

AROMATIC INTERACTIONS IN GAS CHROMATOGRAPHY:
THE USE OF 2,4,6-TRINITROPHENETOLE AS A COLUMN LIQUID

A. O. S. MACZEK* AND C. S. G. PHILLIPS

Inorganic Chemistry Laboratory, Oxford (Great Britain)

(Received December 27th, 1966)

INTRODUCTION

Several workers have tried to take advantage of π -interactions to separate aromatic hydrocarbon isomers—most especially *m*- and *p*-xylene. The most commonly used substrate has been a 1:1 mixture of fluorene and picric acid¹⁻⁶ though FABRIZIO *et al.*⁷ have used dibutylphthalate and picric acid, and SMITH⁸ has used *p*-nitroaniline picrate. PETRANEK AND SLOSAR⁹ have recommended the 3,5-dinitrobenzoate of ethylene glycol, which they claim has better temperature stability than fluorene-picric acid, and is moreover more selective for ethyl benzene and higher alkylbenzenes. NORMAN¹⁰ has advocated 2,4,7-trinitrofluorenone as a selective aromatic phase, and this has been used to separate *o*-, *m* and *p*-nitrotoluenes by ACHE *et al.*¹¹. Other suggested aromatic selective substrates include phenanthrene and 7,8-benzoquinoline¹², α -naphthylamine¹³, nitronaphthalene and chloronaphthalene¹⁴, and *m*-phenylenediamine¹⁵. JANAK AND HRIVNAC¹⁶ have reviewed several cases of aromatic selectivity in terms of π -interactions. The investigations of LANGER *et al.*^{17,18} and PINES AND CHEN¹⁹ have shown that tetrahalophthalate esters provide a good means of separating *m*- and *p*-isomers. These esters appear to act differently from other aromatic selective phases in that they reverse the usual *p*-, *m*-xylene emergence order. More recently LITTLEWOOD²⁰ has questioned the existence of specific aromatic π -interactions in many cases where such interactions are invoked to explain experimental data.

The work described below attempts to determine the existence and extent of some specifically aromatic interactions in gas chromatography. The substrate used, 2,4,6-trinitrophenetole, has a conveniently low melting point (78.5°) and is closely related to picric acid, whose ability to form aromatic π -complexes is well established.

PREPARATION OF THE COLUMN

2,4,6-Trinitrophenetole was produced *in situ* in the column by coating picryl chloride (B.D.H.Ltd.) onto prepared celite from ethanol solution, and then passing carrier gas, saturated at room temperature with ethanol, through the column at 100° for several hours.

The column was originally packed with 30% of picryl chloride by weight. Micro-analysis of the column material after passing ethanol showed less than 0.1% residual chlorine.

* Present address: Department of Physical Chemistry, The University, Leeds 2 (Great Britain).

RESULTS

Several compounds were run on 2,4,6-trinitrophenetole (TNP) at 83.5°. The results are plotted in Fig. 1 with tritolyl phosphate (TTP) as a reference phase. Retentions in both these substrates are measured relative to benzene taken as an arbitrary 100, and the logarithms of relative retentions are compared.

