glacial acetic acid acetic anhydride, and/or acetone; less soluble in methanol; and slightly soluble in water.

Explosive Characteristics of Nonyl. The explosive characteristics of nonyl were determined through testing the sensitivity of the explosive to different stimuli, the explosive performance, and the explosive stability. Results of tests on nonyl compared with similar tests on pentryl (*8*) and tetryl are given.

SENSITIVITY TO DIRECT IMPACT. Results shown by Table XIX indicate that the sensitivity of nonyl, pentryl, and tetryl to direct impact is about the same.

Table XX. Lead Plate Test

Priming Charge 80Pb Azide-20 Pb Styphnate[a]	Diameter of Hole	Priming Charge (80Hg(CNO)$_2$-20KClO$_3$)[b]	Diameter of Hole
Gram	Mm.	Gram	Mm.
	Explosive: Nonyl		
0.025	10.3	0.175	...
0.050	10.5	0.200	10.5
0.075	10.9	0.225	10.7
0.100	10.9	0.250	10.8
	Explosive: Pentryl		
0.025	9.8	0.175	...
0.050	10.3	0.200	10.0
0.075	10.6	0.225	10.4
0.100	10.7	0.250	10.5
	Explosive: Tetryl		
0.025	9.4	0.175	...
0.050	9.8	0.200	9.5
0.075	10.0	0.225	10.0
0.100	10.5	0.250	10.2

[a] Minimum initiating charge required to detonate base charge is 0.025 gram. [b] Minimum initiating charge required to detonate base charge is 0.200 gram.

SENSITIVITY TO FRICTIONAL IMPACT. Above results indicate that the sensitivity of nonyl to frictional impact is somewhat greater than that of either pentryl or tetryl.

SENSITIVITY TO DETONATION BY INITIATING AGENTS. A comparison of the sensitivity to detonation by either 80-20 lead azide–lead styphnate or 80-20 mercury fulminate–potassium chlorate initiating mixtures of nonyl with that of pentryl and tetryl shows that the sensitivity to initiation of the three explosives is the same.

BRISANCE. Thorough comparison of measurements of hole diameters for nonyl, pentyl, and tetryl produced with the lead plate test (Table XX) shows a slight decrease of brisance from nonyl to tetryl.

POWER. Comparison of results determined by the Trauzl lead bloch test (Table XXI) indicates that the power of nonyl is almost greater than that of either pentryl or tetryl.

STABILITY. Results of 75° and 100° heat tests (Table XXI) indicate that nonyl, pentryl, and tetryl resist the decomposition caused by the exposure to the moderately high temperature stability tests.

Table XXI. Comparative Tests.

Explosive	Trauzl Test Expansion, Cc.[a]	Weight Loss, %[b]		
		48 Hr.[c]	48 Hr.[d]	96 Hr.[d]
Nonyl	472	0.127	0.127	0.127
Pentryl	430	0.119	0.119	0.120
Tetryl	395	0.125	0.125	0.125

[a] Mean value of 3 trials corrected to 18° C. [b] Weight losses are corrected for the moisture content of different explosives. [c] After 48 hours, using international test, 75° C. [d] After 48 and 96 hours, using heat test, 100° C.

