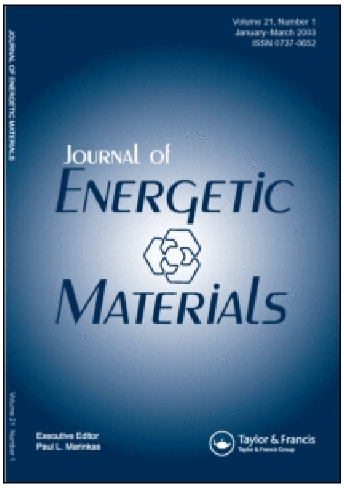

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IMPACT SENSITIVITY OF POLYNITROAROMATICS

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ABSTRACT

A large number of polynitroaromatic compounds have been prepared in these laboratories over the last decade or so during programs to develop new energetic materials. This report documents their impact sensitivities and attempts to rationalize trends in terms of structure/property correlations.

INTRODUCTION

A concentrated effort over the past decade or so has been devoted to the synthesis of new energetic materials in these laboratories. The twofold aims of this synthetic effort have been the development of denser, more powerful explosive and propellant ingredients and the identification of less sensitive and, therefore, safer materials without sacrifice of current standards of performance. This synthetic program

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has been focussed largely on new cyclic and, more recently, caged nitramines[1,2] (which will not be considered here), and on highly substituted polynitroaromatic compounds.[3] Undoubtedly the highlight of this latter work was the successful synthesis of hexanitrobenzene. The strategem employed, namely nitration of a suitably substituted nitroaniline followed by the novel oxidation of the amine functionality using peroxydisulfuric acid, has proven useful in the synthesis of a whole range of polynitroaromatics. Another class of compounds, the nitrated and aminated benzofuroxans, has provided an equally fertile source of new energetic and insensitive ingredients.[4]

The syntheses of these polynitroaromatic energetic materials and related benzofuroxans have been reported in a number of documents, including both Naval Weapons Center (NWC) technical reports and scientific journals. Therefore, these procedures will not be reproduced here. On the other hand, the impact sensitivities of these compounds have been largely unreported. This report documents impact sensitivity for the series of such polynitroaromatics and benzofuroxans prepared at NWC, and attempts to identify underlying structure/property correlations. An understanding of such structure/property relationships is essential for the systematic, scientific formulation of appropriate targets for synthesis as potential new energetic materials.

RESULTS

Table 1 contains the oxygen balance (OB_{100}) and impact sensitivity of the polynitroaromatic compounds considered in this study, together with their chemical names and acronyms. Oxygen balance was calculated using the formula

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO})/MW$$

where n_O = number of oxygen atoms,

n_H = number of hydrogen atoms,

n_C = number of carbon atoms,

n_{COO} = number of carboxyl groups, and

MW = molecular weight.

In this laboratory impact sensitivity is determined using the B of M (Bureau of Mines, Pittsburgh, Pa.) impact machine with the Type 12 tool and 2.5 kg drop weight. The explosive (35 mg) is placed in a roughly conical pile on a 1-inch square of garnet paper and placed on the polished, flat tool steel anvil. The polished, flat surface of the tool steel striker is placed on top of the sample and a 2.5 kg weight is dropped from a predetermined height onto the striker. The result of the event, explosion or otherwise, is determined by a combination of sound, smell, and visual inspection of the sample and paper. The drop height is varied according to the Bruceton "staircase" method, the height being decreased if the previous event was an explosion or increased if it was

TABLE 1. Oxygen balance and impact sensitivity of polynitroaromatics.