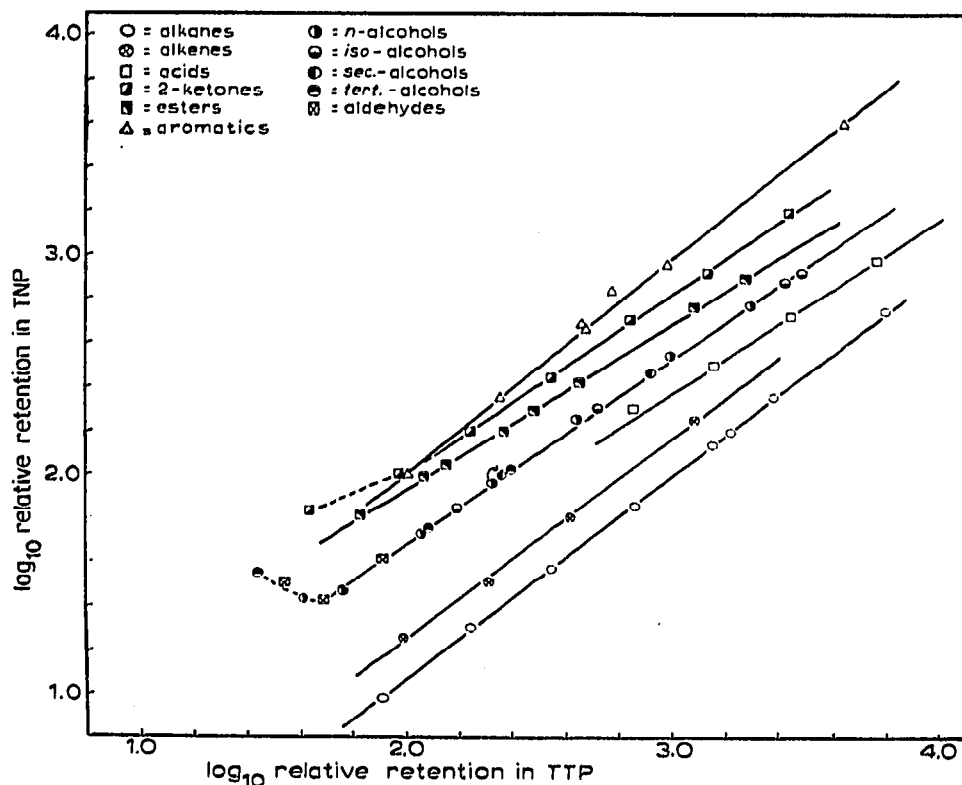


Fig. 1. The selectivity of 2,4,6-trinitrophenetole relative to tritolyl phosphate. Compounds (in order of increasing retention): alkanes: *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *trans*-dekalin, *cis*-dekalin, *n*-tetradecane; alkenes: *n*-octene, *n*-nonene, *n*-decene, *n*-dodecene; acids: formic, acetic, propionic, butyric; alcohols: *tert.*-butyl, methyl, ethyl, *n*-propyl, *tert.*-amyl, isobutyl, *n*-butyl, *sec.*-amyl, *tert.*-hexyl, *n*-amyl, isohexyl, *sec.*-hexyl, *n*-hexyl, *n*-heptyl, isooctyl, isononyl; aldehydes: formaldehyde, acetaldehyde, propionaldehyde; esters: ethyl acetate, propyl acetate, butyl acetate, ethyl propionate, ethyl butyrate, propyl butyrate, amyl butyrate, ethyl caproate; methyl ketones: methyl, ethyl, propyl, amyl, hexyl, heptyl; aromatics: benzene, toluene, *m*-xylene, *p*-xylene, *o*-xylene, mesitylene, tetralin.

Several trends are clear from Fig. 1. Relative to benzene, all classes of compounds other than aromatic hydrocarbons show a preference for the TTP phase. Of these, the most marked preference for TTP is shown by aliphatic hydrocarbons. These are so strongly rejected by the TNP column that on this latter, benzene, boiling at 80.1°, emerges mid-way between *n*-undecane (b.p. = 195.8°) and *n*-dodecane (b.p. = 214.5°). The most strongly alkane/aromatic discriminating columns in the literature are β,β' -oxydipropionitrile (KELKER²¹) and 1,2,3-tris(2-cyanoethoxy)propane (MCNAIR²²), on both of which benzene emerges between *n*-decane and *n*-undecane *i.e.*, one carbon number lower than on 2,4,6-trinitrophenetole. This rejection of alkanes makes the measurement of alkane retentions subject to quite appreciable error—

especially since those *n*-alkanes with appreciable retentions do not give very good peaks due to difficulties of volatilisation. Olefines have a predictably greater preference for the TNP medium than alkanes.

The straight line plots for different classes of compounds (hydrocarbons, acids, alcohols, ketones and esters) are not strictly parallel to each other. The lines for alkanes, alkenes and aromatic hydrocarbons all have a gradient = 1; the remainder have lesser slopes (~ 0.80 – 0.83) and the first member of several homologous series (*e.g.* formaldehyde, methanol, dimethyl ketone, formic acid) shows a preference towards the TNP phase. These trends may be the result of a progressive rejection of polar compounds as their hydrocarbon chains increase in length, a rejection analogous to the overall rejection of aliphatic hydrocarbons by TNP.

o- and *p*-xylene show an appreciable specific retardation on the TNP substrate. The order *p*-, *m*-, *o*- on TTP becomes *m*-, *p*-, *o*- on 2,4,6-trinitrophenetole. Table I shows relative retentions of *o*-, *m*- and *p*-xylene taking *o*-xylene as an arbitrary 100. The bulk of the data are taken from LITTLEWOOD²³ and 2,4,6-trinitrophenetole is shown for comparison.

