

NSWC TR 80-495

LEVEL II

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AD A101203

**RELATIONSHIPS BETWEEN THE IMPACT SENSITIVITY OF
HIGH ENERGY COMPOUNDS AND SOME MOLECULAR
PROPERTIES WHICH DETERMINE THEIR PERFORMANCE;
N, M, AND ρ_0 .**

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RESEARCH AND TECHNOLOGY DEPARTMENT

9 APRIL 1981

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC/TR-86-495	2. GOVT ACCESSION NO. AD-A101 203	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Relationships Between the Impact Sensitivity of High Energy Compounds and Some Molecular Properties Which Determine Their Performance; J. M. and D. A.	5. TYPE OF REPORT & PERIOD COVERED Technical Report	
6. AUTHOR H. G. Adolph J. R. Holden D. A. Cichra	7. PERFORMING ORG. REPORT NUMBER	
8. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center White Oak Laboratory White Oak, Silver Spring, MD 20910	9. CONTRACT OR GRANT NUMBER(s)	
10. CONTROLLING OFFICE NAME AND ADDRESS	11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61152N; 0001; ZRC1309; IR201	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. REPORT DATE 9 Apr 1981	
	14. NUMBER OF PAGES 52	
	15. SECURITY CLASS. (of this Report) UNCLASSIFIED	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Explosives Structure - Property Correlation Sensitivity Density Detonation Gas		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Correlations have been carried out between several parameters related to the sensitivity and performance of several classes of nitro explosives. The parameters include experimental impact sensitivities and crystal densities, and the calculated quantities Q (detonation energy), $M^{\frac{1}{3}}$ (a characteristic of the detonation gas), and NO ₂ % (nitro content). Significant positive trends have been observed for correlations of impact sensitivity (I.S.) with NO ₂ %, $M^{\frac{1}{3}}$, and of NO ₂ % with $M^{\frac{1}{3}}$ and $M^{\frac{1}{3}}$ for series of polynitroaliphatic		

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** crystal or initial density

* sg. root of NM

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compounds and nitramines. The trends in I.S. with ~~NM~~^{*} and ~~Q₀~~^{**} appear to be influenced by the dependence of all 3 parameters on the NO₂[#]. $\Delta\rho$, an increment of exceptional density, is independent of I.S. or may decrease it slightly.

By contrast, in a series of polynitroaromatic compounds the only correlations exhibiting significant trends are between I.S. and NO₂[#].

* sq. root of NM

** crystal or initial density

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FOREWORD

This work was carried out under the NSWC IR Task 201, Task No. ZRC1309, Explosives Chemistry for Weapons. One objective of this Task is the synthesis of new explosives ingredients which will enable the formulation of energetic yet insensitive explosives. In the work described herein, an attempt is made to clarify relationships between molecular characteristics of explosive compounds and their sensitivity and performance properties. A better understanding of these relationships is needed for the successful design of new insensitive high-energy molecules.

Helpful discussions with Drs. M. J. Kamlet and C. Dickinson are gratefully acknowledged.

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INTRODUCTION

Explosives which combine high performance with insensitivity (IHPE)* have been a goal of military explosives development for some time. In one approach, highly energetic but sensitive explosives such as RDX and HMX are desensitized by embedding in elastomeric polymers (binders). The result is a series of explosive compositions with "intermediate" sensitivity and performance attributes which are of great practical value. This approach is currently being refined and extended by the use of energetic binders which are expected to increase the performance of these compositions without significantly raising their sensitivity. Some use has also been made of the kinetic effects present in "non-ideal" explosives to affect the balance of performance and sensitivity, for example in such materials as PBXN-103 and PBXN-105.

Recently, another approach to IHPE has received consideration, in which intrinsically insensitive materials are sought which as a result of their molecular properties also possess useful performance characteristics. TATB and NQ are currently the prototypes of such compounds. Since their energy content is comparable to TNT, their utility is, however, limited. The question arises, can other compounds be made which are as insensitive as TATB and NQ but have higher energy, or, more generally, can we synthesize new explosive compounds with other and more attractive combinations of sensitivity and performance?

To pursue this question, it would be very useful to know how explosive sensitivity and performance are related to each other and to the structure and molecular properties of the explosive compound. Although a number of limited studies relating sensitivity or aspects of performance to molecular structure have been made¹, the only attempts to interrelate sensitivity and performance

*The terms, performance and sensitivity, are used here in their broadest definitions. Sensitivity, for example, encompasses the response to thermal loads, to low strain rate mechanical pulses, and to high strain rate impact phenomena or shockwaves. Performance includes underwater shock and bubble effects, airblast, and metal acceleration.

¹Price, D., Chem. Reviews 59, 801 (1959); Kamlet M. J., and Jacobs, S. J., J. Chem. Physics, 48, 23 (1968); Delpuech, A., and Cherville, J., Propellants and Explosives 3, 169 (1978); Hill, M. E., and Guimont, J. M., "Desensitization of Explosive Materials", Final Report for Contract N0014-76-C-0810, Dec 1979.

appear to be those by Kamlet² and Kamlet and Adolph³ involving correlations of impact sensitivity with oxygen balance. Oxygen balance can be regarded as a molecular parameter qualitatively related to explosive performance although no direct proportionality with any specific explosive effect has been demonstrated. It was shown that $\log(50\% \text{ impact height})$ is a linear function of the oxygen balance for four classes of nitro compounds, but with different coefficients and constants for each of the four regression equations. Thus a relationship between impact sensitivity and performance as well as an effect of molecular structure on this relationship has been demonstrated.

Since the completion of the impact sensitivity vs. oxygen balance correlations², the molecular properties which determine explosive performance of C, H, N, O, F compounds have been identified at least qualitatively if not quantitatively⁴. It appears now that most types of explosive performance of such compounds can be understood in terms of the detonation energy (Q), the number of moles (N) and molecular weight (M) of detonation gas, and the crystal or initial density (ρ_0). Since these molecular parameters are relatively easily accessible*, it appeared that the relationship between sensitivity and performance of explosive compounds could be defined further by investigating the relationship of these molecular properties with explosive sensitivity. Some initial attempts at such an investigation involving the quantities N, M, and ρ_0 are reported here.

²Kamlet, M. J., "The Relationship of Impact Sensitivity with Structure of Organic Explosives. I. Polynitroaliphatic Explosives", Proceedings 6th Symposium (International) on Detonation, San Diego, CA, Aug 1976; ONR Report ACR 221, p. 312.

³Kamlet, M. J. and Adolph, H. G., Propellants and Explosives 4, 30 (1979).

⁴Price, D., Chem. Reviews 59, 801 (1959); Kamlet, M. J., et. al., J. Chem. Physics 48, 23, 43, 3685 (1968).

*In the most simple approach, N, M, and Q can be calculated (using Kamlet's definitions⁵); ρ_0 of new explosive compounds is often routinely determined.

⁵Kamlet, M. J. and Jacobs, S. J., J. Chem. Physics 48, 26-28 (1968).

EXPERIMENTAL

DATA BASE

The major problem in attempting these correlations was the compilation of a suitable data base. It was obvious from the outset that the only sensitivity data available on a sufficiently large and diversified set of nitro compounds were impact sensitivities. The difficulties in comparing impact sensitivities determined at different laboratories are well recognized, and the problems of reproducibility of impact sensitivity data even using the same machine have been amply discussed^{2,3}. Relationships, or the lack thereof, between different types of explosive sensitivity and sensitivity tests have been studied by Urizar, Peterson, and Smith⁶. The impact sensitivity data used in the present work were all determined on the same NSWC (formerly NOL) machine whose operation has been described and discussed in detail⁷, but they were obtained over a period of more than 20 years by several operators who used different means of detecting a "go". Thus the impact sensitivity data were collected under partly favorable and partly unfavorable conditions.

A further complication was the need for additional experimental data besides impact sensitivities. While N and M can be calculated and Q can at least be estimated from the chemical composition and structure of each compound*, the crystal density must be determined experimentally. Unfortunately, for many compounds synthesized during the past 25 years or submitted to NSWC for testing either density or impact sensitivity were determined, but not both. This restricted the set of suitable compounds to no more than 230. To take into account at least some of the structural effects on impact sensitivity noted by Kamlet^{2,3}, this set was subdivided into nitramines (76, Table 1), nitroaromatic (59, Table 2), and nitroaliphatic compounds (64, Table 3). Compounds from the original set of 230 which did not belong to one of these classes are not included in the present analysis.

²See Reference 2 on page 2 .

³See Reference 3 on page 2 .

⁶Urizar, M. J., Peterson, S. W., and Smith, L. C., "Detonation Sensitivity Tests", LA-7193-MS, Los Alamos Scientific Laboratory, April 1978.

⁷Ref 3., p 34, and Ref 3., footnote 14.

* See the previous footnote, p. 2 .

TABLE 1. LIST OF NITRAMINES*

C-N-N-O-X	I.S.	NO ₂ #	NM ^{1/2}	ρ_0	$\Delta\rho$	
104040400	1.05	1.47	19.7	1.743	-.059	METHYLFNF DINITRAMINE (MFNINA)
204040400	1.43	1.33	18.0	1.710	.064	ETHYLFNF DINITRAMINE (FNNA)
304040400	.95	1.67	17.9	1.764	-.002	TRINITROETHYL METHYL NITRAMINE
304070000	1.18	1.50	18.0	1.770	-.030	TRINITROETHYLNITROGUANIDINE
306060600	1.30	1.35	17.6	1.806	.009	1,3,5-TRINITRAZACYCLOHEXANE (ROX)
309040400	1.05	1.27	16.9	1.520	-.081	N-METHYL ETHYLFNEDINITRAMINE
404040400	1.41	1.30	17.7	1.890	.054	TRIFLUOROETHYL TRINITROETHYL NITRAMINE
404060400	1.05	1.51	17.0	1.751	-.003	TRINITROETHYL CYANOMETHYL NITRAMINE
404061000	1.20	1.50	17.7	1.910	.051	BIS(FLUOROPDINITROETHYL)NITRAMINE
404081400	.90	1.80	17.6	1.970	.072	BIS(TRINITROETHYL) NITRAMINE (BTNEN)
405041000	1.23	1.41	17.5	1.724	-.057	N-METHYL-N-NITRO-(TRINITROETHYL)CARBAMATE
406040600	1.40	.97	16.4	1.640	.012	N,NP-DINITROETHYL-N,NP-DINITRO-OXAMIDE
406060900	1.23	1.42	17.5	1.770	-.082	N-NITRO-N-(TRINITROETHYL)GLYCINEAMIDE
406061100	.82	1.59	17.8	1.830	.043	TRINITROETHYL NITRATOETHYL NITRAMINE
407041000	.91	1.26	15.9	1.800	.045	N-NITRO-N-(TRINITROETHYL)ETHANESULFONAMIDE
409040400	1.41	1.05	17.6	1.900	.118	1,3,5,7-TETRANITRAZACYCLOOCTANE (PMX)
410040400	1.50	1.26	17.1	1.630	.037	3-NITRAZA-1,5-PENTANEDINITRAMINE
506061000	1.15	1.61	17.0	1.823	.024	N,3,3,5,5-PENTANITROPIPERIDINE
506081400	.78	1.74	17.6	1.842	.016	TRINITROETHYL TRINITROPROPYL NITRAMINE
507051000	1.20	1.35	17.0	1.698	-.003	TRINITROETHYL N-ETHYL-N-NITROCARBAMATE
508061100	1.09	1.57	17.4	1.770	.056	1,1,1-TRINITRO-6-NITRATO-3-NITRAZAHXANE
509040900	1.33	1.41	17.0	1.725	.095	(2,2-DINITROPROPYL) NITRATOETHYL NITRAMINE
509050900	1.62	1.41	17.0	1.623	-.007	TRINITROETHYL 2-METHOXYETHYL NITRAMINE
509071000	1.02	1.53	17.4	1.770	.081	1,1,1-TRINITRO-3,6-DINITRAZAHXANE
510060800	1.44	1.42	16.9	1.620	.016	4,4-DINITRO-2,6-DINITRAZAHXANE
510060800	1.54	1.42	16.9	1.654	.031	3,3-DINITRO-1,5-PENTANE DINITRAMINE
510101400	1.00	1.30	18.1	1.803	.020	1,9-DINITRATO-2,4,6,8-TETRANITRAZACHANE
606081400	.78	1.69	17.2	1.840	-.011	1-NITRO-2,5-BIS(TRINITROMETHYL)PYRROLIDINE
606081600	.95	1.57	17.4	1.840	.014	TRINITROETHYL N-(TRINITROETHYL)NITRAMINOACETATE
606081600	.90	1.57	17.4	1.816	-.014	TRINITROETHYL N-NITRO-N-(TRINITROPROPYL)CARBAMATE
609051000	1.54	1.29	16.6	1.600	-.034	TRINITROETHYL 4-NITRAZAPENTANOATE
609071200	1.74	1.62	17.1	1.650	-.044	TRINITROPROPYL (2,2-DINITROPROPYL) NITRAMINE
609071200	1.16	1.85	17.1	1.740	.032	TRINITROETHYL 2,5-DINITRAZAHXANOATE
609071200	1.29	1.67	17.1	1.736	.034	TRINITROETHYL (3,3-DINITROBUTYL) NITRAMINE
610061000	1.45	1.53	16.7	1.726	.090	BIS(2,2-DINITROPROPYL)NITRAMINE
614060400	2.22	1.01	16.6	1.548	.032	1,7-DIMETHOXY-2,4,6-TRINITRAZAHXANE
614080800	1.77	1.23	16.8	1.660	.090	3,6-DINITRAZA-1,8-OCTANEDINITRAMINE
704040400	1.41	1.39	16.9	1.730	.000	N-METHYL-N,2,4,6-TETRANITROANILINE (TETRYL)
704102000	1.02	1.49	17.3	1.887	.018	BIS(TRINITROETHYL) 2,4-DINITRAZAPENTANEDIOATE
709071400	1.20	1.45	16.9	1.700	-.018	2,2-DINITROPROPYL 5,5,5-TRINITRO-2-NITRAZAPENTANOATE
709071400	1.18	1.45	16.9	1.733	.015	TRINITROETHYL 5,5-DINITRO-2-NITRAZAHXANOATE
709071400	1.39	1.45	16.9	1.700	-.018	TRINITROETHYL 5,5-DINITRO-3-NITRAZAHXANOATE
709091500	1.32	1.52	17.2	1.770	.009	N-NITRO-N,NP-BIS(TRINITROPROPYL)UREA
709091500	1.76	1.47	17.3	1.790	.021	TRINITROETHYL 6,6-DINITRO-2,4-DINITRAZAHXANOATE
806061200	1.00	1.72	16.5	1.790	-.001	N-(TRINITROETHYL)-N-NITRO-N-NITROBENZENESULFONAMIDE
809081000	1.15	1.39	17.0	1.770	-.011	BIS(TRINITROETHYL) 3-NITRAZAPENTANEDIOATE

TABLE 1. (continued)