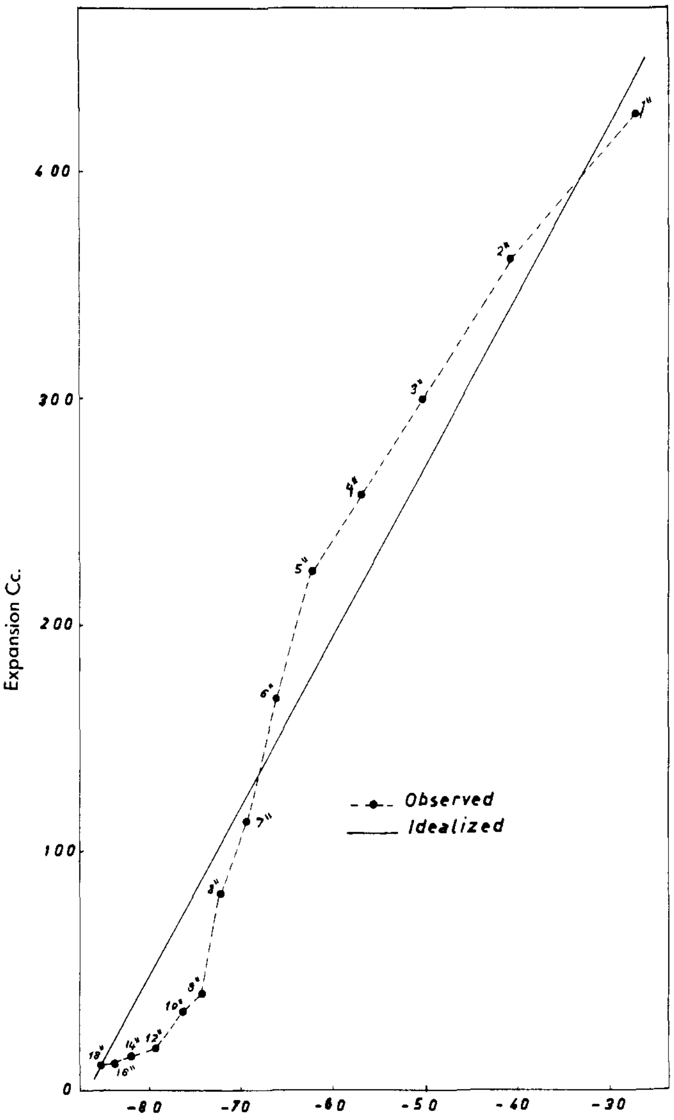


Figure 9. Effect of oxygen balance on power and brisance of hexyl and its analogs determined by the Trauzl test

Numbers refer to explosives in Table XVII

LITERATURE CITED

(1) Blanksma, J.J., *Rec. Trav. Chim.* **21**, 265 (1902).
(2) *Ibid.*, 321 (1902).
(3) *Ibid.*, 325 (1902).
(4) *Ibid.*, **23**, 129 (1904).
(5) *Ibid.*, **27**, 40 (1908).
(6) Blanksma, J.J., Terwogt, P.C.E.M., *Ibid.*, **21**, 286 (1902).
(7) Boyer, R., Spencer, E.Y., Wright, G.F., *Can J. Research* **24**, 200 (1946).
(8) Clark, L.V., *Ind. Eng. Chem.* **25**, 1385 (1933).
(9) Clarkson, C.E., Holden, I.G., Malkin, T., *J. Chem. Soc.* 1556 (1950).
(10) Davis, T.L., "The Chemistry of Powder and Explosives," p. 21 4th. ed. John Wiley, New York, 1956.
(11) Davis, T.L., U. S. Patent **1,607,059** (Nov. 16, 1926).
(12) Desseigne, G., Mem. Poudres **28**, 156 (1938).
(13) *Ibid.*, **31**, 43 (1949).
(14) *Ibid.*, **33**, 255 (1951).
(15) Engelbertz, P., Chemiche Fabrik Griesheim, Ger. **767,510** (Sept. 15, 1952).
(16) Franchimont, A.P.N., *Rec. Trav. Chim.* **29**, 300 (1910).
(17) Giuas, M., Pansini, P., Ann. Chim. (Rome) **49**, 1311 (1959).
(18) Grant, R.L., Tiffany, J.E., *Ind. Eng. Chem.* **37**, 633 (1945).
(19) Grotta, B., *Chem. Met. Eng.* **26**, 1126 (1922).
(20) Henkin, H., McGill, R., *Ind. Eng. Chem.* **44**, 1391 (1952).
(21) Hill, M.E., Taylor, Jr., F., *J. Org. Chem.* **25**, 1037 (1960).
(22) Kirk, R.E., Othmer, D.F., "Encyclopedia of Chemical Technology," Vol. **6**, p. 88, Interscience Encyclopedia, New York, 1951.
(23) Kostevitch, M., *Z. Ges. Schiess-Sprengstoffw.* **23**, 156 (1928).
(24) Lothrop, W.C., Handrick, G.R., *Chem. Revs.* **44**, 419 (1949).
(25) Marshall, A., "Explosives," Vol. **2** J. and A. Churchill, London, 1917.
(26) Martin, A.R., Yallop, H.J., *Trans. Faraday Soc.* **54**, 257 (1958).
(27) Mertens, K.H., *Ber.* **10**, 995 (1877).
(28) Meyer, M., "Science of Explosives," p. 296, Thomas Y. Crowell Co., New York, 1943.