#	Acronym	Chemical Name	OB_{100}	$h_{50\%}$ (cm)	log h
1	HNB	Hexanitrobenzene	3.45	11	1.04
2	PNB	Pentanitrobenzene	2.97	11	1.04
3	TetNB	1,2,3,5-Tetranitrobenzene	1.55	28	1.45
4	TNB	1,3,5-Trinitrobenzene	-1.41	71	1.85
5	Picric Acid	2,4,6-Trinitrophenol	-0.48	64	1.81
6	PNA	Pentanitroaniline	1.89	22	1.35
7	TetNA	2,3,4,6-Tetranitroaniline	0.37	47	1.67
8	TNA	2,4,6-Trinitroaniline	-1.75	141	2.15
9	DATB	1,3-Diamino-2,4,6-trinitrobenzene	-2.06	>200	>2.30
10	TATB	1,3,5-Triamino-2,4,6-trinitrobenzene	-2.33	>200	>2.30
11	HNBP	2,2',4,4',6,6'-Hexanitrobiphenyl	-0.92	70	1.84
12	DIPAM	3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl	-1.32	67	1.83
13	CL-12	4,4'-Diamino-2,2',3,3',5,5',6,6'-octanitrobiphenyl	0.74	20-95*	
14	DNBP	2,2',3,3',4,4',5,5',6,6'-Decanitrobiphenyl	2.65		
15	DNBF	4,6-Dinitrobenzofuroxan	-0.88	76	1.88
16	ADNBF	7-Amino-4,6-dinitrobenzofuroxan	-1.25	100	2.00
17	CL-14	5,7-Diamino-4,6-dinitrobenzofuroxan	-1.56	120	2.08
18	CL-17	7-Amino-4,5,6-trinitrobenzofuroxan	0.70	56	1.75
19	CL-18	8-Amino-7-nitrobenzobisfuroxan	-0.79	56	1.75
20	BTF	Benzotrisfuroxan	0.00	53	1.72
21	PNT	Pentanitrotoluene	0.95	18	1.25
22	2,3,4,5-TetNT	2,3,4,5-Tetranitrotoluene	-0.74	15	1.16
23	2,3,4,6-TetNT	2,3,4,6-Tetranitrotoluene	-0.74	19	1.27
24	2,3,5,6-TetNT	2,3,5,6-Tetranitrotoluene	-0.74	25	1.39
25	2,4,6-TNT	2,4,6-Trinitrotoluene	-3.08	98	1.99
26	2,3,4-TNT	2,3,4-Trinitrotoluene	-3.08	56	1.75
27	3,4,5-TNT	3,4,5-Trinitrotoluene	-3.08	107	2.03
28	TetN-*o*-Tol	2-Amino-3,4,5,6-tetranitrotoluene	-1.05	36	1.55
29	TetN-*m*-Tol	3-Amino-2,4,5,6-tetranitrotoluene	-1.05	37	1.57
30	TetN-*p*-Tol	4-Amino-2,3,5,6-tetranitrotoluene	-1.05	47	1.67
31	HNDPM	2,2',4,4',6,6'-Hexanitrodiphenylmethane	-1.80	39	1.59
32	Picryl Azide	2-Azido-1,3,5-trinitrobenzene	-0.79	19	1.28
33	CL-16	Azidopentanitrobenzene	2.33	17	1.23
34	DDNP	2-Diazo-4,6-dinitrophenol	-1.84	9	0.97
35	5-Cl-DDNP	5-Chloro-2-diazo-4,6-dinitrophenol	-0.82	8	0.90
36	Me-NO_2-DDNP	3-Methyl-2-diazo-4,5,6-trinitrophenol	-1.12	8	0.89
37	Tetryl	*N*-Methyl-*N*,2,4,6-tetranitroaniline	-1.04	25	1.40
38	($MeNO_2N$)-22	*N*-Methyl-2-amino-*N*,3,4,5,6-pentanitrotoluene	-0.58	21	1.34
39	($MeNO_2N$)-23	*N*-Methyl-3-amino-*N*,2,4,5,6-pentanitrotoluene	-0.58	18	1.26

*CL-12 shows a marked dependence of impact sensitivity on particle size.

not. Drop heights are equally spaced in the logarithm of the height at 0.1 log unit intervals. (The log of a 10 cm drop is taken as 1.0.) A sequence of 25 tests is carried out, and the result is quoted as $h_{50\%}$, the height at which 50% of tests result in explosions.

DISCUSSION

While satisfactory (or at least adequate) models are available to estimate the density[5] and performance (detonation velocity and pressure)[6] of a potential new energetic material, our understanding of explosive structure/sensitivity relationships is less well developed. Superficially, one of the simplest tests available for screening new explosives for sensitivity to accidental and environmental stimuli and for identifying potential roles in which they might be usefully employed is the drop-weight impact test, and consequently, this is one of the first tests carried out.