C-N-N-O-Y	I.S.	NO ₂ #	NM ^{1/2}	ρ_0	$\Delta\rho$	
800101000	.95	1.50	17.1	1.803	.006	BIS(1-TRINITROPROPYL) N,NP-DINITROOXAMIDE
800122200	1.10	1.44	17.4	1.710	-.143	BIS(1-TRINITROETHYL) 2,4,6-TRINITRAZAHEPTANEDIOATE
817061200	1.67	1.30	16.2	1.610	.006	2,2-DINITROPROPYL 4,5-DINITRO-2-NITRAZAHFXANOATE
814061000	1.90	1.41	15.9	1.707	.170	BIS(2,2-DINITROBUTYL)NITRAMINE
814081000	1.96	1.04	16.1	1.690	.110	N,NP-DINITRO-N,NP-BIS(3-NITRAZABUTYL)OXAMIDE
814081200	1.05	1.44	16.6	1.510	-.092	2,2,9,9-TETRAZITRO-4,7-DINITRAZADECANE
818101000	1.57	.90	17.5	1.854	.208	BIS(4-AMINO-2,7-DINITROBUTYL)NITRAMINE DINITRATE (SALT)
900001200	1.26	1.30	15.8	1.760	.027	1,3,5-TRIS(METHYLNITRAMINO)-2,4,6-TRINITROBENZENE
910101000	1.11	1.46	16.9	1.800	.049	N,NP-DINITRO METHYLENE BIS(4,4,4-TRINITROBUTYRAMIDE)
910142200	1.18	1.50	17.5	1.859	.037	BIS(5,5,5-TRINITRO-3-NITRAZAPENTANYL)METHYLENEDINITRAMINE
917121000	1.36	1.49	17.1	1.755	-.001	METHYLENE BIS(5,5,5-TRINITRO-3-NITRAZAPENTANOAMIDE)
912122000	1.04	1.44	17.3	1.811	.050	1,1,1,6,6,11,11,11-OCTANITRO-3,9-DINITRAZAUNDECANE
912177000	1.00	1.64	17.3	1.810	.049	1,1,1,6,6,11,11,11-OCTANITRO-4,8-DINITRAZAUNDECANE
1012001000	1.45	1.32	16.5	1.630	-.062	BIS(1-TRINITROETHYL) 4-NITRAZAHEPTANEDIOATE
1012102000	1.45	1.45	16.4	1.730	-.005	BIS(1-TRINITROETHYL) 3,6-DINITRAZADECANEDIOATE
1012122200	1.74	1.30	17.2	1.775	-.006	BIS(1-TRINITROETHYL) 2,5,8-TRINITRAZANONANEDIOATE
1014001000	1.57	1.78	16.0	1.630	.020	N,NP-DINITRO-N,NP-BIS(3,3-DINITROBUTYL)OXAMIDE
1016001000	1.46	1.70	16.5	1.669	.055	4,4,8,8-TETRAZITRO-1,11-DINITRATO-6-NITRAZAUNDECANF
1016142000	1.20	1.93	17.3	1.720	.001	1,1,1,14,14,14-HEXANITRO-3,6,9,12-TETRAZITRAZATETRADECANE
1112122400	1.31	1.44	17.1	1.746	-.027	2,7-DINITROPROPANEDIOL BIS(5,5,5-TRINITRO-2-NITRAZAPENTANOATE)
1112122400	1.09	1.44	17.1	1.763	-.010	BIS(1-TRINITROETHYL) 5,5-DINITRO-2,8-DINITRAZANONANEDIOATE
1118101000	1.04	1.46	16.4	1.700	.107	2,2,7,7,12,12-HEXANITRO-4,10-DINITRAZATRIDECANE
1118101000	1.47	1.46	16.4	1.676	.075	2,2,7,7,12,12-HEXANITRO-5,9-DINITRAZATRIDECANE
1212102000	1.20	1.30	16.2	1.650	-.029	1,4-BIS(5,5,5-TRINITRO-2-NITRAZAPENTANOATE)-2-BUTYNE
1216102000	2.10	1.74	16.5	1.770	.061	BIS(1-TRINITROETHYL) 4,7-DINITRAZADECANEDIOATE
1216142400	1.29	1.85	17.0	1.780	.045	BIS(1-TRINITROETHYL) 2,5,8,11-TETRAZITRAZADODECANEDIOATE
1216162400	1.36	1.67	17.3	1.740	-.019	1,1,1,6,6,10,10,10,10,10,10,10-DECANITRO-3,8,13-TRINITRAZAPENTADECANE
1318102000	2.14	1.76	16.2	1.660	.027	2,2-DINITROPROPANEDIOL BIS(5,5-DINITRO-2-NITRAZAHXANOATE)
1416163000	1.09	1.46	17.1	1.767	-.002	BIS(1-TRINITROETHYL) 5,5,9,9-TETRAZITRO-2,7,12-TRINITRAZATRIDECANEDIOATE
1518102700	1.11	1.06	16.8	1.769	.013	1,3,5-TRIS(1-OXO-5,5,5-TRINITRO-3-NITRAZAPENTYL)-5-TRIAZACYCLOHEXANE

*I.S. = $\log_{10} h_{50}$ NO₂ # = MOLAR NUMBER OF NITRO GROUPS PER 100g OF EXPLOSIVENM^{1/2} = SEE TEXT ρ_0 = CRYSTAL DENSITY, g/cm³ $\Delta\rho$ = DENSITY DIFFERENCE (OBSERVED-CALCULATED), SEE TEXT

TABLE 2. LIST OF NITROAROMATIC COMPOUNDS*

C-M-N-O-X	I.S.	NO ₂	NM ^{1/2}	ρ_0	$\Delta\rho$	
303050400	2.19	1.16	14.3	1.676	-.065	4-METHYL-3,5-DINITROTRIAZOLE
402020400	1.43	1.27	14.6	1.690	-.125	2,5-DINITROFURAN
404060600	1.44	1.29	16.4	1.757	.010	4-(2-NITROETHYL)-3,5-DINITROTRIAZOLE
407040700	1.34	1.30	15.3	1.670	.011	2,4,6-TRINITROPYRIDINE-N-OXIDE
400030603	1.92	1.12	13.9	2.000	.067	1,3,5-TRIFLUORO-2,4,6-TRINITROBENZENE
401030602	1.68	1.20	14.4	1.660	.004	1,3-DIFLUORO-2,4,6-TRINITROBENZENE
402040602	2.33	1.14	15.1	1.920	.051	2,4,6-TRINITRO-3,5-DIFLUOROANILINE
402041000	1.14	1.57	15.9	1.700	-.135	PENTANITROANILINE
403030600	2.00	1.41	13.9	1.680	-.039	1,3,5-TRINITROBENZENE
403030700	1.94	1.31	14.4	1.763	-.009	2,4,6-TRINITROPHENOL
403030800	1.63	1.22	14.9	1.029	.016	STYPHNIC ACID
403040400	1.61	1.46	15.3	1.870	.020	2,3,4,6-TETRANITROANILINE
404040600	2.25	1.32	14.4	1.762	.014	2,4,6-TRINITROANILINE
404040601	2.36	1.15	15.2	1.940	.114	2,4,6-TRINITRO-3,5-DIAMINOFLUOROBENZENE
404060800	1.66	1.39	15.6	1.880	.026	1,3,4,5-TETRANITRO-2,6-DIAMINOBENZENE
404050600	2.41	1.23	14.8	1.837	.070	1,3-DIAMINO-2,4,6-TRINITROBENZENE (DATB)
404050700	2.08	1.16	15.2	1.965	.159	3,5-DIAMINO PICRIC ACID
406060600	2.51	1.15	15.2	1.940	.156	1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE (TATB)
702040600	2.15	1.26	13.4	1.710	-.008	2,4,6-TRINITROBENZONITRILE
702051001	1.26	1.49	15.5	1.870	.009	2,4,6-TRINITROFLUORODINITROMETHYLBENZENE
704040700	1.62	1.17	14.2	1.710	.024	2,4,6-TRINITROBENZALDOXYME
704030600	2.02	1.32	13.5	1.610	-.023	1-(DINITROMETHYL)-3-NITROBENZENE
704030600	2.20	1.32	13.5	1.654	.021	2,4,6-TRINITROTOLUENE (TNT)
705030700	2.28	1.23	14.0	1.690	.013	3-METHYL-2,4,6-TRINITROPHENOL
404061200	1.11	1.60	15.5	1.830	.023	TRINITROETHYL-2,4,6-TRINITROBENZENE
405030600	1.41	1.25	12.8	1.607	-.000	2,4,6-TRINITROSTYRENE
407051001	2.27	1.10	13.8	1.700	-.037	N-(TRINITROETHYL)-M-NITROBENZENESULFONAMIDE
407051001	1.91	1.10	13.8	1.790	.053	N-(TRINITROETHYL)-P-NITROBENZENESULFONAMIDE
404061400	1.38	1.43	15.5	1.800	-.013	TRINITROETHYL 2,4,6-TRINITROBENZOATE
404061001	2.02	1.15	14.6	1.700	.053	FLUORODINITROETHYL 3,5-DINITROBENZOATE
405051200	1.86	1.33	15.0	1.666	-.007	TRINITROETHYL 3,5-DINITROBENZOATE
405051300	1.65	1.24	14.2	1.640	-.139	TRINITROETHYL 3,5-DINITROSALICYLATE
404070800	1.98	1.18	14.2	1.750	.036	4-(2,4-DINITROBENZYL)-3,5-DINITRO-1,2,4-TRIAZOLE
406060600	2.51	1.02	13.3	1.484	-.698	4-(P-NITROBENZYL)-3,5-DINITRO-1,2,4-TRIAZOLE
406061200	1.32	1.54	15.2	1.700	-.043	1-(TRINITROPROPYL)-2,4,6-TRINITROBENZENE
407051000	1.44	1.45	14.6	1.650	-.025	1-(TRINITROPROPYL)-2,4-DINITROBENZENE
1004040000	2.00	1.30	12.9	1.800	.067	1,4,5,8-TETRANITRONAPHTHALENE (TNN)
1007051200	2.33	1.08	14.7	1.600	-.094	2,2-DINITROPROPYL 2,4,6-TRINITROBENZOATE
1204061200	1.91	1.41	13.7	1.780	.004	2,2P,4,4P,6,6P-HEXANITROBIPHENYL
1204061400	1.68	1.37	14.2	1.820	-.000	3,3P-DIHYDROXY-2,2P,4,4P,6,6P-HEXANITROBIPHENYL
1204080400	1.93	1.03	12.9	1.880	.069	TACOT
1205071200	1.68	1.37	14.0	1.780	.001	BIS(2,4,6-TRINITROPHENYL) AMINE
1206041200	2.12	1.32	14.2	1.790	-.005	3,3P-DIAMINO-2,2P,4,4P,6,6P-HEXANITROBIPHENYL (DIPAM)
1204051100	1.73	1.23	13.8	1.760	.039	2,2P,4,4P,6,6P-PENTANITROBENZOPHENONE (PENCO)
1404081700	1.30	1.22	13.6	1.770	-.009	2,5-DIPICRYL-1,3,4-OXADIAZOLE
1406061200	1.44	1.31	13.2	1.740	.036	2,2P,4,4P,6,6P-HEXANITROSTILBENE (HNS)

TABLE 2. (continued)

P-H-N-O-X	I.S.	NO ₂	NM ^{1/2}	ρ_o	$\Delta\rho$	
1A04071201	1.92	1.14	12.1	1.718	-.003	2,5-DIPICRYLTHIAZOLE
1A04071401	1.66	1.27	12.4	1.740	-.000	2,5-DIPICRYL-3-NITROTHIOPHENE
1A04091400	1.76	1.20	13.4	1.750	.002	2,4,6,4P,2PP,4PP,6PP-HEPTANITRO-2P,6P-DIAZA-M-TERPHENYL
1A05091400	1.76	1.20	13.4	1.740	.042	2,4,6,2P,2PP,4PP,6PP-HEPTANITRO-4P,6P-DIAZA-M-TERPHENYL
1A06061201	1.72	1.19	11.7	1.700	.007	2,5-DIPICRYLTHIOPHENE
1A06061700	1.76	1.22	12.0	1.720	-.017	2,5-DIPICRYLFURAN
1A06091000	1.49	1.42	13.7	1.701	-.013	2,2P,2PP,4,4P,4PP,6,6P,6PP-NONANITRO-M-TERPHENYL (NONA)
1A06091500	1.80	1.36	13.2	1.800	.045	2,2PP,4,4P,4PP,6,6P,6PP-OCTANITRO-M-TERPHENYL
1A06091600	1.60	1.36	13.2	1.720	-.035	2,2P,2PP,4,4PP,6P,6,6PP-OCTANITRO-P-TERPHENYL
1A06091600	1.77	1.36	13.2	1.760	.005	2,2P,2PP,4,4PP,6,6P,6PP-OCTANITRO-P-TERPHENYL
7A06171000	1.91	1.26	13.4	1.774	-.028	TRIPICRYL-S-TRIAZENE
7A06122400	1.60	1.42	13.6	1.650	-.142	DONFCANITROQUATERPHENYL (DONFCA)
7A06142400	1.60	1.37	13.0	1.700	-.007	AZO BIS(2,2P,4,4P,6,6P-HEXANITROBIPHENYL) (ASH)

*SEE FOOTNOTE TO TABLE 1

TABLE 3. LIST OF NITROALIPHATIC COMPOUNDS*

C-H-N-O-Y	I.S.	NO ₂	NM ^{1/2}	P ₀	ΔP	
283038400	1.23	1.82	17.4	1.672	-.107	1,1,1-TRINITROETHANE
384048400	1.26	1.34	17.7	1.797	-.022	TRINITROETHYL CARBAMATE
384048400	1.52	1.70	17.7	1.749	-.021	1,1,1,1-TETRANITROPROPANE
386048401	1.18	1.16	17.7	1.740	-.026	N-(TRINITROETHYL)METHANESULFONAMIDE
404061501	1.36	1.47	16.1	1.881	-.035	BIS(TRINITROETHYL) SULFITE
404071300	.82	1.67	17.7	1.884	-.019	N,N-BIS(TRINITROETHYL)HYDROXYLAMINE
406040700	1.60	1.35	16.8	1.754	-.075	TRINITROBUTYRAMIDE
406040700	1.56	1.26	17.1	1.650	-.038	METHYL N-(TRINITROETHYL) CARBAMATE
408040801	1.70	1.10	15.3	1.710	-.029	N-(TRINITROETHYL)ETHANESULFONAMIDE
404061500	1.20	1.45	17.2	1.880	-.015	BIS(TRINITROETHYL)CARBONATE (BTNEC)
404061400	.96	1.50	17.3	1.850	-.047	N,NP-BIS(TRINITROACETYL)METHYLENEDIAMINE
504071400	1.70	1.81	17.4	1.898	-.064	1,1,1,3,5,5,5-HEPTANITROPENTANE
506061400	1.23	1.60	17.5	1.770	-.087	BIS(TRINITROETHOXY)METHANE
508040700	2.05	1.27	16.7	1.665	-.120	N-(2-PROPYL) TRINITROACETAMIDE
604061700	.85	1.70	16.6	1.734	-.013	1,1,1,6,6,6-HEXANITRO-3-HEXYNE
604061600	1.18	1.44	17.0	1.830	-.021	BIS(TRINITROETHYL) OXALATE
606051201	1.24	1.39	16.9	1.731	-.025	FLUORODINITROETHYL TRINITROBUTYRATE
606051201	1.11	1.34	16.9	1.726	-.030	TRINITROETHYL FLUORODINITROBUTYRATE
606051200	1.23	1.69	16.8	1.774	-.029	1,1,1,6,6,6-HEXANITRO-3-HEXYNE
606061400	1.26	1.55	17.1	1.783	-.003	TRINITROETHYL 4,4,4-TRINITROBUTANOATE (TNETB)
606061400	1.11	1.45	17.2	1.750	-.073	BIS(TRINITROETHYL)OXAMIDE
606092201	1.18	1.54	16.6	1.736	-.000	TRIS(TRINITROETHYL)PHOSPHATE
607051300	1.18	1.40	17.0	1.620	-.114	TRINITROETHYL 2,2-DINITROPROPYL CARBONATE
607071300	1.26	1.56	17.1	1.754	-.012	N-(TRINITROETHYL)-4,4,4-TRINITROBUTYRAMIDE
607091400	1.30	1.40	17.4	1.840	-.016	1,5-BIS(TRINITROETHYL)BIURF
608061401	1.26	1.43	16.0	1.761	-.020	BIS(TRINITROPROPYL) SULFONE
610040700	2.04	1.20	15.6	1.442	-.077	N-(1-BUTYL)TRINITROACETANIDE
707092100	.83	1.63	17.4	1.800	-.091	TRIS(TRINITROETHYL) ORTHOFORMATE
708061300	1.53	1.55	16.6	1.707	-.005	1,1,1,7,7,7-HEXANITRO-4-HEPTANONE
708081400	1.26	1.63	16.9	1.813	-.024	N-(TRINITROETHYL)-3,3,5,5-TETRANITROPIPERIDINE
708081600	1.43	1.30	17.2	1.696	-.097	METHYLENE BIS(TRINITROETHYL CARBAMATE)
709051200	2.18	1.41	16.4	1.690	-.026	2,2-DINITROPROPYL TRINITROBUTYRATE
709051200	1.85	1.41	16.4	1.680	-.054	TRINITROETHYL 4,4-DINITROVALERATE
710081300	1.37	1.45	16.9	1.718	-.006	BIS(TRINITROPROPYL)UREA
710081300	1.28	1.45	16.9	1.661	-.151	BIS(1,1,1-TRINITRO-2-PROPYL)UREA
806061400	1.15	1.36	16.5	1.722	-.045	ATS(TRINITROETHYL) FUMARATE
807092200	.78	1.55	17.2	1.780	-.049	TRINITROETHYL BIS(TRINITROETHOXY)ACETATE
808040801	2.08	.94	17.0	1.640	-.024	N-(TRINITROETHYL)HEPTANESULFONAMIDE
808061500	1.48	1.40	16.5	1.720	-.002	TRINITROBUTYRIC ANHYDRIDE
808061600	1.54	1.35	16.6	1.687	-.052	BIS(TRINITROETHYL) SUCCINATE
810081400	1.65	1.36	16.6	1.692	-.018	N,NP-ATS(1,1,1-TRINITROPROPYL)OXAMIDE
810081400	1.46	1.54	16.6	1.707	-.030	N-(TRINITROPROPYL)-1,3,5,5-TETRANITROPIPERIDINE
811051200	2.08	1.35	16.1	1.690	-.078	2,2-DINITROBUTYL 4,4,4-TRINITROBUTANOATE
811051200	2.14	1.35	16.1	1.690	-.058	TRINITROETHYL 4,4-DINITROBUTANOATE
807038400	2.35	1.80	13.9	1.604	-.030	TRINITROETHYL SALICYLATE
808122400	1.30	1.64	17.3	1.840	-.035	TRINITROETHYL ORTHOCARBONATE (TNOFC)