It may be seen that TNP gives a very good *o*-xylene/*m*-xylene separation, though its *m*-/*p*-separation (= 0.966) is not so good as that of dipropyl tetrachlorophthalate (= 0.959). It seems probable, in view of the reverse *m*-/*p*-elution order, that 2,4,6-trinitrophenetole exerts on both *o*- and *p*-xylene a specific effect involving aromatic π -bonding. This point will be discussed further in the next section.

TABLE I
RELATIVE RETENTIONS OF XYLENES

	<i>Squalane</i>	<i>Benzyl-diphenyl</i>	<i>Tritolyl phosphate</i>	<i>7,8-Benzo-quinoline</i>	<i>Dipropyl tetrachloro-phthalate</i>	<i>Methyl propyl tetrachloro-phthalate</i>	<i>2,4,6-Trinitrophenetole</i>
	78.5°	78.5°	78.5°	78.5°	110°	110°	83.5°
<i>o</i> -Xylene	100	100	100	100	100	100	100
<i>m</i> -Xylene	83.9	80.0	78.2	78.0	75.7	75.0	68.8
<i>p</i> -Xylene	82.8	76.2	76.1	72.2	79.0	78.0	71.1

AROMATIC INTERACTIONS

Aromatic interactions of the kind considered here can conveniently be presented in the form of a special plot developed by ROHRSCHEIDER²⁴, an example of which is shown in Fig. 2. In such a plot, $\log r$, the logarithm of the retention of any substance relative to a standard (*n*-octane in this case), is measured along the vertical axis. The standard itself is represented by a horizontal line $\log r = 0$. The vertical axis then represents a paraffinic stationary phase (*e.g.* squalane). A line of unit slope is now drawn from a point on the vertical axis at a value of $\log r$ for a reference compound (*n*-octene here). This line now represents this reference compound. Any line drawn parallel to the vertical axis intersects both the reference and the standard lines; the distance between the two intersections gives a particular value for $\log r$ for these two compounds. Therefore, if such lines are fitted along the standard line such that the

distance between the intersections is an experimental value of $\log r$ for a given stationary phase, stationary phases will be arranged in order along an axis calibrated in terms of the relative retentions of the two (reference and standard) compounds.

LITTLEWOOD²⁰ has surveyed the selectivity of stationary phases in GC using such plots. As a part of his survey he has extended the data of ROHRSCHEIDER²⁴ to include an examination of the assumed π -interactions of aromatic hydrocarbons.

Table II shows the retentions of *n*-octene (reference) and benzene, relative to

TABLE II

RETENTIONS RELATIVE TO *n*-OCTANE = 1.00

Stationary phase	<i>n</i> -Octene		Benzene		Source
	Relative retention	$\log r$	Relative retention	$\log r$	
BDP (benzylidiphenyl)	1.135	0.055	0.892	-0.05	McNAIR AND DEVRIES ²³
TTP (tritolyl phosphate)	1.218	0.086	1.235	0.092	
DNP (dinonyl phthalate)	1.021	0.009	0.616	-0.210	
TCEP [1,2,3-tris(2-cyanoethoxy)propane]	1.890	0.276	8.34	0.921	
SQN (squalane)	0.886	-0.053	0.332	-0.480	McNAIR AND DEVRIES ²³
DBTCP (di- <i>n</i> -butyl tetrachlorophthalate)	1.071	0.030	0.871	-0.060	LANGER <i>et al.</i> ¹⁸
TNP (2,4,6-trinitrophenetole)	1.845	0.266	10.41	1.017	