However, although the drop-weight impact test is easy to carry out, and although it has proven useful as a crude screening procedure to classify explosives as sensitive, moderately sensitive, or insensitive, it has proven frustratingly inaccurate and seemingly irreproducible. Thus, a material can give different results on two apparently identical machines, or even on the same machine on different days. Some probable causes of variation include the base on which the apparatus stands, minor differences in the guide rails and friction on the falling weight, confinement of the sample, humidity, and operator differences in determination of explosion or otherwise. Considerable effort has been expended in an attempt to instrument the test, measuring *inter alia* noise production and gas evolution on explosion, endeavoring to eliminate potential operator variables, but with only limited success. Indeed, drop-weight impact sensitivities for twice recrystallized TNT have varied from below 100 cm to above 250 cm. It is small wonder that Bowden declared[7] that hitting a material with a hammer is a pastime more befitting a carpenter than a scientist! However, all impact testing reported here was carried out using the same machine under the same conditions and largely by the same skilled operator. Further it was hoped that, while too much should not be made of the precise impact sensitivity of an individual compound, if a sufficiently large number of structurally related compounds are tested these individual oddities and vagaries might tend to offset each other, and meaningful trends might evolve.

It must always be remembered that the drop-weight impact test does not yield an unequivocal and unencumbered measure of the sensitivity of an explosive, since the criterion for an explosion depends on a critical propagation of reaction. (Indeed in the Rotter impact test, in which the criterion for explosion is the evolution of gas, the volume of gas evolved is interpreted as an indication of the ease of propagation of the explosive reaction.[8]) It was concluded long ago that the impact initiation of explosives involves the creation of hot spots, which must reach a localized temperature of about 500°C if propagation of the explosive reaction is to be sustained.[9] Factors which might contribute to the critical generation of hot spots include

- kinetics of decomposition
- heat evolved in decomposition
- heat capacity
- thermal conductivity
- latent heats of fusion and evaporation
- crystal hardness
- crystal shape, etc.

By restricting the study to organic solids and by resting the explosive samples on sand paper, it was hoped that the effects of crystal properties would be minimized, as would the variations in physical properties.

Several groups have published results of studies into relationships between the structure of energetic materials and their sensitivity to impact initiation. The first studies were by Kamlet and Adolph, who studied a large number of nitroaliphatics and nitramines,[10] and nitroaromatics.[11] They were able to identify a broad general trend in which the logarithm of 50% drop height (log $h_{50\%}$) decreased with increasing oxygen balance (OB_{100}). If the explosives were restricted to a single class of compounds, where a common decomposition pathway might be inferred, reasonably good linear correlations were found. Jain considered a variant of this approach and found good correlations of his "valence parameter" with impact sensitivity, velocity of detonation, and heat of explosion.[12] Storm and Stine reconsidered the data of Kamlet and Adolph for polynitroaromatics and claimed that a very much improved correlation of log $h_{50\%}$ with OB_{100} (-0.97 to -1.00) could be obtained if the explosives were restricted to a series of very closely related compounds and that these correlations could be used to predict very accurately the impact sensitivity of a new member of that series.[13] These results look very impressive but, given the accepted reliability of log $h_{50\%}$ (± 0.10), such outstanding correlations may be fortuitous and misleading. Mullay reported a correlation between impact sensitivities and molecular electronegativities of energetic materials.[14] Nielsen[2] extended Stals' work[15] and proposed a correlation between impact sensitivity and the dissociation energy for the weakest bond, which could be calculated empirically if all bond lengths were known. However the accuracy of these empirical calculations was limited, and bond lengths were not necessarily available. Delpuech and Cherville carried out quantum mechanical calculation of critical bond polarities and reported correlations of shock sensitivity within families of explosives.[16]