TABLE 3. (continued)

C-N-N-O-X	I.S.	NO ₂	NM ^{1/2}	ρ_0	$\Delta\rho$	
909050700	2.85	1.00	13.4	1.587	-.887	TRINITROETHYL PHENYL UREA
910040001	2.11	.90	12.7	1.625	.020	N-(TRINITROETHYL)-P-TOLUENESULFONAMIDE
912041700	1.37	1.26	14.7	1.496	.177	PENTAFRUITRITOLYTRINITRATE TRINITROBUTYRATE
912041400	2.05	1.32	16.3	1.606	.625	METHYLENE BIS(TRINITROBUTYRAMIDE)
912121000	1.15	1.56	17.1	1.901	.126	1,3,5-TRIS(TRINITROETHYL)-1,3,5-TRIAZACYCLOHEXANE
1009092200	1.15	1.48	16.9	1.795	-.026	BIS(TRINITROETHYL) 2-(TRINITROETHYL)BUTANEDIOATE
1010122000	1.00	1.61	17.4	1.830	-.007	1,1,2,2-TETRAKIS(TRINITROETHOXY)ETHANE
1012061600	2.00	1.27	16.1	1.630	-.812	ETHYLENE BIS(TRINITROBUTYRATE) (NFNA)
1014001900	2.00	1.44	16.2	1.620	-.802	N,N-BIS(2,2-DINITROPROPYL) TRINITROBUTYRAMIDE
1014001000	2.20	1.19	16.4	1.579	-.874	BUTAN-1,4-DIOL BIS(4,4,4-TRINITRO-2-AZABUTANOATE)
1014101000	1.30	1.51	16.5	1.603	-.009	1,3-BIS(TRINITROPROPYL)-5,5-DINITROHEXAHYDRO-1,3-DIAZINE
1112042000	1.70	1.39	16.4	1.604	-.816	2,2-DINITROPROPYLENEGLYCOL BIS(TRINITROBUTYRATE)
1117002000	1.83	1.59	16.4	1.710	.010	BIS(TRINITROETHYL) 4,4-DINITROHEPTANEDIOATE
1200061600	1.44	1.22	15.0	1.619	-.897	BIS(TRINITROETHYL)PHTHALATE
1217061600	1.91	1.21	15.3	1.690	.097	BUTYNE-1,4-DIOL BIS(TRINITROBUTYRATE)
1218121000	1.30	1.46	16.4	1.657	-.807	1,3,5-TRIS(TRINITROPROPYL)-1,3,5-TRIAZACYCLOHEXANE
1311092100	1.20	1.47	15.9	1.620	-.124	TRIS(TRINITROETHYL) ORTHOBENZOATE
1516122000	1.51	1.44	16.5	1.750	.032	BIS(TRINITROETHYL) 4,4,6,6,8,8-HEXANITROUNDECANEDIOATE

*SEE FOOTNOTE TO TABLE 1

Following Kamlet's arguments^{2,3}, impact sensitivities are plotted as $\log_{10}(\text{50\% height})$. Crystal densities were determined by flotation or x-ray diffraction. N and M were calculated according to Kamlet⁵, using the CO_2 arbitrary as the basis for determining the detonation stoichiometry, except that HF was added as the first product in C, H, N, O, F compounds, and that N as used herein represents the number of moles of gas per 100g of explosive.

COMPUTATIONAL TECHNIQUES

All calculations, data handling and plotting for this study were performed with the CDC 6500 at the Naval Surface Weapons Center, White Oak, using an expanded version of the code, DENSTY, used to develop our method of "normal" density estimation⁸. This code produces and uses a data base consisting of packed, variable length compound records containing the number of words in the record, a reference number, sort code, the density, melting point, impact sensitivity (stored as \log_{10} 50% height), class designation, molecular contents (atom types and number of nitro groups), and text (name of the compound). For this study, the class designations used were nitramines, aromatics and aliphatics. Between runs, the data base was stored on magnetic tape as a file containing 1000 word physical records.

As this data base file is read by DENSTY, the calculated "normal" density, number of nitro groups per 100g ($\text{NO}_2\#$), moles of detonation gas per 100g (N), and $\text{NM}^{1/2}$ where M is the average molecular weight of product gases are calculated for each compound and stored in the computer memory along with the data from the file. The density is calculated as previously described⁸.

The PLOTR subroutine of the DENSTY code can be called to plot (using the line printer) any two of these quantities stored in the computer core (Fig. 1-18). In these plots a letter denotes a single data point; a O indicates multiple points. In like manner, subroutine TRENDR can be called to calculate a two parameter, slope-intercept least-squares line between any two quantities. Weighting schemes can be applied to the data for determination of these line parameters; and the lines can be included in subsequent plots as shown in Fig. 1-18. TRENDR also calculates two types of correlation coefficients between the unweighted data as given in Table 4. The "least-squares" correlation coefficient is calculated with the following formula:

$$\text{LSCC} = \frac{n \sum X_i Y_i - \sum X_i \sum Y_i}{\sqrt{n \sum X_i^2 - (\sum X_i)^2} \sqrt{n \sum Y_i^2 - (\sum Y_i)^2}}$$

²See Reference 2 on page 2.

³See Reference 3 on page 2.

⁵See Reference 5 on page 2.

⁸Cichra, D. A., Holden, J. R., and Dickinson, C., NSWC TR 79-273, Feb 1980.

where n is the number of compounds and X_i and Y_i are the values of the designated quantities for (compound) i . Possible values of LSCC range from +1.000 for a perfect direct linear correlation down to -1.000 for a perfect inverse linear correlation. A value of 0.000 means no correlation - perfectly random values.

The "rank difference" correlation coefficient does not depend upon a linear relationship, but measures the extent to which one quantity increases or decreases as the second specified quantity increases. It is given by the following formula:

$$RDCC = 1 - \frac{6 \sum (R_i - S_i)^2}{n(n^2 - 1)}$$

where n is the number of compounds and R_i and S_i are sorted list locations of the two designated quantities for compound i - that is, 1 for the largest value down to n for the smallest value of the quantity. Values of RDCC range from +1.000 if the sort orders of the two quantities are identical down to -1.000 if the sort orders are exactly reversed - the compound with the largest value of the first quantity has the smallest value of the second quantity, etc..

Another subroutine of the expanded DENSITY code, LSTSQR, can be called to perform a multiparameter least-squares fit to an equation of the following type:

$$Y = C_1X_1 + C_2X_2 + C_3X_3 + \dots$$

where Y , X_1 , X_2 ,.... are measured or calculated quantities stored in the computer core associated with each compound of the data base. One of the X quantities can be specified as unity so that the relation is of the following type:

$$Y = C_1 + C_2X_2 + C_3X_3 + \dots$$

This option was used to determine the coefficients of the multiparameter equations relating $\log_{10}h_{50}$ to $NO_2\#$, $NM^{1/2}$ and ρ_0 given later in this report (p.13,14,15). A calculated value of Y (in this case, $\log_{10}h_{50}$) determined with the derived values of C_1 , C_2 , etc. is stored in the computer core for each compound. These calculated values of $\log_{10}h_{50}$ were then compared to the measured values by subroutine TRENDR to determine the correlation coefficients given for each relationship.

RESULTS AND DISCUSSION

The first correlations investigated were between impact sensitivity (as $\log_{10} h_{50}$) and N, the number of moles of detonation gas per 100g of explosive as calculated by the CO_2 arbitrary. These plots showed very low least squares correlation coefficients (0.26 for the nitramines, 0.05 for the nitroaromatics, and 0.19 for the nitroaliphatic compounds), indicating complete lack of correlation between these two parameters. It was tempting to conclude from this observation that optimization of N might be a mechanism for increasing performance but not sensitivity, until it was realized that N is not an independent variable because in a system restricted to C, H, N, O, F it is coupled to M via the CO_2 arbitrary.

Kamlet has shown that, for C, H, N, O, F compounds, detonation pressure, detonation velocity, cylinder wall energies and velocities, and a number of other explosive effects⁴ are a function of the parameter \mathcal{R} which is defined by the expression $\mathcal{R} = \text{NM}^{1/2}\text{Q}^{1/2}$. This appears to be the only instance where a direct and quantitative relationship has been established between the amount and character of the detonation gas and explosive performance. Therefore, the quantity, $\text{NM}^{1/2}$, appeared to be the most reasonable function with which to study the relationships between detonation gas and other explosive phenomena. Our next series of plots were, therefore, of impact sensitivity vs. $\text{NM}^{1/2}$. These plots are shown in Fig. 1-3. In interpreting these and the other impact sensitivity plots, the statement made about the consistency of the data should be noted. Second, since impact sensitivity depends on many other parameters, only broad trends can reasonably be expected in single parameter correlations unless this parameter is dominant. The initial objective here was not to obtain an optimized multiparameter description of impact sensitivity but rather to discern effects of single molecular properties on it. Thirdly, since impact sensitivity is a strong function of oxygen balance, it was important to determine the relationship, if any, between $\text{NM}^{1/2}$ and oxygen balance. For the sake of convenience, we have used the molar number of nitro groups per 100g of explosive ($\text{NO}_2\#$)* as an approximate measure of oxygen balance, and the dependence of impact sensitivity on this parameter for the three classes of

⁴See Reference 4 on page 2 .

$$*\text{NO}_2\# = \frac{\text{\# of Nitro groups per molecule} \times 100}{\text{molecular weight}}$$

nitro compounds studied here is shown in Figures 4-6. It is seen that the relationship is qualitatively identical to that found by Kamlet for impact sensitivity and oxygen balance: in each case, the $\log_{10} h_{50}$ decreases linearly with increasing $\text{NO}_2\#$, with almost identical least squares correlation coefficients (Table 4). The plots of $\text{NM}^{1/2}$ vs. $\text{NO}_2\#$ are shown in Figures 7-9.

Comparison of Figures 1-3 with Figures 7-9 shows a parallel between the I.S./ $\text{NM}^{1/2}$ and $\text{NM}^{1/2}/\text{NO}_2\#$ plots: if there is a trend in the $\text{NM}^{1/2}$ vs. $\text{NO}_2\#$ plot, there is also one in the I.S. vs. $\text{NM}^{1/2}$ plot. This is clearly the case for the nitroaliphatics; a lesser trend is noted in both plots for the nitramines, and no trend is apparent in either plot for the aromatic compounds. This visually detectable parallel is also apparent in the least squares correlation coefficients (Table 4), which increase in the order, aromatics < nitramines < nitroaliphatics for both series of plots. We interpret these two sets of plots and the correspondence in correlation coefficients to mean that proportionality between I.S. and $\text{NM}^{1/2}$ is observed only when $\text{NM}^{1/2}$ is a function of $\text{NO}_2\#$, and that this proportionality is basically one between I.S. and $\text{NO}_2\#$. In other words, if $\text{NM}^{1/2}$ could be varied with no change of $\text{NO}_2\#$, there would be no effect on impact sensitivity. Whether this finding has utility in the design of new IHPE molecules has not yet been ascertained.

The above conclusion is substantiated by the results of simultaneous 2-parameter least squares fits of impact sensitivity to $\text{NO}_2\#$ and $\text{NM}^{1/2}$ for the three classes of compounds. The equations and coefficients are as follows:

Nitramines

$$\log_{10} h_{50} = 4.512 - 1.224(\text{NO}_2\#) - 0.085(\text{NM}^{1/2})$$

correlation coefficient 0.67

Aromatics

$$\log_{10} h_{50} = 3.764 - 1.739(\text{NO}_2\#) + 0.021(\text{NM}^{1/2})$$

correlation coefficient 0.62

Aliphatics

$$\log_{10} h_{50} = 4.636 - 0.809(\text{NO}_2\#) - 0.123(\text{NM}^{1/2})$$

correlation coefficient 0.68

Note that the correlation coefficients are not significantly higher than those listed in Table 4 for the plots of I.S. against $\text{NO}_2\#$ alone (0.65, 0.62, and 0.65). Therefore, treating $\text{NM}^{1/2}$ as an additional "independent" variable does not affect the observed relationship between I.S. and $\text{NO}_2\#$.

The next sets of plots shown in Figures 10-12 and 13-15 are the corresponding correlations of impact sensitivity with ρ_0 , and of ρ_0 with $\text{NO}_2\%$. Again, as in the case of the $\text{NM}^{1/2}$ plots, there is a parallel between the two series; i.e. significant correlation for the nitramines and nitroaliphatics but no correlation for the nitroaromatics. Again, this visual analysis is confirmed by the least squares correlation coefficients (Table 4). Using an analogous interpretation, one concludes that impact sensitivity is only a function of ρ_0 to the extent that ρ_0 is dependent on the NO_2 content of the molecule. However, the results from 2-parameter least squares fits of impact sensitivity to $\text{NO}_2\%$ and ρ_0 are not as clear in their implications:

Nitramines

$$\log_{10} h_{50} = 5.855 - 0.916(\text{NO}_2\%) - 1.853(\rho_0)$$

correlation coefficient 0.79

Aromatics

$$\log_{10} h_{50} = 4.403 - 1.704(\text{NO}_2\%) - 0.222(\rho_0)$$

correlation coefficient 0.62

Aliphatics

$$\log_{10} h_{50} = 5.480 - 0.861(\text{NO}_2\%) - 1.624(\rho_0)$$

correlation coefficient 0.74

Adding ρ_0 as a second "independent" variable has no effect on the correlation coefficient between I.S. and $\text{NO}_2\%$ for the aromatic compounds. However, this action increases the correlation coefficient for the nitramines from 0.65 to 0.79 and nitroaliphatics from 0.65 to 0.74.

Whether this increase is significant is not clear, but greater caution is required in the interpretation of the I.S. vs ρ_0 plots than for the I.S. vs $\text{NM}^{1/2}$ correlations. Certainly, among the aromatic compounds, no sensitivity penalty is to be expected when performance is maximized by choosing the densest compound at any selected nitro group content. For the other classes of compounds, Figures 10 and 12 indicate that I.S. is, at worst, a linear function of ρ_0 . When performance parameters are functions of a higher power of ρ_0 , as is the case in metal acceleration, high density compounds will permit favorable performance sensitivity trade-offs in these classes as well.

Holden⁸ has recently developed an empirical method for the calculation of crystal densities of nitro compounds from chemical composition and bonding environments of the constituent atoms. This method, because it rests on a large

⁸ See Reference 8 on page 7 .

data base, permits a meaningful identification of compounds with "exceptional densities", i.e., densities that are larger or smaller than the norm for a given chemical composition and molecular structure. It was of interest in the present context to examine the relationship between impact sensitivity and $\Delta\rho$, the difference between observed and calculated density. These plots are shown in Figures 16-18. Both visual analysis and least squares correlation coefficients (Table 4) indicate little correlation and an inverse relationship, if any (tendency toward decreased I.S. with increasing $\Delta\rho$). This observation is substantiated by the following 3-parameter least squares fits of I.S. to $\text{NO}_2\%$, $\text{NM}^{1/2}$ and $\Delta\rho$.