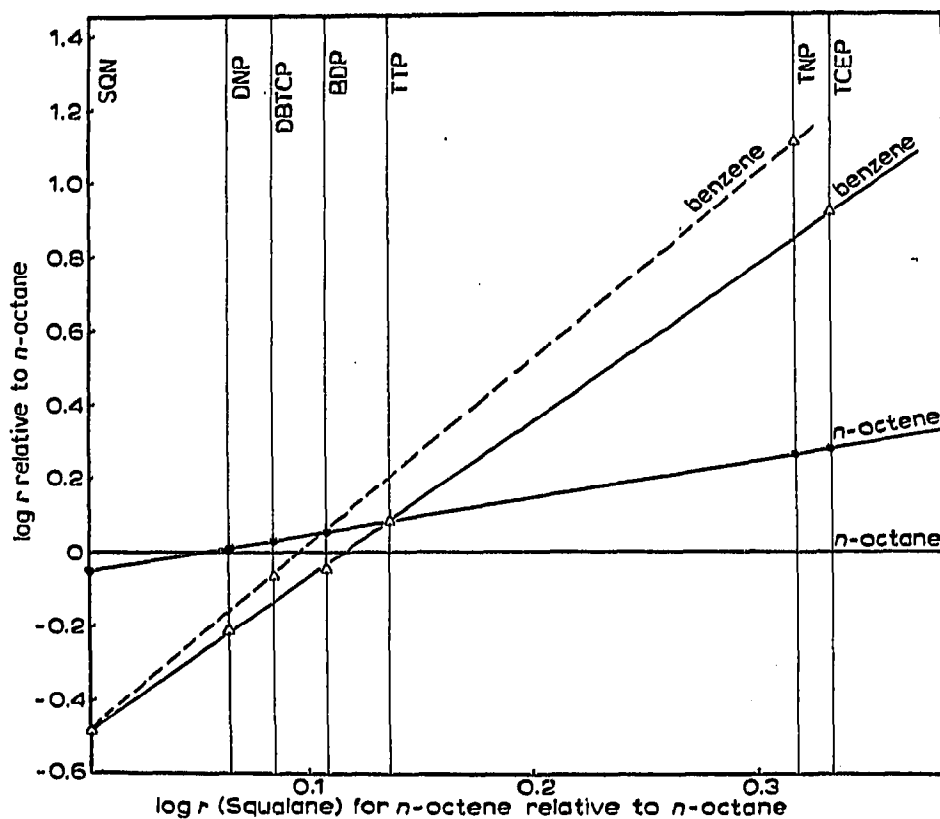


Fig. 2. ROHRSCHEIDER plot: benzene relative to *n*-octane and *n*-octene. SQN = Squalane; DNP = dinonyl phthalate; DBTCP = dibutyl tetrachlorophthalate; BDP = benzylidiphenyl; TTP = tritolyl phosphate; TNP = 2,4,6-trinitrophenetole; TCEP = 1,2,3-tris(2-cyanoethoxy)propane.

n-octane (standard). These include our results on TNP, and values taken from the references indicated. The Rohrschneider plot of these data is shown in Fig. 2; it has an extended horizontal scale for added clarity.

It may be seen that on five phases (squalane, dinonyl phthalate, benzyldiphenyl, tritoyl phosphate and 1,2,3-tris(2-cyanoethoxy)propane) the order of elution of benzene is the same as for octene. This has already been pointed out by LITTLEWOOD²⁰ who deduced from his results that there was no specific aromatic π -bonding in such solvents. 1,2,3-tris(2-cyanoethoxy)propane in particular is surprisingly normal, despite its apparent preferential strong retention of benzene mentioned earlier. Two substrates in Fig. 2, however, retain benzene appreciably more than the others. On dibutyl tetrachlorophthalate (DBTCP) and on 2,4,6-trinitrophenetole (TNP) (for which the benzene points lie on a straight line which passes through the point for benzene on the squalane reference phase) there is probably a real π -aromatic interaction effect. It is significant that on both of these substrates the *m*-xylene-*p*-xylene elution order is different from that on all the other phases (see Table I).

It is unfortunately not possible to include any other supposedly π -interacting substrates on Fig. 2 owing to a lack of suitable data (*n*-octane: *n*-octene: benzene) in the literature. Fig. 3 however, shows a ROHRSCHEIDER plot of benzene relative to cyclohexane and cyclohexene; retention values are taken from RAUPP⁵ and BROOKS²⁵. The linearity of the benzene plot is once again remarkably good, and this time covers six substrates: nujol, diethylhexyl sebacate, dinonyl phthalate, polypropylene glycol, trixylenyl phosphate, and fluorene-picric acid.