We chose to consider here the simple procedure of Kamlet and Adolph.[10,11] These authors were able to identify a relationship between the impact sensitivity of a polynitroaromatic and its oxygen balance, OB_{100}, which can be related to the energy available in the explosive.[11] Further, they were able to account for the increased sensitivity over simple polynitroaromatics, in which the initiating step is presumably a scission of the C-NO_2 bond, of those compounds which contained a C-H bond alpha to the polynitroaromatic ring. In the latter group of compounds, the initiating step was identified as scission of the C-H bond. Support for this mechanism was derived from studies of the thermal decomposition of TNT, in which products formed by reaction at the methyl group were isolated and identified,[17] and for which a primary kinetic isotope effect was observed when the methyl group was labelled with deuterium.[18] Kamlet and Adolph coined the term "trigger linkage" for the site of the initiating step; Delpuech and Cherville designate it as the "privileged bond."[16] Kamlet and Adolph also concluded, not unreasonably, that if a compound contains structural features of more than one sensitivity category, then its impact behavior should conform more closely with the more sensitive.

With only two exceptions, the nitroaromatics considered by Kamlet and Adolph in 1979 contained no more than three nitro groups on one ring.[11] Since that time many more-highly nitrated compounds have become available, most of which are included in this study. Indeed of the 40-odd compounds considered here, about half contain four or more nitro groups on the same ring. The relationship of the impact sensitivity of these more-highly substituted compounds with their oxygen balance is illustrated in Figure 1.

The first point to be noted, after the expected general tendency towards increased sensitivity with increased oxygen balance, is that direct comparisons should be restricted in the first place to structurally similar materials. Thus the diazophenols and the aromatic azides are much more sensitive to impact than are the general body of polynitroaromatics, and the dependence on oxygen balance is less pronounced. It is reasonable to infer that the "trigger linkages" in these compounds are associated with the diazonium and azido functionalities and that they are relatively little influenced by the remainder of the molecule. A similar result is observed for polynitroaromatics containing the nitramine grouping. Once again these compounds are considerably more sensitive, and the initial reaction on impact is believed to be cleavage of the $N\text{-}NO_2$ bond.

Second, the results for those compounds which do not contain an alpha C-H bond may be fitted to a linear relationship

$$\log(h_{50\%}) = 1.72 - 0.21(OB_{100})$$

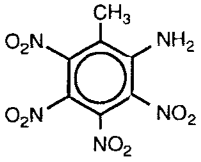
with a correlation coefficient of 0.96 and a standard error of 0.10. These results are quite comparable with those of Kamlet and Adolph,[11] although the constants are slightly different because the impact sensitivities were determined on a different drop-weight machine. It should be stressed again that the standard error corresponds with the height increment on the drop-weight machine, the commonly accepted accuracy and reproducibility of the test procedure. It is noteworthy that the benzofuroxans correlate well with the polynitroaromatics in this investigation, and that the amine groups appear to show little desensitizing effect over that indicated by the reduction in oxygen balance.

The polynitroaromatic compounds containing an alpha C-H group are consistently more sensitive to impact than are similar compounds with the same oxygen balance but without the alpha C-H group, and appear to form a separate class. These results can also be fitted to a linear relationship,

$$\log(h_{50\%}) = 1.33 - 0.17(OB_{100}),$$

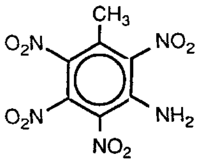
but here the correlation coefficient is only 0.87 and the standard error is increased to 0.14. This increased spread of data was not unexpected since most of the results were for positional isomers. However since the impact sensitivities for each set of isomers were measured at the same time and by the same operator, we are able to use this divergence of results to draw some interesting conclusions about the effects of positional isomerism.

The first compounds considered were the isomeric tetranitrotoluidines (**28**-**30**). The *ortho* and *meta* derivatives (**28**,**29**) had impact sensitivities of 36 and 37 cm respectively, while the *para* isomer (**30**) had an impact sensitivity of 47 cm. The obvious structural difference is that (**28**,**29**) each contain three contiguous nitro groups about the aromatic ring, whereas (**30**) lacks this feature. It is known that the central of three contiguous nitro groups is rendered more prone to chemical reaction by a combination of electronic and steric factors, and it has been suggested that this group may be more activated towards rearrangement to a nitrito functionality,[19] where O-N bond cleavage should be facilitated.