Nitramines

$$\log_{10}h_{50} = 4.409 - 1.181(\text{NO}_2\%) - 0.083(\text{NM}^{1/2}) + 0.713(\Delta\rho)$$

correlation coefficient 0.68

Aromatics

$$\log_{10}h_{50} = 3.655 - 1.639(\text{NO}_2\%) + 0.019(\text{NM}^{1/2}) + 0.560(\Delta\rho)$$

correlation coefficient 0.63

Aliphatics

$$\log_{10}h_{50} = 4.602 - 0.849(\text{NO}_2\%) - 0.116(\text{NM}^{1/2}) + 0.7411(\Delta\rho)$$

correlation coefficient 0.69

As can be seen, the correlation coefficients are only insignificantly higher than those for the I.S. fits to $\text{NO}_2\%$ and $\text{NM}^{1/2}$ (0.67, 0.62 and 0.68).

These results indicate that $\Delta\rho$ does not have a significant effect on impact sensitivity. The positive values of the $\Delta\rho$ coefficients in the least squares equations above suggest that if $\Delta\rho$ has any effect, it is that positive values tend to lower the sensitivity (produce larger values of $\log_{10}h_{50}$). Therefore, explosive performance can be increased with no sensitivity penalty by choosing compounds with exceptionally high densities for their molecular composition; that is compounds with large, positive values of $\Delta\rho$.

A curious feature of the correlations carried out here is the similarity in the variation of the correlation coefficients for the I.S. vs $\text{NM}^{1/2}$ and the I.S. vs ρ_0 plots among the three classes, i.e., significant correlations for the nitramines and nitroaliphatics, but no correlation for the nitroaromatics in both series. Whether this is coincidence or a peculiarity of the set of compounds used in this work is not clear at this point.

It is of interest to examine the structures of those compounds which show the largest positive deviation from the regression lines in the I.S./ ρ_0 and the I.S./ $\text{NM}^{1/2}$ plots, and are thus the least sensitive for a given $\text{NM}^{1/2}$ or ρ_0 . These compounds are listed in Tables 5, 6, and 7. In the aromatic series, because of lack of correlations, these compounds are those with the lowest impact sensitivities, and are the same for both plots. However, it is

noted that even for the nitramines and the nitroaliphatic compounds the same exceptional structures are often present in both the $NM^{1/2}$ and ρ_o plots. In these cases a likely reason is the dependence of both $NM^{1/2}$ and ρ_o on $NO_2^\#$, and indeed many of these compounds are also exceptional in the I.S./ $NO_2^\#$ plots. Beyond this, the structures in the three series of compounds appear to have little else in common. The structures common to the $NM^{1/2}$ and ρ_o plots should represent potential IHPE's and are worthy of further investigation.

SUMMARY AND CONCLUSIONS

Significant positive trends have been observed for correlations of impact sensitivity (I.S.) with $\text{NO}_2\#$, ρ_0 , $\text{NM}^{1/2}$, and of $\text{NO}_2\#$ with ρ_0 and $\text{NM}^{1/2}$ for series of polynitroaliphatic compounds and nitramines. The trends in I.S. with $\text{NM}^{1/2}$ and ρ_0 appear to be caused by the dependence of all three parameters on the $\text{NO}_2\#$. $\Delta\rho$, an increment of exceptional density, is found to be independent of I.S., or may decrease it slightly.

By contrast, in a series of polynitroaromatic compounds, the only correlations exhibiting significant trends are between I.S. and $\text{NO}_2\#$.

The trends observed are in general quite broad. This is believed to be due, in part, to variations in the conditions under which the impact sensitivities were determined. Despite this shortcoming inherent to the data set, a number of tentative conclusions relevant to the design of IHPE's are drawn from the correlations carried out herein, and are offered for consideration:

1. The overriding factor determining both performance in metal acceleration and impact sensitivity is the $\text{NO}_2\#$, or more generally the oxygen balance of the compound.

2. To the extent that $\text{NM}^{1/2}$ and/or ρ_0 can be increased independent of $\text{NO}_2\#$, favorable performance/sensitivity ratios should be possible. This appears most feasible for polynitroaromatic compounds because of a general absence of significant correlations between ρ_0 , $\text{NM}^{1/2}$, and $\text{NO}_2\#$.

3. Other possibilities for increasing performance without paying a penalty in I.S. are compounds with exceptionally high crystal densities, compounds with exceptionally high products $\text{I.S.} \times \text{NM}^{1/2}$ and $\text{I.S.} \times \rho_0$, and possibly compounds with high $\text{NM}^{1/2}$ for a given $\text{NO}_2\#$ (the existence of the latter type of compounds has not been ascertained).

FUTURE PLANS

The remaining important molecular property which undoubtedly affects both I.S. and performance, and which has not been considered here, is the energy of detonation (Q). In future efforts correlations involving this quantity and I.S. will be attempted.

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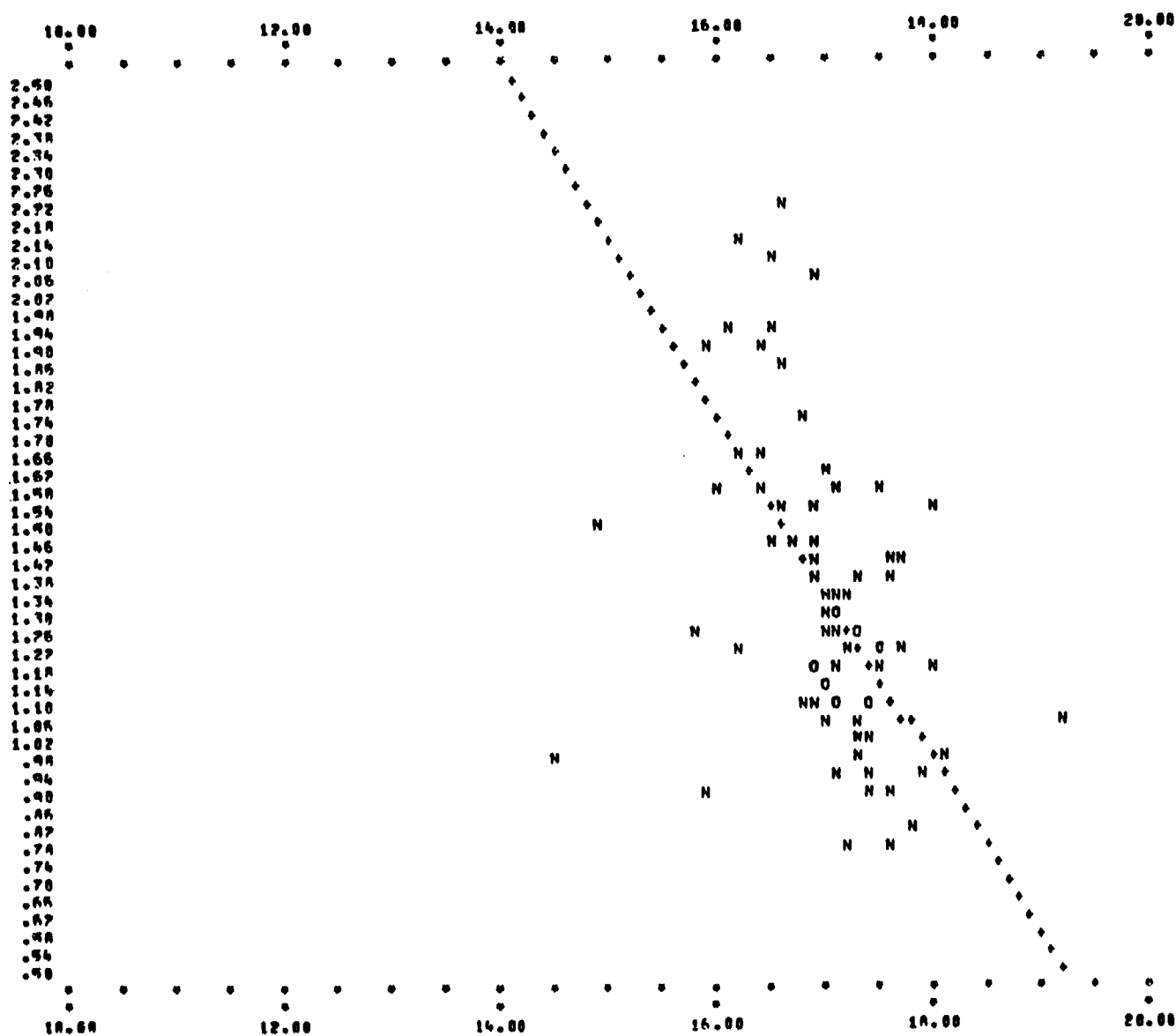
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FIGURE 1. $\log_{10} h_{50} \text{ UP, NM}^{1/2} \text{ ACROSS, NITRAMINES}$

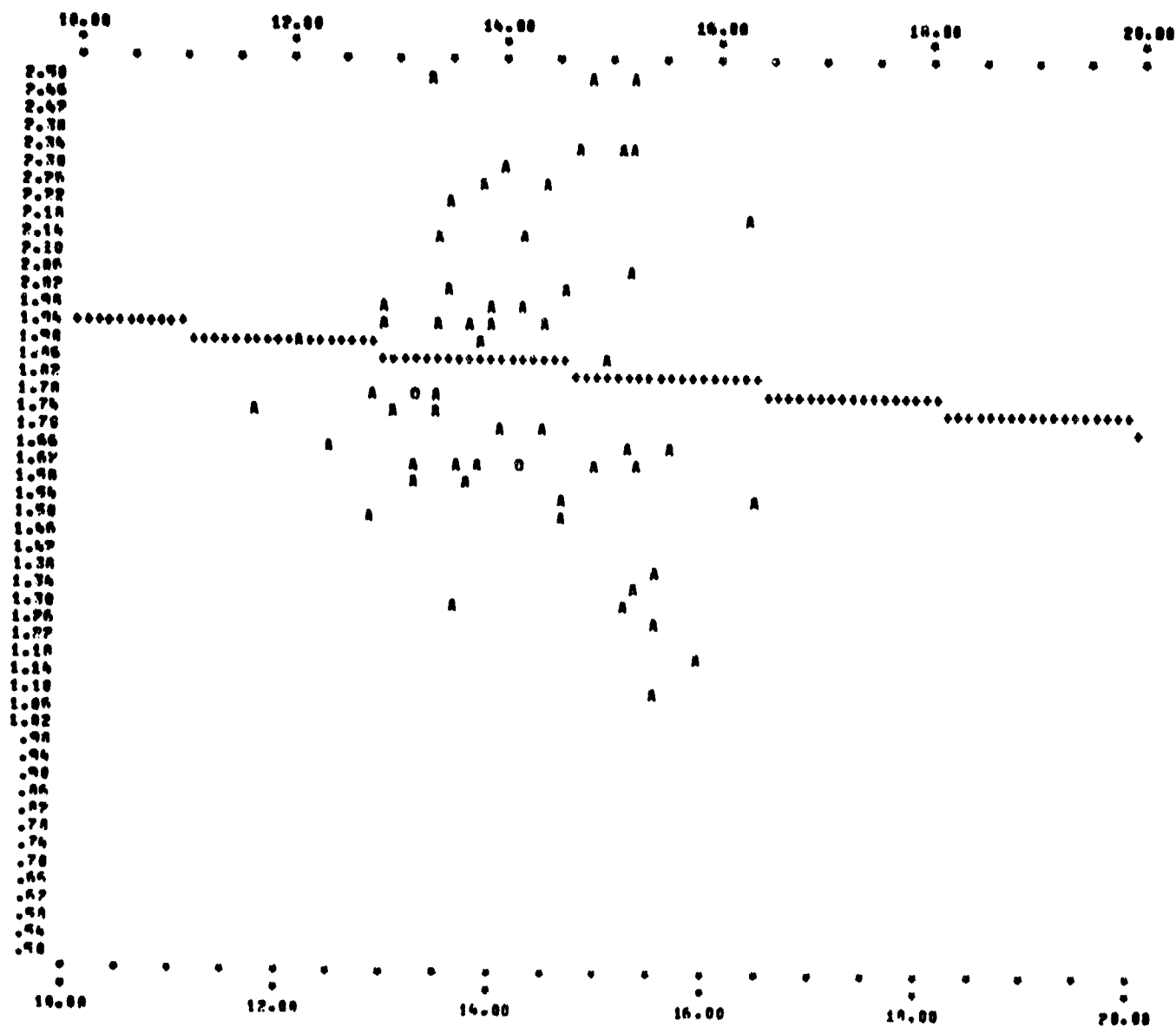


FIGURE 2. $\log_{10} h_{50}$ UP, $NM^{1/2}$ ACROSS, NITROAROMATICS

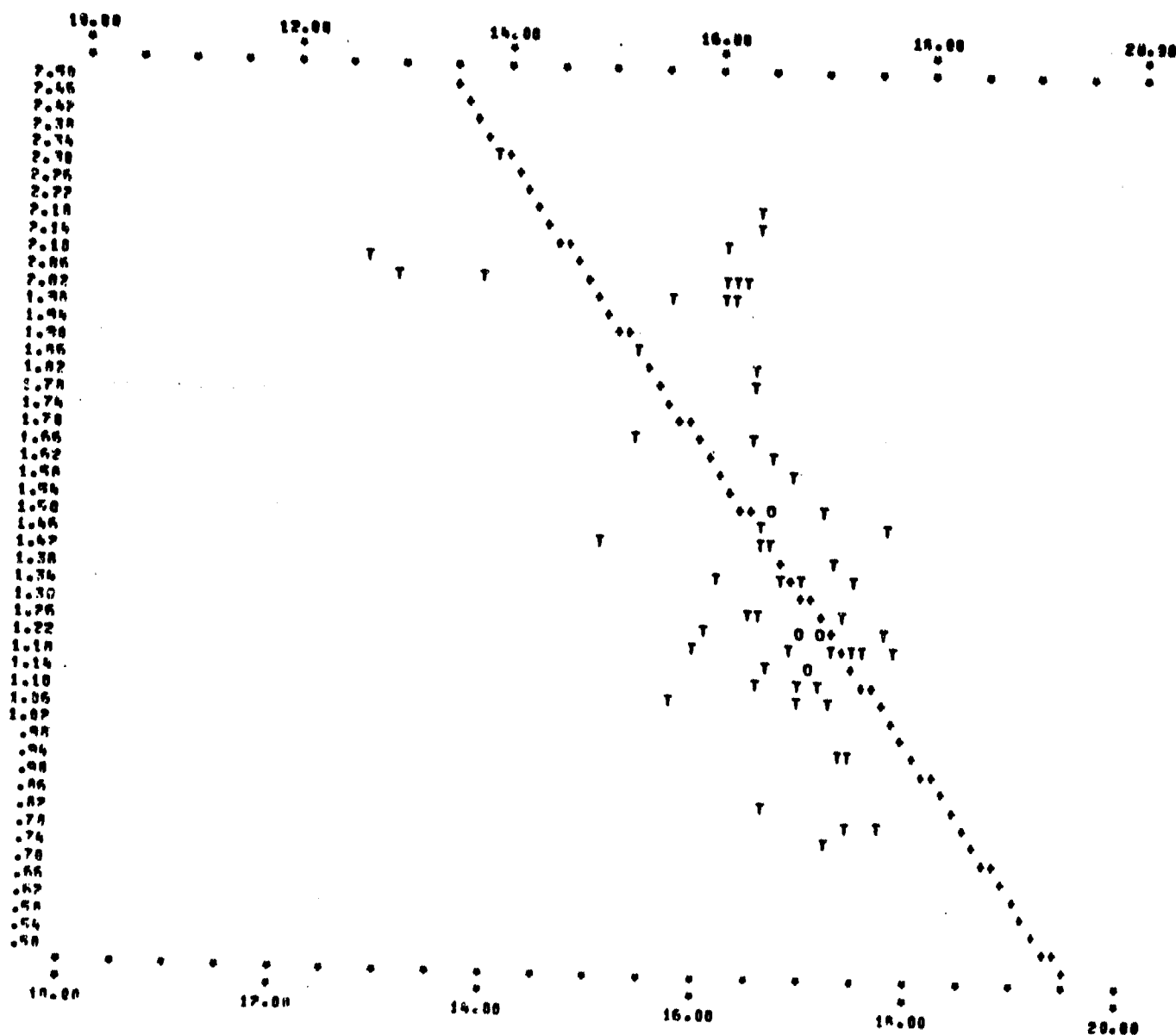


FIGURE 3. $\log_{10} h_{50} \text{ UP, NM}^{1/2} \text{ ACROSS, NITROALIPHATICS}$