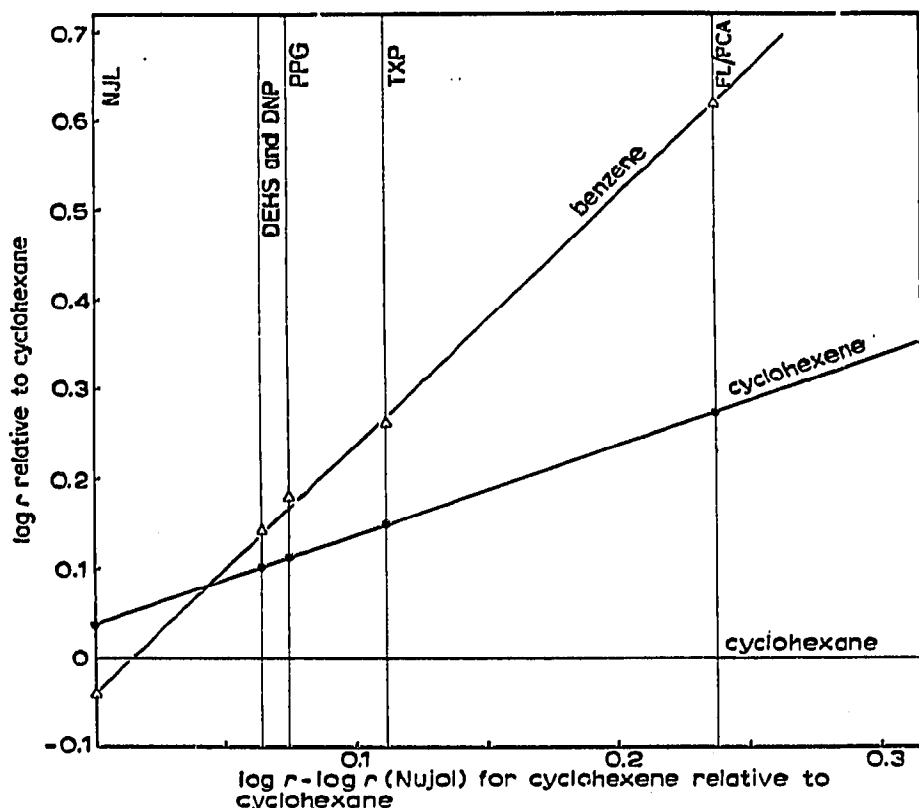


Fig. 3. ROHRSCHEIDER plot: benzene relative to cyclohexane and cyclohexene. NJL = Nujol; DEHS = diethylhexyl sebacate; DPN = dinonyl phthalate; PPG = polypropylene glycol; TXP = trixylenyl phosphate; FL/PCA = fluorene-picric acid.

trixylenyl phosphate and 1:1 fluorene-picric acid (*i.e.* the fluorene picrate π -complex). This latter liquid behaves no differently from the others so far as aromatic selectivity is concerned, which could perhaps have been foretold from its quite normal elution order (*p*-, *m*-, *o*-xylene). Moreover it is perhaps too optimistic to expect the strong fluorene picrate complex to dissociate in favour of a weaker benzene complex, which would have to happen for there to be a specific selective effect on benzene. A substrate with more than 1:1 picric acid in fluorene may well belong to the DBTCP, TNP π -complexing class of compounds.