(29) Munroe, C.E., Tiffany, J.E., U. S. Bur. Mines, Bull. **346**, 148 (1931).
(30) Nietzki, R., Schedler, A., *Ber.* **30**, 1666 (1897).
(31) Reilly, J., Hickinbottom, W.J., *J. Chem. Soc.* **117**, 103 (1920).
(32) Robertson, A.J.B., *Trans. Faraday Soc.* **44**, 677 (1948).
(33) Roth, J.F., *Z. Ges. Schiess-U. Sprengstoffw.* **36**, 4, 28, 52 (1941).
(34) Schiino, K., Oinuma, S., *Repts. Govt. Chem. Ind. Research Inst. Tokyo.* **51**, 74 (1956).
(35) Semenczuk, A., Urbanski, T., *Bull. Acad. Polon. Sci.* Vol. **VI** No. 5, 309 (1956).
(36) Storm, C.G., *Bur. Mines. Bull.* **96**, 11 (1916).
(37) Taylor, J., Hall, C.R.L., Thomas, H., *J. Phys. Colloid Chem.* **51**, 580 (1947).
(38) Thorpe, J.F., Whiteley, M.A., "Thorpe's Dictionary of Applied Chemistry," Vol. **IV**, p. 551-2 (1955).
(39) Urbanski, T., Semenczuk, A., Bull. Acad. Polon. Sci., Classe III **5**, 649 (1957).
(40) Van Romburgh, P., *Rec. Trav. Chim.*, **2**, 103 (1883); **8**, 215 (1889).
(41) *Ibid.*, **4**, 191 (1885).
(42) *Ibid.*, **7**, 4 (1888).
(43) *Ibid.*, **8**, 274 (1889).
(44) Vogel, A.I., "Practical Organic Chemistry," p. 1045, Longmans, Green, London, 1957.
(45) Wride, H.B., Arms and Explosives **28**, 6 (1920).

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Molecular Structure of Conjunct Polymers

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Conjunct polymers are incidental by-products of acid-catalyzed hydrocarbon reactions. The structures of these oils were determined with the aid of physical property correlations, ultraviolet, infrared, and mass spectroscopy, and various chemical methods, including hydrogenation. The conjunct polymers were thus shown to be cyclic polyolefinic hydrocarbons with a high proportion of conjugated double bonds, no two of which are in the same ring ("heteroannular conjugation'). Five-membered ring systems predominate, but larger, and possibly also smaller, rings are believed to be present. Both condensed and uncondensed ring systems are assumed. An average molecule may be considered to be dicyclic, with one pair of conjugated double bonds and one-half to one and one-half isolated double bonds. About 60% of the carbon atoms are in side chains. Polymer distillate fractions with as many as five rings and four double bonds per mole have been observed.

CONJUNCT polymers are highly olefinic oils which are produced by acid-catalyzed reactions of hydrocarbons. Under the proper conditions they may be formed from any type of hydrocarbon except aromatics. The nature of the acid is not critical. Usually, however, the catalyst involved is hydrofluoric acid, sulfuric acid, phosphoric acid, boron trifluoride, aluminum chloride, or combinations of these.

As a rule, the conjunct polymer is an undesired by-product of some other reaction, such as alkylation, polymerization, or isomerization. The polymer forms a complex with the catalyst. It is liberated by neutralization or hydrolysis of the catalyst phase, and appears as a light yellow to dark red oil with a characteristic odor. It is also commonly referred to as "red oil," "sludge," or "acid oil."

Conjunct polymers are exceedingly complex mixtures of highly olefinic, conjugated cyclic hydrocarbons. Ipatieff and Grosse (*14*) first recognized that these materials are polymeric in nature. They also realized that the process of forming them is different from conventional polymerization, since it involves such additional reactions as hydrogen transfer and cyclization, and the starting material is not necessarily olefinic. They employed the term "conjunct polymerization" to define this combination of reactions. Since then, many workers have used the term "conjunct polymer" to refer to the polyolefinic oil produced in acid-catalyzed reactions of hydrocarbons.

The technical literature on conjunct polymers is largely concerned with utilization. It is, therefore, restricted mainly to patents, only a few of which are pertinent to the work described in this article (*3, 12, 15, 16, 19, 20, 21, 29*). Apparently the only reported studies on the analysis of these oils are by Bloch and his associates (*2, 3, 12, 15, 29*). On the basis of ultraviolet and infrared spectra and certain other properties, they concluded that the conjunct polymers are five-membered ring hydrocarbons with from two to over four double bonds per mole, two of which are conjugated. They also reached the significant conclusion that the conjugated double bonds are probably distributed between a ring and a side chain, and that the polymers have a high degree of alkyl and/or alkenyl substitutions.

Workers in this field undoubtedly realized that conjunct

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