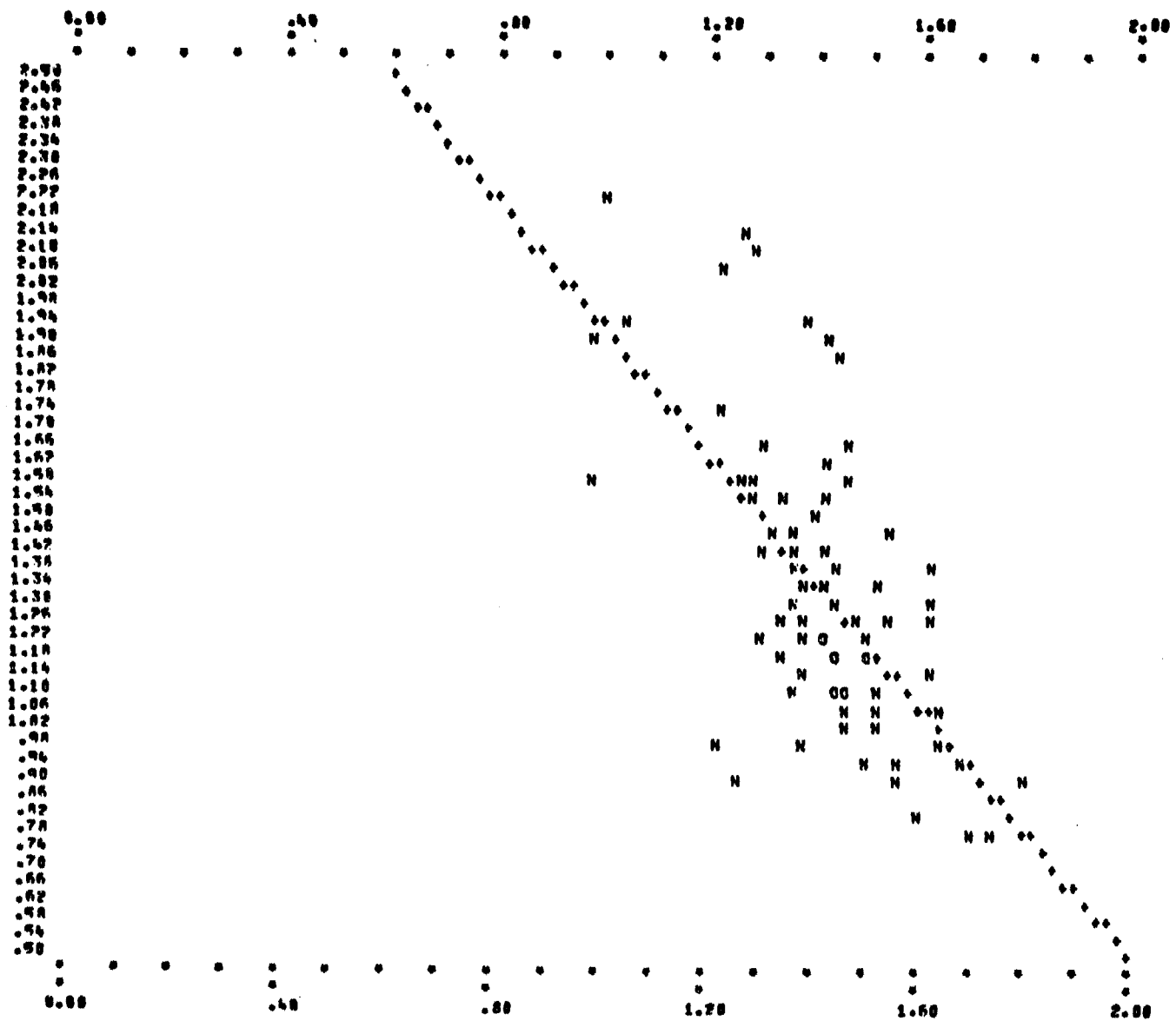


FIGURE 4. $\log_{10} h_{50}$ UP, NO_2 # ACROSS, NITRAMINES

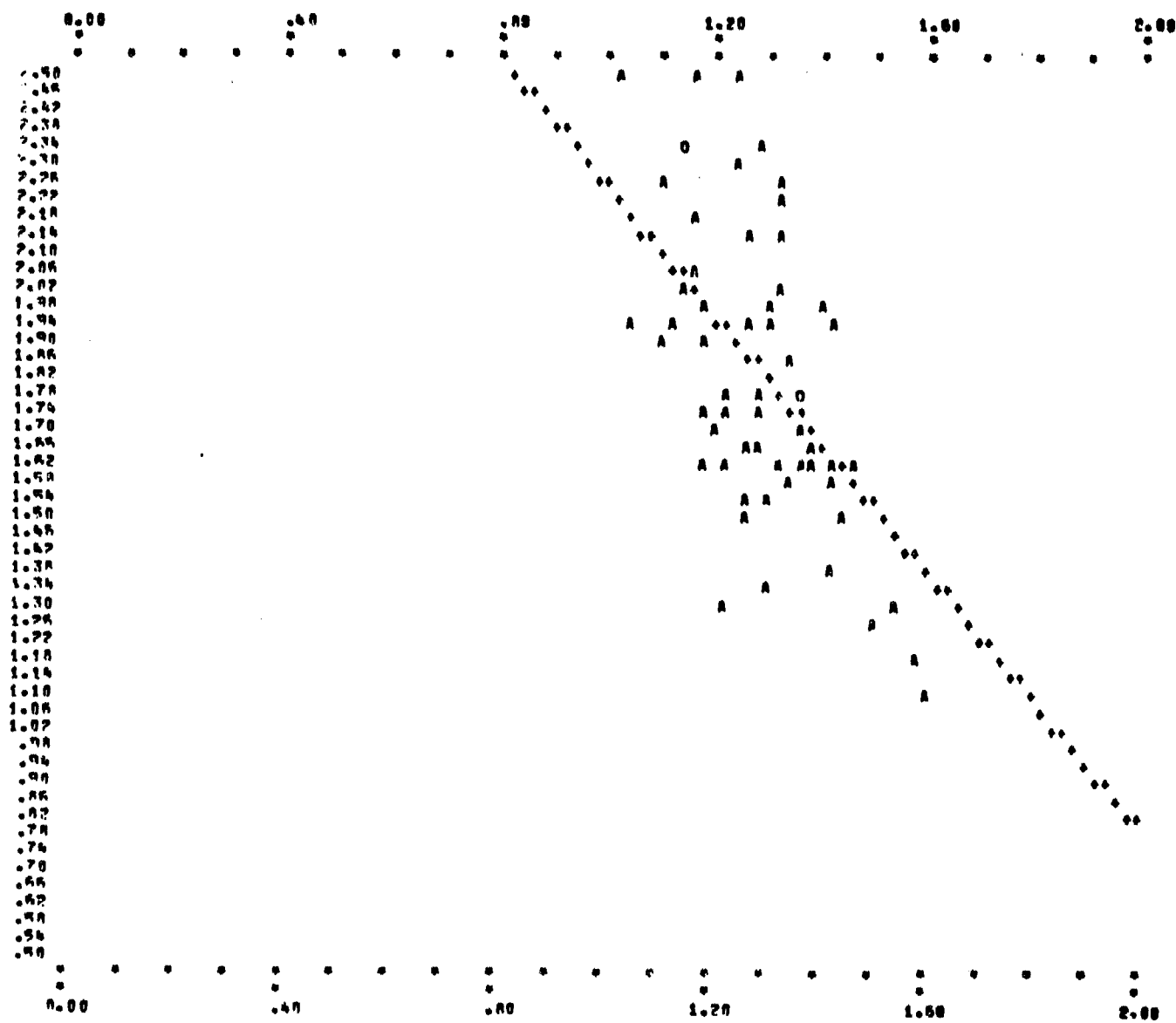
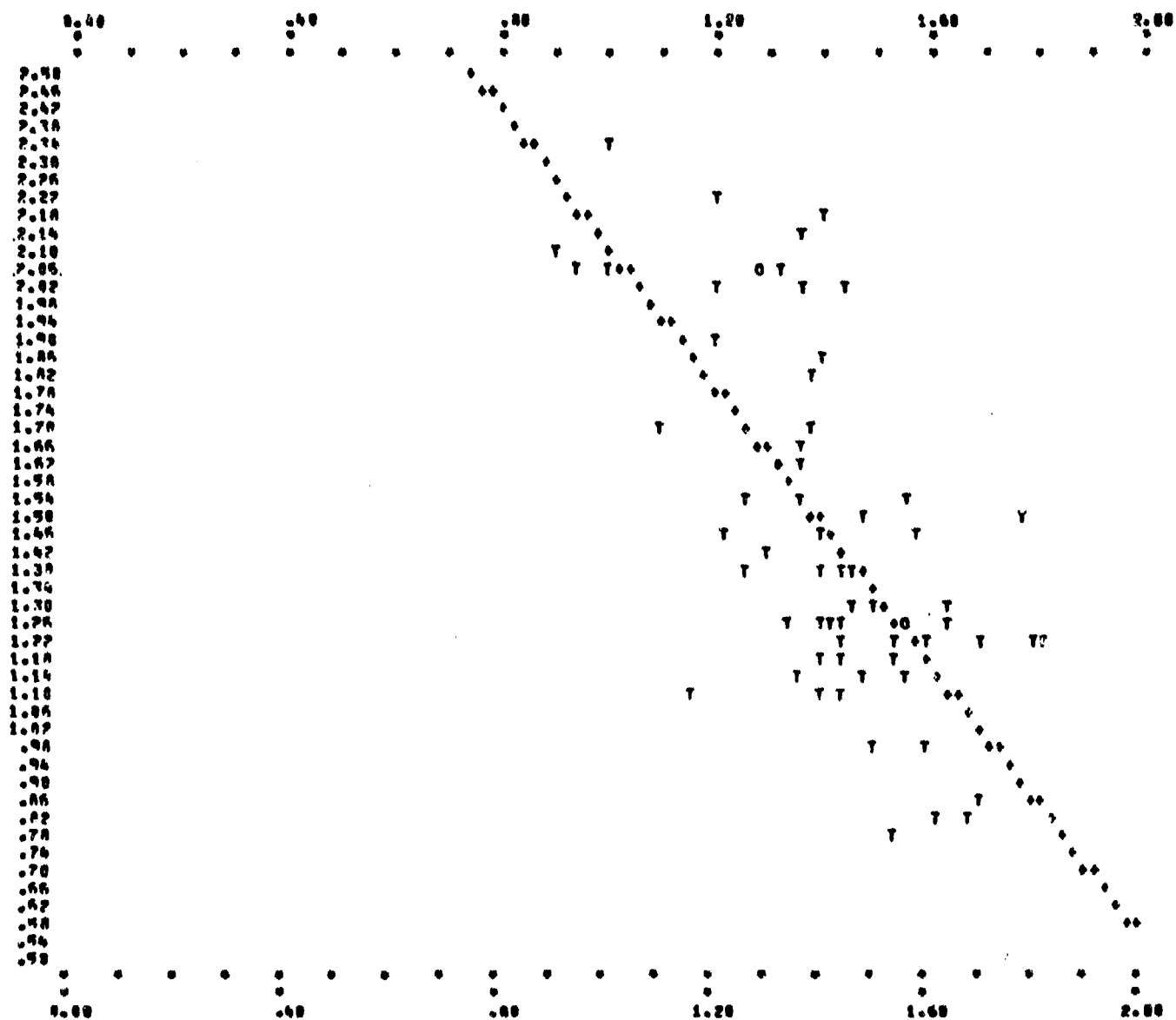


FIGURE 5. $\log_{10} h_{50}$ UP, $\text{NO}_2\#$ ACROSS, NITROAROMATICS

FIGURE 6. $\log_{10} h_{50}$ UP, $\text{NO}_2\#$ ACROSS, NITROALIPHATICS

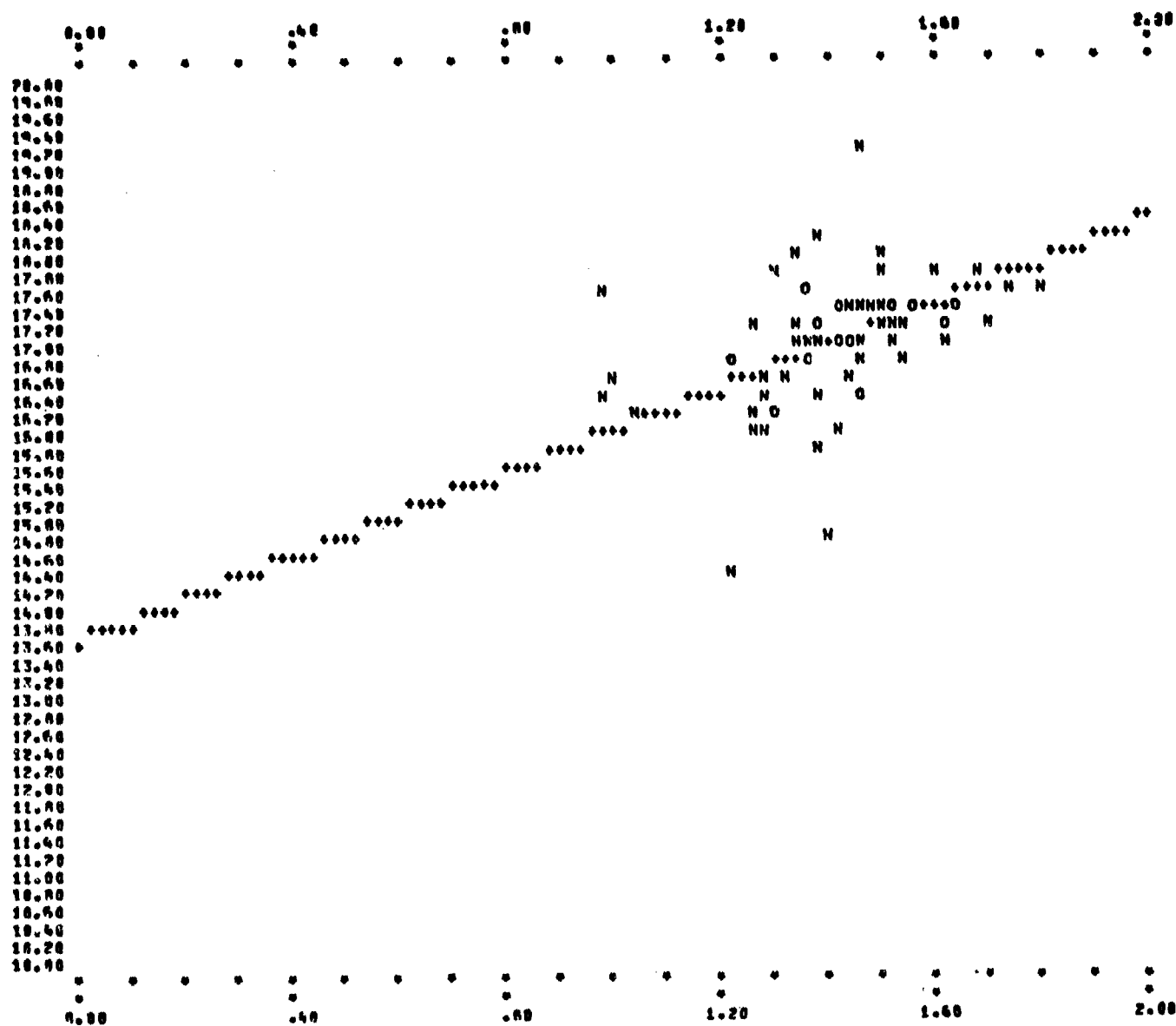
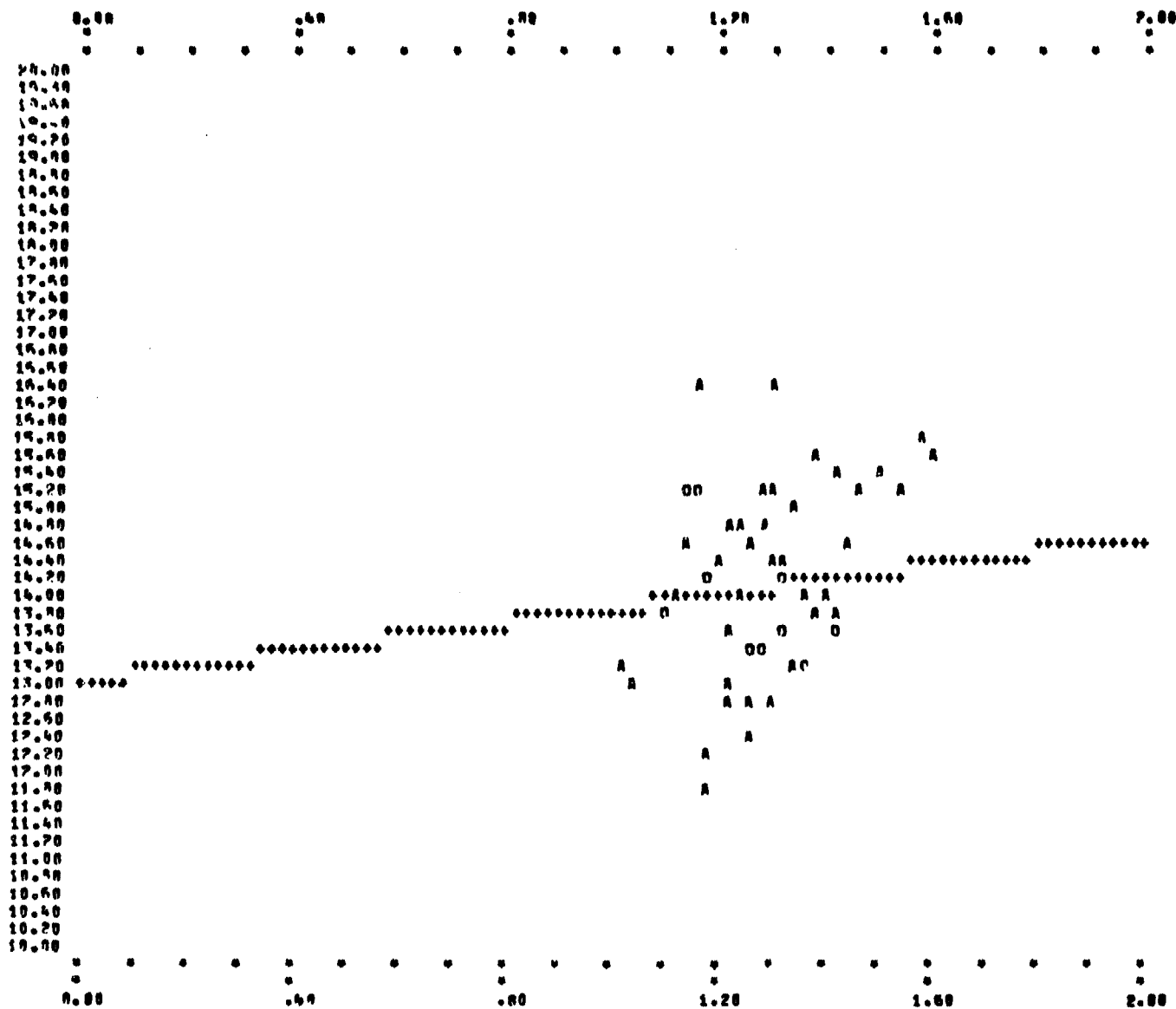