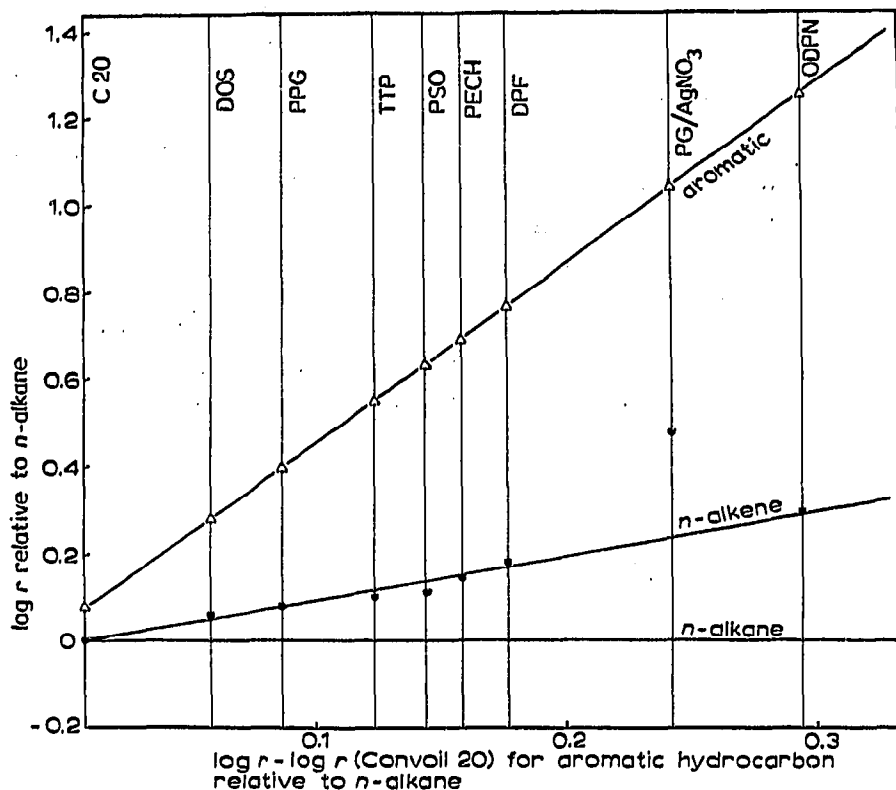


Fig. 4. ROHRSCHEIDER plot: aromatic hydrocarbon relative to *n*-alkane and *n*-alkene all at a common boiling point of 100°. C20 = Convoll 20; DOS = dioctyl sebacate; PPG = polypropylene glycol; TTP = tritolyl phosphate; PSO = polystyrene oxide; PECH = poly-epichlorohydrin; DPF = diphenyl formamide; PG/AgNO₃ = propylene glycol-AgNO₃; ODPN = β,β' -oxydipropionitrile.

Finally, Fig. 4 illustrates specific olefine selectivity. This plot is for three hypothetical compounds, an *n*-alkane, an *n*-alkene, and an aromatic hydrocarbon at a common boiling level of 100°, and shows the effect of silver nitrate on olefine retentions. Retention values are from the data of TENNEY²⁶ in which the hypothetical retentions of compounds at a common boiling level of 100° are obtained from plots of log retention against boiling point. In this case, however, substrates are arranged in the order of their retention of the aromatic relative to the alkane. The gradient of the aromatic line is arbitrarily fixed at a value of 4 for convenience.

It is clear that there is still a general overall agreement between the retentions of alkanes, aromatics and alkenes (though it is a less accurate agreement than in the previous figures—polystyrene oxide, for example, seems either to reject alkenes or to

retard aromatics specifically) except in the case of propylene glycol-silver nitrate. In this phase, the *n*-alkene is retained appreciably beyond the retention predicted from the trend in the other substrates. It can be seen that the presence of silver nitrate causes the *n*-alkene to be retained selectively by a factor of 1.74 ($\log r = 0.24$) on propylene glycol-silver nitrate, and that the well established use of silver nitrate for olefine separations is based on a real specific interaction.

FURTHER AROMATIC INTERACTIONS ON 2,4,6-TRINITROPHENETOLE

The results obtained with aromatics in the two previous sections and particularly the enhanced *o*-xylene-*m*-xylene separation, have prompted an investigation of a wider range of alkyl benzenes on 2,4,6-trinitrophenetole. Table III shows some relative retentions on TNP and tritolyl phosphate (TTP). In Fig. 5, relative retentions on TNP are plotted against those on TTP.

TABLE III

RETENTIONS OF SOME AROMATIC HYDROCARBONS RELATIVE TO BENZENE (= 100)

	2,4,6-Trinitro- phenetole (TNP) (78.5°)	Tritolyl phosphate (TTP) (100°)
1. Benzene	100	100
2. Toluene	224	224
3. Ethylbenzene	308	448
4. <i>p</i> -Xylene	480	440
5. <i>m</i> -Xylene	464	468
6. <i>o</i> -Xylene	675	585
7. Isopropylbenzene	320	640
8. <i>n</i> -Propylbenzene	428	790
9. 1,3,5-Trimethylbenzene	900	920
10. 1,2,3-Trimethylbenzene	746	680
11. 1,2,4-Trimethylbenzene	1,290	1,090
12. <i>tert.</i> -Butylbenzene	437	985
13. <i>sec.</i> -Butylbenzene	390	1,090
14. <i>n</i> -Butylbenzene	730	1,590
15. <i>tert.</i> -Amylbenzene	633	1,690
16. 1,2,4,5-Tetramethylbenzene	3,800	2,730
17. Pentamethylbenzene	14,600	8,860
18. Styrene	905	731
19. Tetralin	3,870	4,300

In addition to the already mentioned *p*- and *o*-xylene selectivity which 2,4,6-trinitrophenetole exhibits, Fig. 5 shows that this substrate is specifically selective towards several inter-related categories. The first and largest division is between the set of compounds containing benzene, its methylated homologues and styrene, and the set consisting of other alkyl benzenes, each with more than one carbon residue in the alkyl chain. Within the two sets formed by these compounds there is further discrimination.