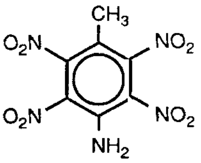
28

36 cm



29

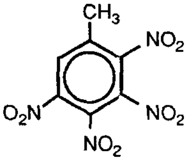
37 cm



30

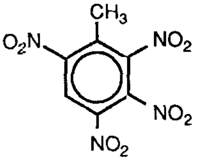
47 cm

The second group of compounds considered consisted of the isomeric tetranitrotoluenes (**22**-**24**). The 2,3,4,5-tetranitro isomer (**22**), with four contiguous nitro groups around the aromatic ring, had an impact sensitivity of 15 cm; the 2,3,4,6 isomer (**23**), with three contiguous nitro groups, had an impact sensitivity of 18 cm; the 2,3,5,6 isomer (**24**), with only two contiguous nitro groups, had an impact sensitivity of 25 cm. The differences in sensitivity are not large, but the variation follows the expected trend. Given that they were determined by the same operator on the same machine at the same time, we believe that these results support our hypothesis that, in a polynitroaromatic containing three contiguous nitro groups, the central nitro group is activated to reaction, probably nitro/nitrito rearrangement, and this functional group provides the "trigger linkage" for impact initiation. (It should also be noted that the tetranitrotoluenes (**22**-**24**) are more sensitive than the tetranitrotoluidines (**28**-**30**). Clearly in this class of compounds, the amine functionality acts as a desensitizing group; as is discussed later, this is not universally the case.)



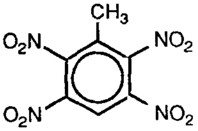
22

15 cm



23

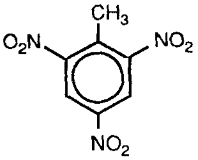
18 cm



24

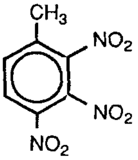
25 cm

The results of Kamlet and Adolph indicate strongly that the alpha C-H bond is involved in the initiating reaction,[11] and some of the results reported here certainly support that contention; at the same time other results we have obtained indicate that contiguous nitro groups contribute to the sensitivity of the compounds. In an attempt to evaluate the relative importance of these effects, three of the isomeric trinitrotoluenes were examined. 2,4,6-TNT (α) (**25**), with no adjacent nitro groups but with the methyl group having two nitro group neighbors, had an impact sensitivity of 98 cm. 2,3,4-TNT (β) (**26**), with three contiguous nitro groups and with the methyl group having one nitro group neighbor, had an impact sensitivity of 56 cm. 3,4,5-TNT (δ) (**27**), with three contiguous nitro groups but with the methyl group having no adjacent nitro group, had an impact sensitivity of 107 cm. These results tend to suggest that the interaction between three contiguous nitro groups imparts the same degree of sensitivity as does the interaction between adjacent methyl and nitro groups, but that a synergistic effect is produced when both features are present in the same molecule.



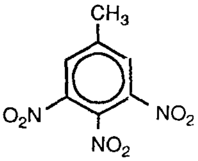
25

98 cm



26

56 cm



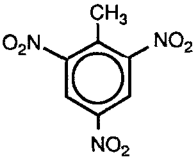
27

107 cm

Oxygen balance, OB_{100}, is related to the volume and type of gaseous products on explosion (either detonation or deflagration) of an energetic material and to the energy released. It is, therefore, probably more directly relevant to the *propagation* of reaction in an explosive than to its *initiation*. The latter is more closely related to the strength of the critical bond and the energy required for its rupture. (This bond need not necessarily be the first bond broken, but probably usually is.) Thus, the approaches of Stals[15] and Delpuech and Cherville[16] are probably more valid scientifically, but they are more complex and require data not readily available for a new or proposed explosive, and they are consequently less usable as predictive tools. The observed and undeniable correlation between oxygen balance and impact sensitivity, which is heightened by restricting the explosives to a very closely related series of compounds, is probably more coincidental than causal. Thus, in such a set of compounds, the features which increase oxygen balance probably also decrease the energy required to break the critical bond to initiate reaction. However these parallel effects may be expected to diverge as dissimilar features are incorporated into the molecule, and particularly so when new trigger linkages are introduced.