FIGURE 7. $NM^{1/2}$ UP, NO_2 # ACROSS, NITRAMINES

FIGURE 8. $NM^{1/2}$ UP, NO_2 # ACROSS, NITROAROMATICS

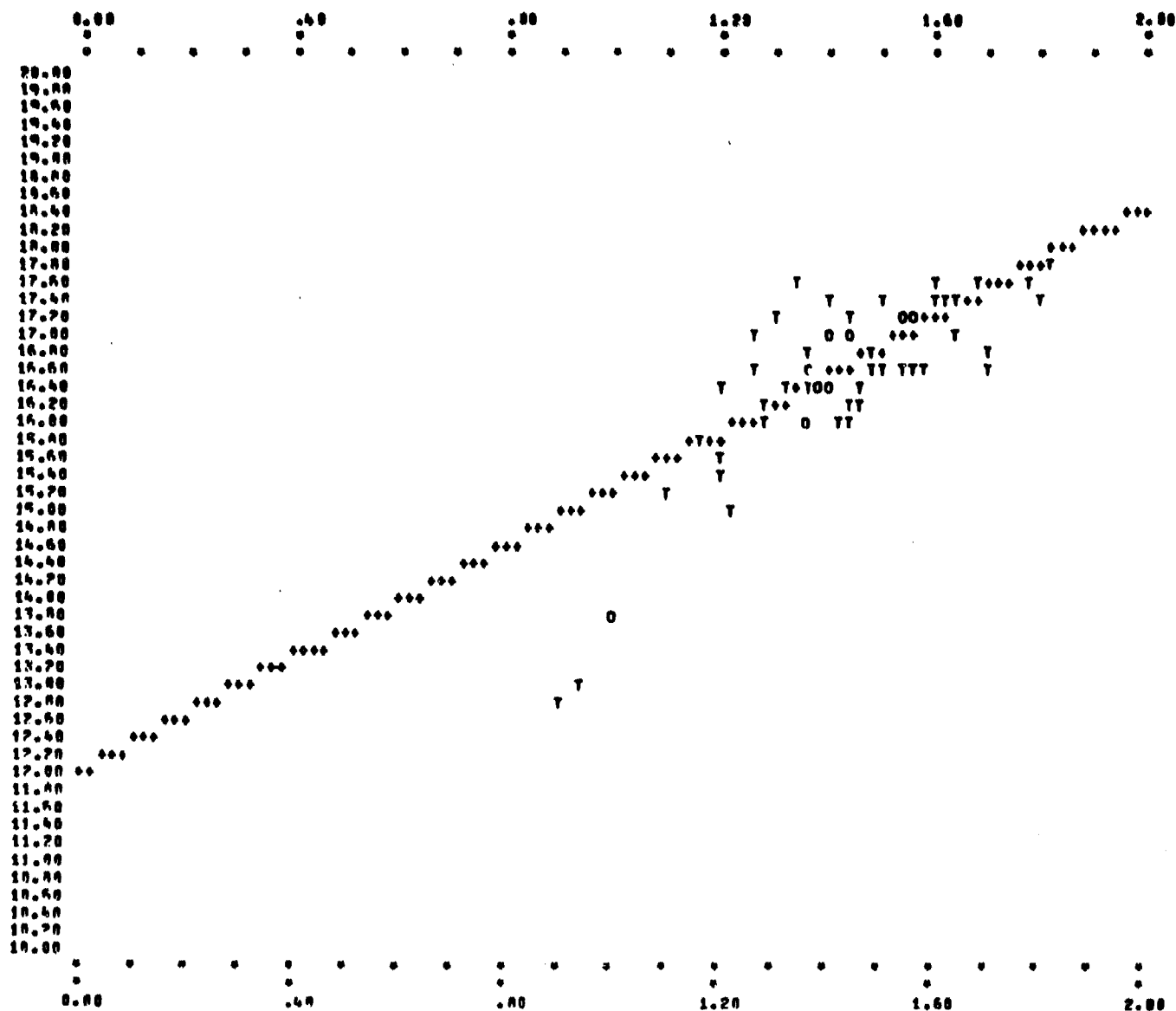


FIGURE 9. $NM^{1/2}$ UP, NO_2 # ACROSS, NITROALIPHATICS

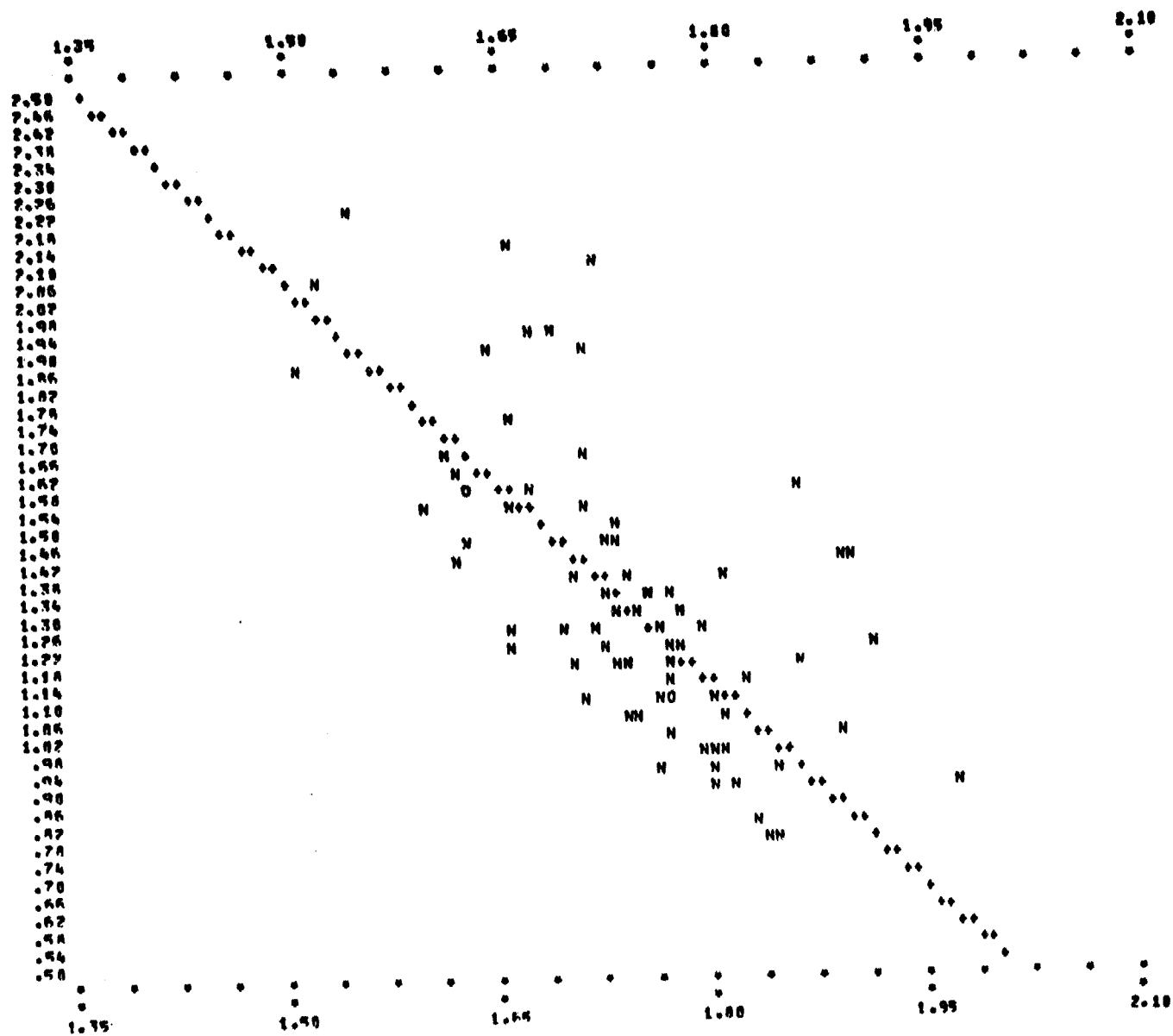


FIGURE 10. $\log_{10} h_{50}$ UP, ρ_o ACROSS, NITRAMINES

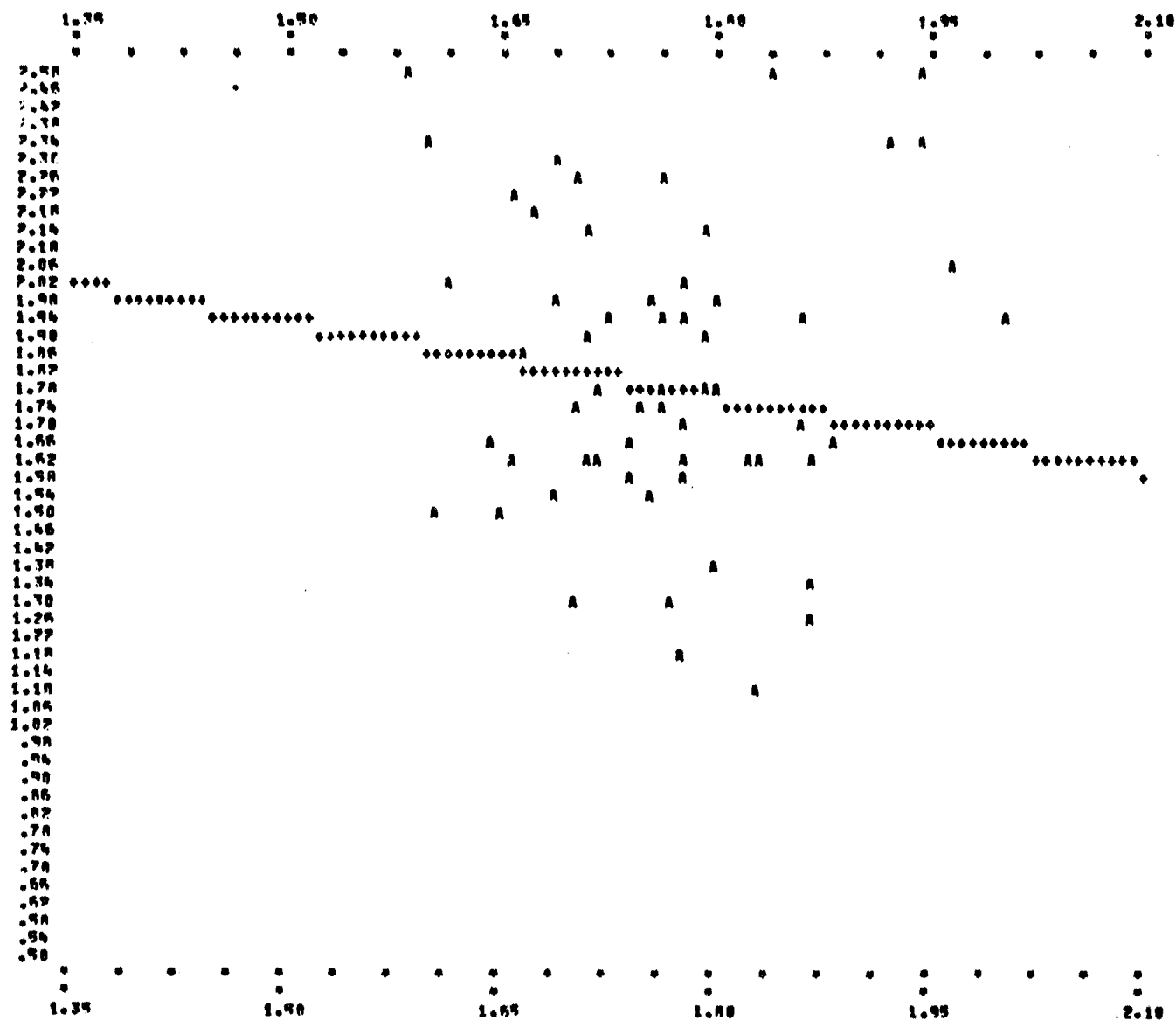
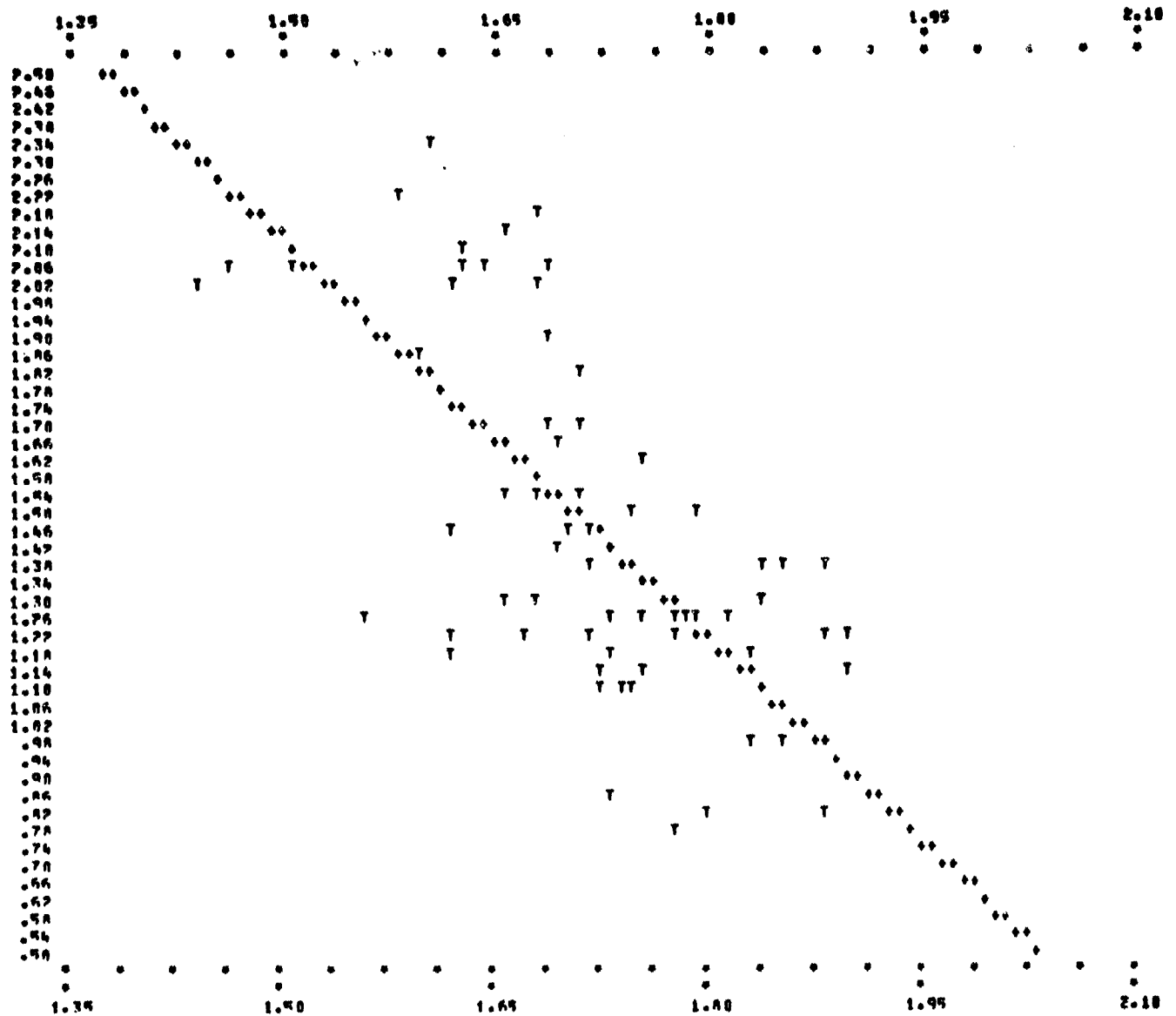


FIGURE 11. $\log_{10} h_{50} \text{ UP}, \rho_o \text{ ACROSS, NITROAROMATICS}$

FIGURE 12. $\log_{10} h_{50} \text{ UP}, \rho_o \text{ ACROSS, NITROALIPHATICS}$

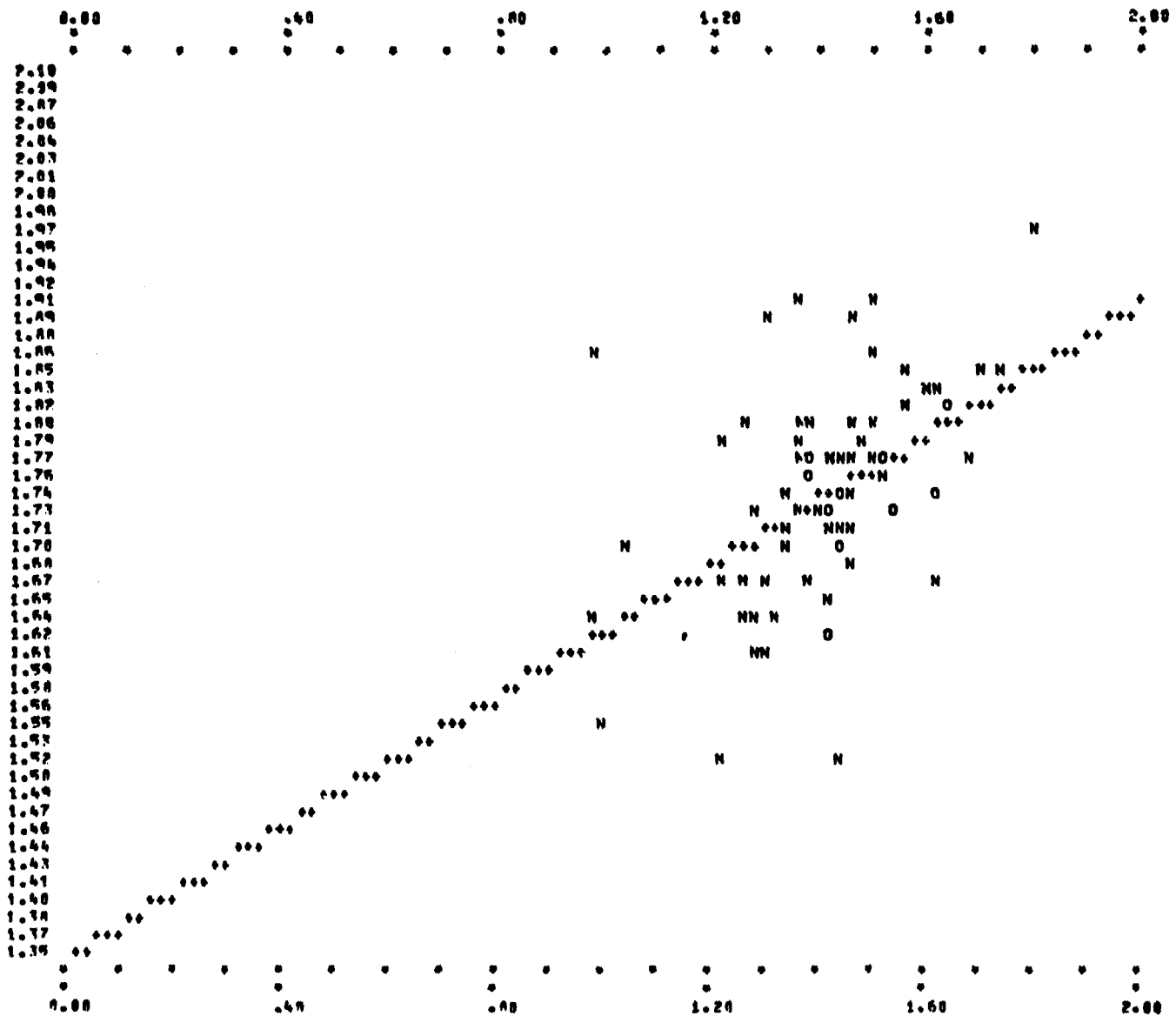
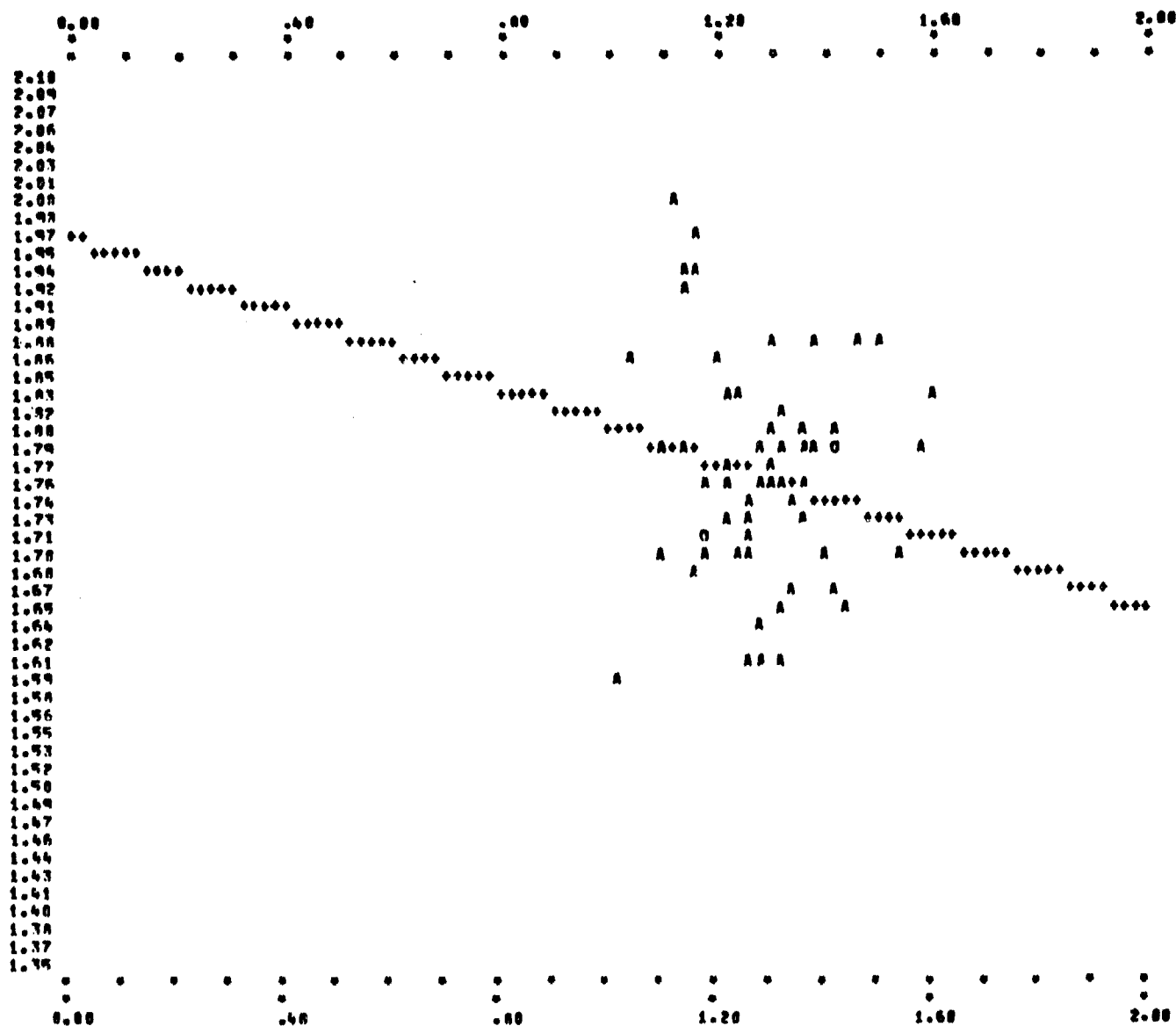
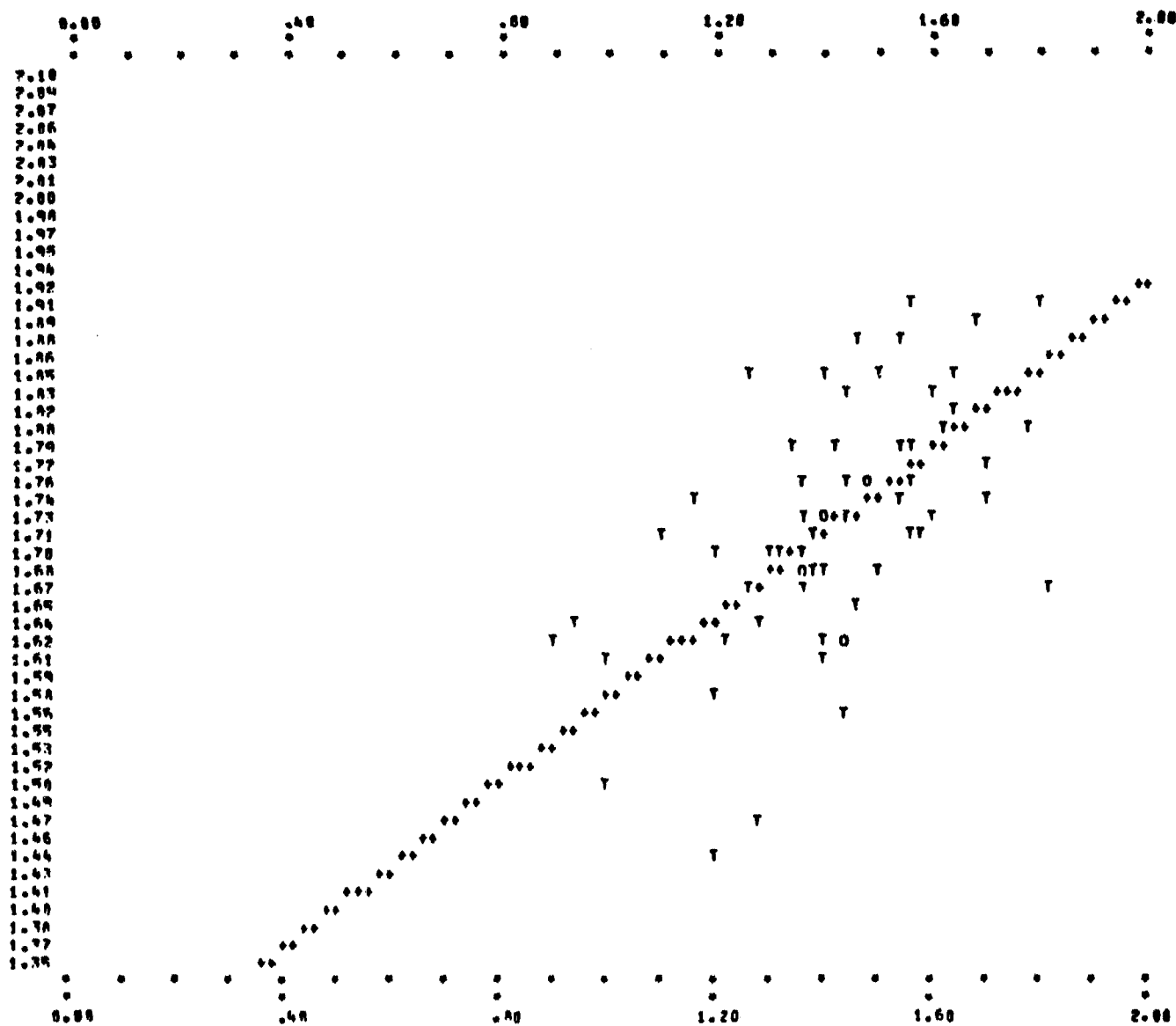
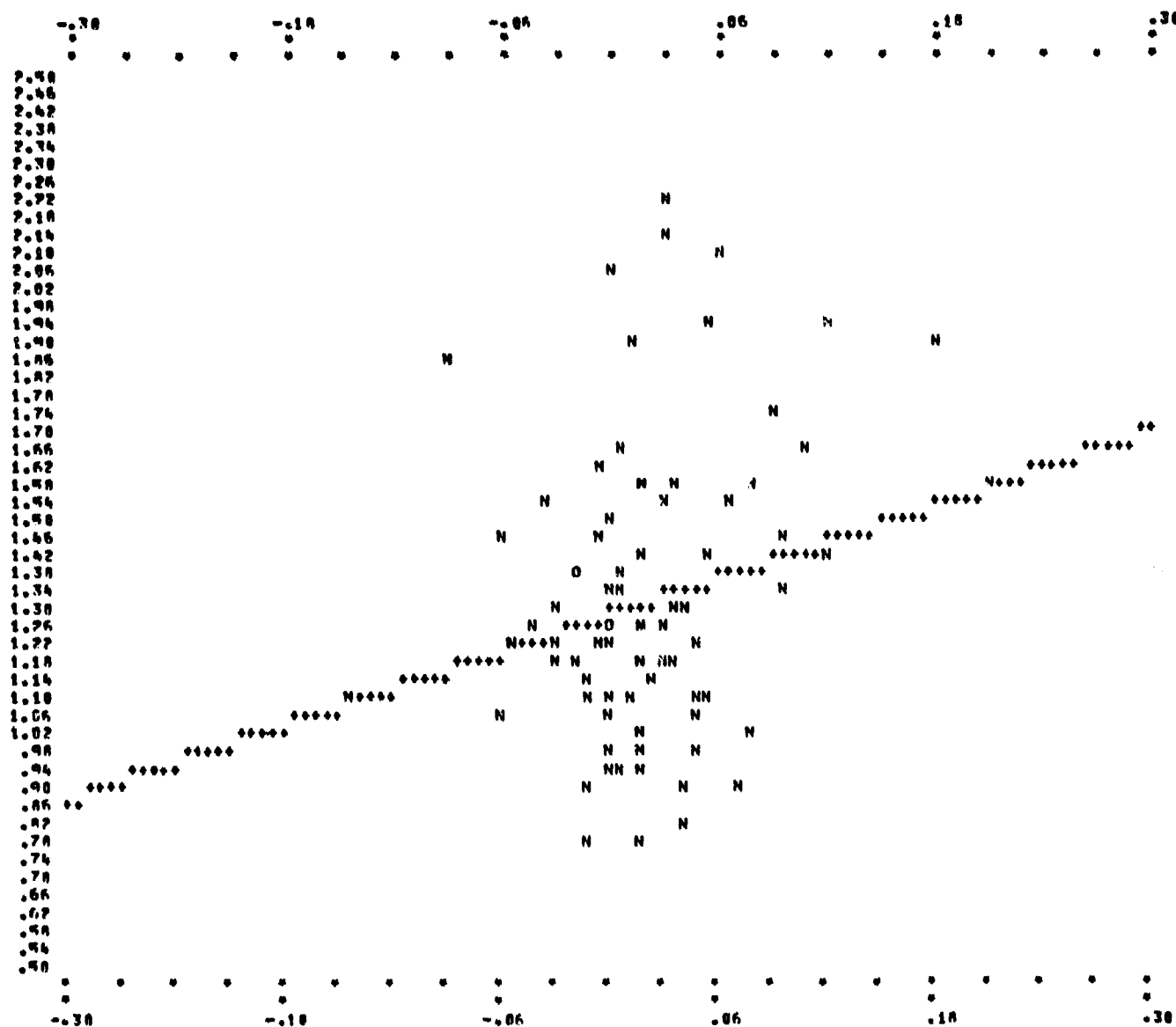
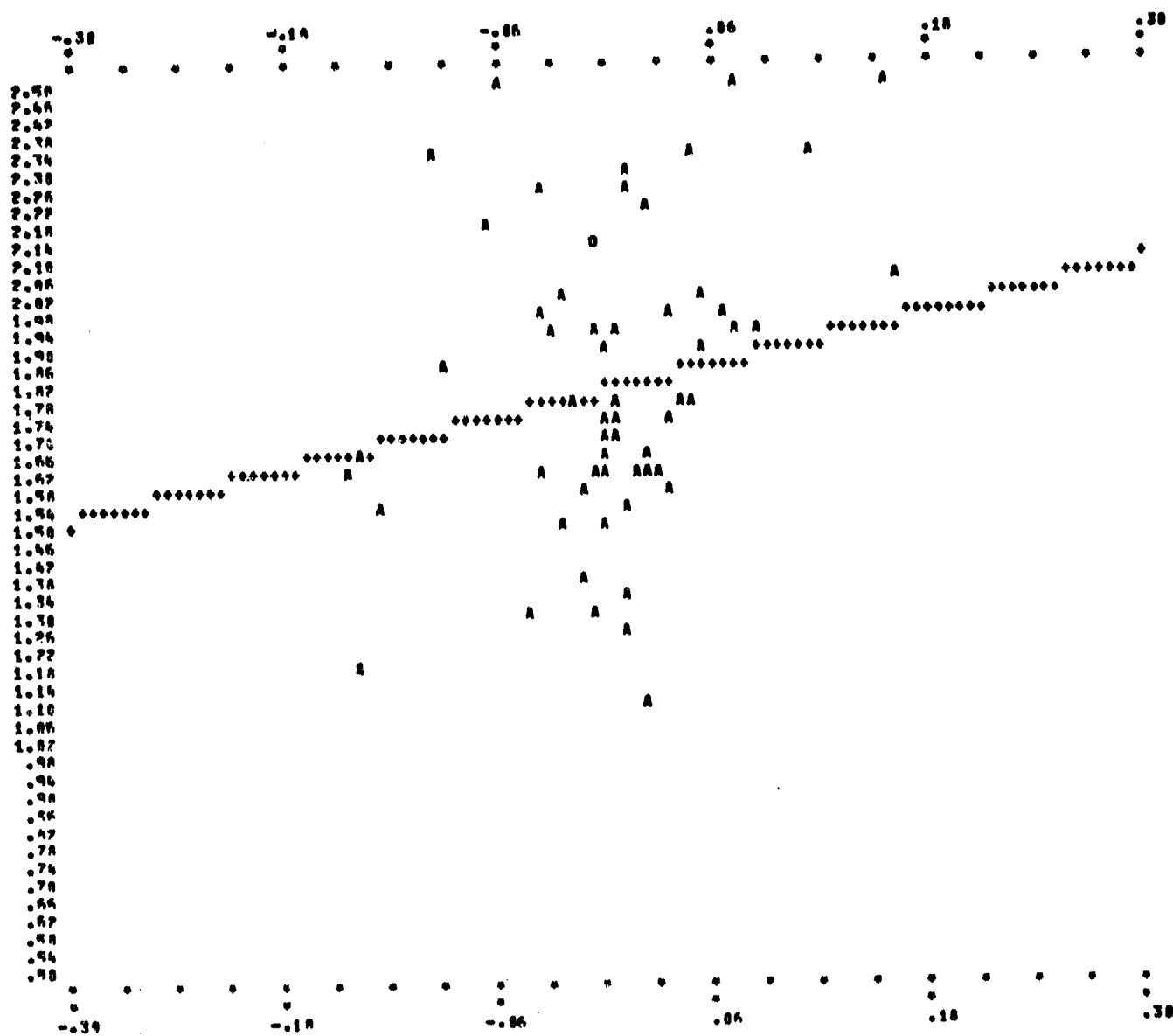