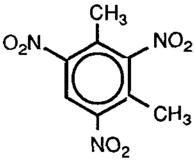
Experience and intuition tell us that a number of features contribute to the sensitivity and instability of explosives in general, and polynitroaromatics in particular. In the polynitroaromatics the initial reaction is believed to involve cleavage of the C-NO_2 bond; an increase in the number of nitro groups leads to an increase in the number of potential initiation sites, while an accumulation of contiguous nitro groups leads to a weakening of the central C-NO_2 bond by both electronic and steric effects. The inclusion of an azido, diazonium, or nitramine group markedly increases the impact sensitivity, but this is achieved only by the presence of a new and more sensitive trigger linkage. An increase in the number of nitro groups in a molecule is reflected in an increase in oxygen balance; their accumulation in vicinal positions is not. Inclusion of an azido or diazonium group, or the replacement of a nitro group by a nitramine, also has a relatively minor effect on oxygen balance. Other features which contribute to sensitivity include low melting point (decomposition takes place more rapidly in the liquid state than in the solid) and molecular asymmetry.

It also appears that the presence of an alpha C-H bond, as in the methyl or methylene group, leads to increased sensitivity, and the very plausible justification of Kamlet and Adolph[11] has already been discussed. However this conclusion is only valid if compounds with the same oxygen balance are considered. There is no evidence in the current work that the addition of a methyl group to trinitrobenzene, tetranitrobenzene, pentanitrobenzene, or tetranitroaniline results in any large increase in impact sensitivity. The methyl group appears to act essentially as an inert diluent which happens to decrease the oxygen balance of the compound, and therefore gives the *appearance* of a sensitizer if oxygen balance is the other variable. Support for this hypothesis may be derived from the impact sensitivities of trinitroxylene (**40**) and trinitromesitylene (**41**), which are indistinguishable from that of TNT (**25**).



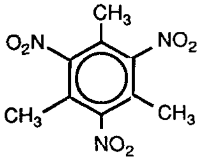
25

100 cm



40

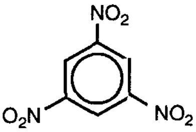
100 cm



41

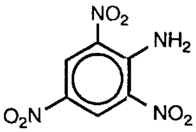
110 cm

Physical features which appear to contribute to insensitivity and stability include high molecular weight and melting point and a high degree of symmetry. The outstanding chemical feature which leads to insensitivity in polynitroaromatics is the presence of amino groups between the nitro groups around the aromatic ring. (The presence of an amino group will, of course, result in a decrease in oxygen balance.) This effect is observed most dramatically as amino groups are added sequentially in the series trinitrobenzene/picramide/DATB/TATB (**4**,**8**,**9**, **10**), with the remarkable increase in stability and insensitivity, and has been attributed to strengthening and stabilizing the C-NO_2 by the electron donating amines, and to intra- and intermolecular hydrogen bonding.



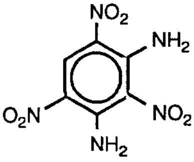
4

71 cm



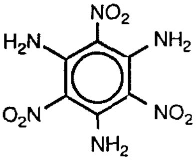
8

141 cm



9

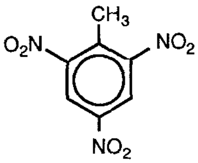
>200 cm



10

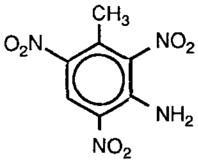
>200 cm

A similar effect was observed by Iyer for the series trinitrotoluene/aminotrinitrotoluene/diaminotrinitrotoluene (**25**,**42**,**43**),[20] and indeed can be seen in all the polynitroanilines examined here.



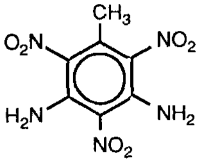
25

61 cm



42

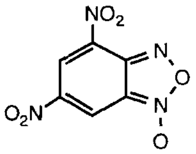
174 cm



43

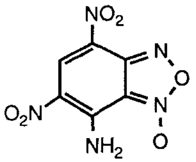
239 cm (Ref. 20)

A corresponding decrease in sensitivity is also to be seen on inclusion of amino groups in benzofuroxans, going from DNBF to ADNBF to CL-14 (**15**,**16**,**17**).