FIGURE 13. Po UP, NO₂ # ACROSS, NITRAMINES

FIGURE 14. p_0 UP, NO_2 # ACROSS, NITROAROMATICS

FIGURE 15. ρ_0 UP, NO₂ # ACROSS, NITROALIPHATICS

FIGURE 16. $\log_{10} h_{50}$ UP, ΔP ACROSS, NITRAMINES

FIGURE 17. log₁₀ h₅₀ UP, Δρ ACROSS, NITROAROMATICS

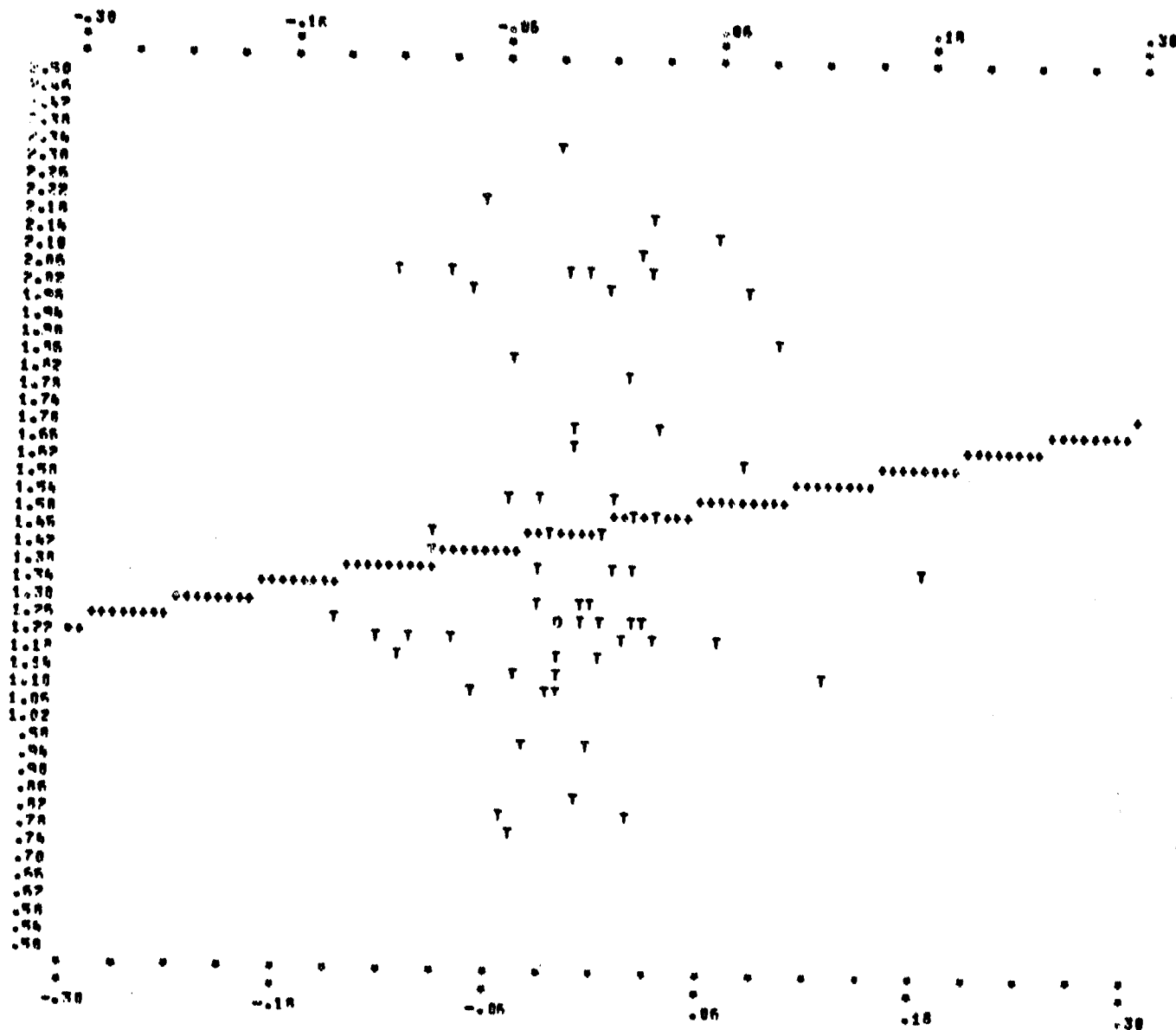
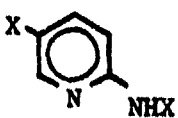


FIGURE 18. $\log_{10} h_{50}$ UP, $\Delta\rho$ ACROSS, NITROALIPHATICS

TABLE 4. LEAST SQUARES CORRELATION COEFFICIENTS AND RANK DIFFERENCE COEFFICIENTS FOR ONE-PARAMETER CORRELATIONS

Class \ Plot	I.S./ NO ₂ #	I.S./ NM ^{1/2}	NM ^{1/2} / NO ₂ #	I.S./ ρ _o	ρ _o / NO ₂ #	I.S./ Δρ
Nitramines	-0.65	-0.41	0.40	-0.68	0.44	0.24
	-0.61	-0.52	0.48	-0.71	0.44	0.19
Nitroaromatics	-0.62	-0.11	0.28	-0.01	0.08	0.31
	-0.55	-0.14	0.21	-0.04	0.04	0.25
Nitroaliphatics	-0.65	-0.63	0.81	-0.64	0.56	0.09
	-0.63	-0.64	0.68	-0.65	0.57	0.15

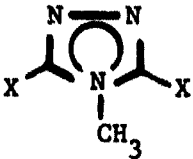
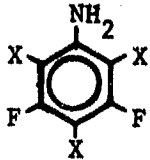
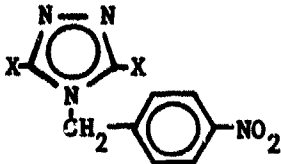
TABLE 5. EXCEPTIONAL COMPOUNDS - NITRAMINES*

Compds from Fig. 1 (I.S./NM ^{1/2})	log ₁₀ 50 xNM ^{1/2}	Compds from Fig. 10 (I.S./ρ ₀)	log ₁₀ 50 xρ ₀	Compds from Fig. 4 (I.S./NO ₂ *)
$\begin{array}{c} \text{X} \quad \text{O} \\ \quad \\ \text{CX} \text{ CH} \text{ N} \text{ COCH} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CX} \text{ CH} \text{ N} \text{ COCH} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{X} \quad \text{O} \end{array}$	36.0		3.86	$\begin{array}{c} \text{X} \\ \\ \text{CH} \text{ CX} \text{ CH} \text{ N} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH} \text{ CX} \text{ CH} \text{ N} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{X} \end{array}$
$\begin{array}{c} \text{X} \\ \\ \text{CH} \text{ OCH} \text{ NCH} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH} \text{ OCH} \text{ NCH} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{X} \end{array}$	36.8	$\begin{array}{c} \text{CH} \text{ CH} \text{ CX} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH} \text{ CH} \text{ CX} \text{ CH} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{N-X} \end{array}$	3.24	SAME
$\begin{array}{c} \text{X} \quad \text{O} \\ \quad \\ \text{CH} \text{ CX} \text{ CH} \text{ CH} \text{ N} \text{ CO} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH}_2 \\ \\ \text{CX}_2 \\ \\ \text{CH}_2 \end{array}$	35.5	SAME	3.55	SAME
$\begin{array}{c} \text{X} \quad \text{O} \\ \quad \\ \text{CH} \text{ CX} \text{ CH} \text{ CH} \text{ N} \text{ CO} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{X} \quad \text{O} \end{array}$				
$\begin{array}{c} \text{O} \quad \text{X} \\ \quad \\ \text{CX} \text{ CH} \text{ OCH} \text{ CH} \text{ N} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$	34.6	SAME	3.61	SAME
$\begin{array}{c} \text{O} \quad \text{X} \\ \quad \\ \text{CX} \text{ CH} \text{ OCH} \text{ CH} \text{ N} \\ 3 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{O} \quad \text{X} \end{array}$				
		$\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ \text{CH} \text{ NCH} \text{ CH} \text{ N} \text{ C=O} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{CH} \text{ NCH} \text{ CH} \text{ N} \text{ C=O} \\ 3 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{X} \quad \text{X} \end{array}$	3.31	$\begin{array}{c} \text{O} \text{ NOCH} \text{ CH} \text{ CH} \text{ CX} \text{ CH} \\ 2 \quad 2 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{O} \text{ NOCH} \text{ CH} \text{ CH} \text{ CX} \text{ CH} \\ 2 \quad 2 \quad 2 \quad 2 \quad 2 \quad 2 \\ \quad \\ \text{N-X} \end{array}$
$\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ \text{CH} \text{ N} \text{ CH} \text{ CH} \text{ N} \text{ H} \\ 3 \quad 2 \quad 2 \quad 2 \end{array}$	34.6	SAME	3.12	SAME

*X = NO₂

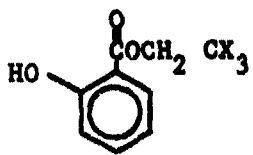
"SAME" means the nearest structure to the left

TABLE 6. EXCEPTIONAL COMPOUNDS - NITROAROMATICS*

Structure	$\log h_{50}$ $\times \text{NM}^{1/2}$	$\log h_{50}$ $\times \rho_0$
TATB	38.1	4.86
DATB	37.2	4.60
Fluoro - DATB	35.8	4.57
	35.6	3.67
	35.2	4.47
2,2-Dinitropropyl trinitrobenzoate	34.2	--
	33.4	3.97
Picramide	32.4	3.96
Trinitro-m-cresol	32.0	3.85
Diamino picric Acid	--	4.09

*X = NO₂

TABLE 7. EXCEPTIONAL COMPOUNDS - NITROALIPHATICS*

Compds from Fig. 3 (I.S./NM ^{1/2})	logh ₅₀ xNM ^{1/2}	Compds from Fig. 12 (I.S./ρ ₀)	logh ₅₀ xρ ₀	Compds from Fig. 6 (I.S./NO ₂ #)
$\begin{array}{c} \text{CX} \text{ CH} \text{ NHCO-CH} \text{ CH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{CX} \text{ CH} \text{ NHCO-CH} \text{ CH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{O} \end{array}$	36.1		3.77	---
2,2-Dinitropropyl 4,4,4-trinitro- butyrate	35.8	SAME	3.66	SAME
Trinitroethyl 4,4-dinitrohexa- noate	34.4	SAME	3.55	SAME
$\begin{array}{c} \text{CX} \text{ CH} \text{ CH} \text{ CO-CH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{CX} \text{ CH} \text{ CH} \text{ CO-CH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{O} \end{array}$	33.5	SAME	3.39	---
$\begin{array}{c} \text{CX} \text{ CH} \text{ CH} \text{ C-NH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{CX} \text{ CH} \text{ CH} \text{ C-NH} \\ \text{3} \quad \text{2} \quad \text{2} \quad \text{2} \\ \text{O} \quad \text{CH}_2 \end{array}$	33.4	SAME	3.46	SAME
$\begin{array}{c} \text{CX} \text{ C-NH-C} \text{ H} \\ \text{3} \quad \text{3} \quad \text{7} \end{array}$	33.2	--	--	---
2,2-Dinitrobutyl 4,4,4-trinitro- butyrate	32.2	--	--	SAME
Bis (2,2-Dinitro- propyl) 4,4,4-trinitro - butyramide	32.4	--	--	SAME

*X = NO₂

"SAME" means the nearest struture to the left.

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