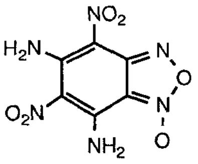
15

76 cm



16

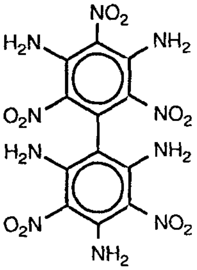
100 cm



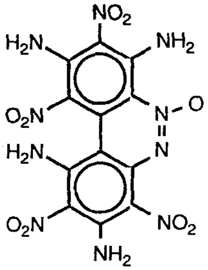
17

120 cm

However the effect is not universal. Read found that the impact sensitivity of hexanitrobiphenyl was actually *increased* by the presence of amines.[21] This result may be due to steric factors, with the orthogonality of the biphenyl ring system and steric crowding of the substituents forcing one of the *ortho* nitro groups into an unfavorable configuration and weakening the C-NO_2 bond, and has prompted Read to consider benzo[c]cinnoline oxides such as **45**, in which the rings are constrained in a planar configuration, as alternatives to the orthogonal biphenyls (e.g., **44**).[22]

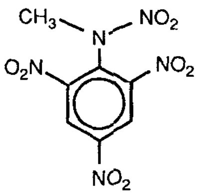


44

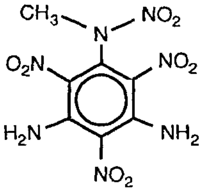


45

Hutchinson found that the addition of amine groups to tetryl (**37**) to give **46** also caused an increase in sensitivity.[23] However, it must be recalled that in tetryl it is the N-NO_2 bond rather than a C-NO_2 bond which provides the initial reaction, and it is not unreasonable that a substituent which strengthens the latter bond might weaken the former.



37

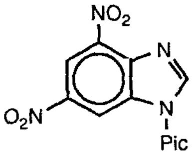


46

Figure of Insensitivity (F of I): 37 — 100; 46 — 75 (Ref. 23)

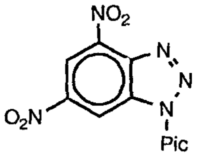
In summary, then, it seems likely that the apparent correlation between the oxygen balance of an energetic material and its sensitivity to impact is an indirect and rather fortuitous one, both factors being related to the number of various sensitizing and desensitizing features. Within a closely related series in which the mode of chemical reaction and "trigger linkage" remain constant, and in which change is restricted to only the number of nitro or amino groups, a good correlation might be expected. In a more diverse collection of compounds, the correlations may not be so good; when new trigger linkages are introduced any correlation would be considered surprising.

In this context it seems worth while commenting on the impact sensitivity of some picryl and nitro substituted heterocycles synthesized recently in these laboratories. In the light of the discussion above, it is recognized that polynitroheterocycles are distinctly different from the polynitroaromatics already considered. However, 1-picryl-4,6-dinitrobenzimidazole (**47**), with an oxygen balance of -2.63 and an impact sensitivity of 91 cm, lies surprisingly close to the trend for the polynitroaromatics in Figure 1. It is believed that the trigger linkage is a C-NO_2 bond, probably one of those in the picryl moiety. On the other hand, the corresponding 1-picryl-4,6-dinitrobenzotriazole (**48**) and its 5,7-dinitro isomer (**49**) (BTX), with oxygen balance of -1.90 and impact sensitivities of 35 and 40 cm, are much more sensitive than indicated by the trend. (Interestingly, 1-picrylbenzotriazole (**50**) has an even lower oxygen balance and a higher sensitivity.) In these compounds, it is believed that the initial reaction on impact involves cleavage of nitrogen from the triazole segment rather than scission of a C-NO_2 bond.[24] It is worth noting that picrylpolynitroimidazoles and 1,2,4-triazoles also tend to be somewhat more sensitive than might be predicted from the trend in Figure 1, although not as sensitive as the benzotriazoles since they do not contain the N=N-N atomic grouping.[25] Perhaps this suggests that the initial reaction on impact is cleavage of a nitro group from the heterocycle rather than from the picryl moiety in these compounds.



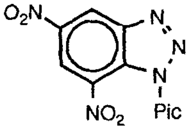
47

91 cm



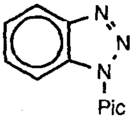
48

35 cm



49

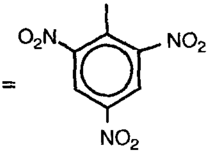
40 cm



50

11 cm

Pic =



CONCLUSIONS

The impact sensitivity of polynitroaromatic materials ranges from about 8 cm to over 230 cm, with a general tendency to greater sensitivity (smaller drop height) with increasing oxygen balance. When the class of materials is tightly restricted to those containing only nitro, amino, and furoxan functional groupings, the correlation between impact sensitivity and oxygen balance is excellent. However, when other functional groups such as azido, diazonium, methyl, and methylnitramino are included this correlation is not so good, and it appears that the relation between impact sensitivity and oxygen balance is coincidental rather than causal.

It seems more likely that impact sensitivity is dependent on the energy of the weakest bond (the "trigger linkage"), but identification of the weakest bond and estimation of its strength are not yet amenable to routine simple calculation. Features which add to the sensitivity of a polynitroaromatic include the number and proximity of nitro groups, furoxan rings, azido, diazonium, and methylnitramino groups. Amino groups act as desensitizers, particularly when interspersed between the nitro groups. An additional decomposition pathway is provided by the presence of an alpha-methyl group, but extra methyl groups appear to have no further effect on impact sensitivity.

ACKNOWLEDGMENT

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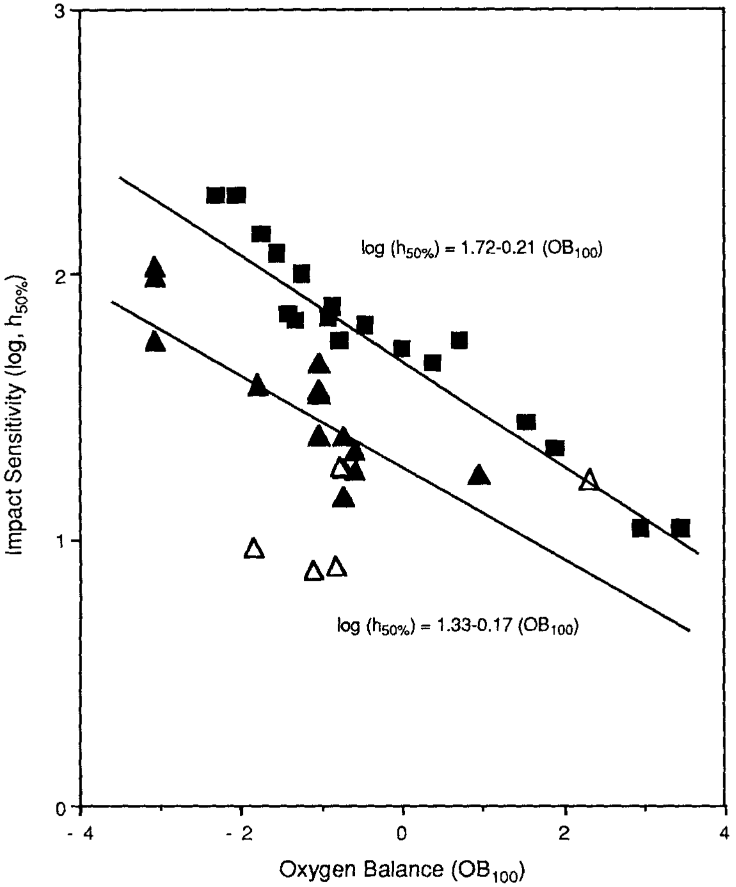

■ Compounds without α-CH, to which is fitted the line log ($h_{50\%}$) = 1.72 - 0.21 (OB_{100}).

▲ Compounds with α-CH, to which is fitted the line log ($h_{50\%}$) = 1.33 - 0.17 (OB_{100}).

△ Azides and diazonium compounds.

FIGURE 1

Correlation of Impact Sensitivity With Oxygen Balance.

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