Thus, benzene, toluene, *m*-xylene and mesitylene all fall on the same line of gradient 1, whereas *p*-xylene, *o*-xylene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene show an increasing retardation greater than the first set. The second set con-

sists of methyl compounds which contain one or more *o*- or *p*-grouping, whereas those without substituents of the latter kind are all in the first set. Styrene is selectively retarded even more than any of these *o*- and *p*-substituted methylbenzenes, probably as a result of its additional double-bond. The alkylbenzenes with more complex side chains fall into three interrelated sets which derive from toluene. Thus the *n*-alkylbenzenes fall on one straight line, *tert.*-alkylbenzenes on another and *sec.*-alkylbenzenes on a third.

Since benzene shows a specific interaction with TNP (Fig. 2) it is probable that benzene, toluene, and the other similarly retarded homologues all interact specifically with TNP to a similar extent. It seems that an *o*- or *p*-disposal of methyl groups enhances this specific interaction, and that it is further enhanced by the presence of an olefinic grouping in the alkyl chain.

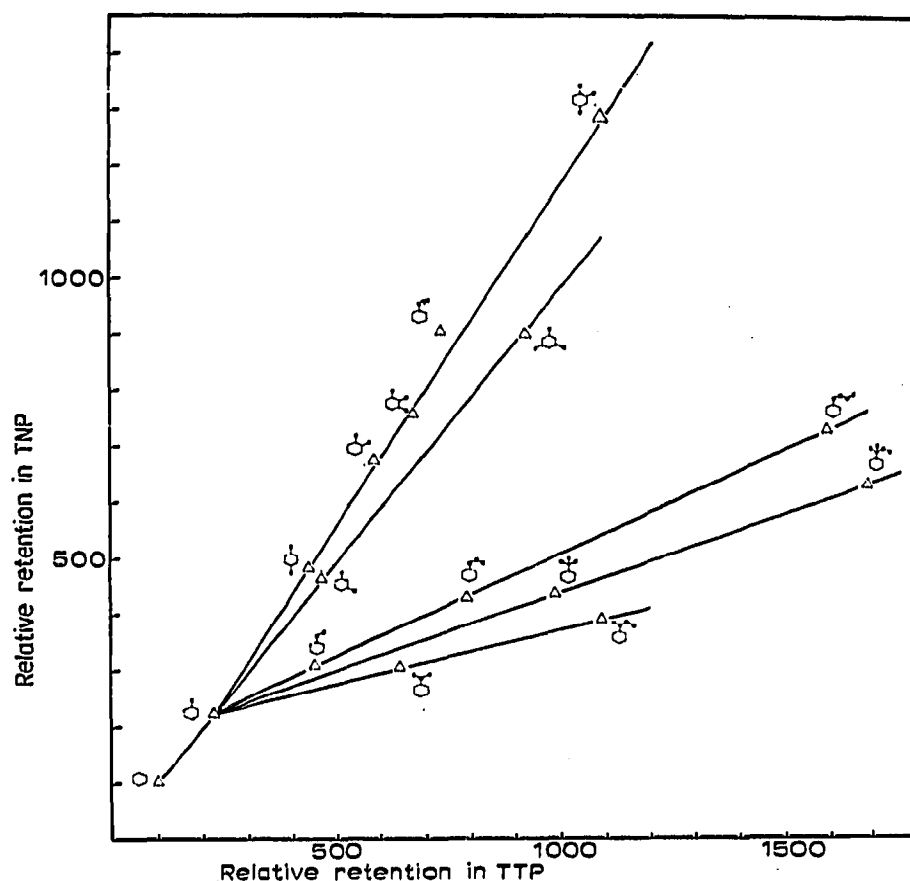


Fig. 5. Aromatic selectivity in 2,4,6-trinitrophenetole.

An increase in the length of the side chain beyond one carbon atom markedly decreases the affinity of the aromatics for TNP. This is almost certainly a size consideration; the bulk of an interacting molecule must play a large part in the resultant strength of π -interactions. The effect, though regular, is not altogether simple, for although these alkyl benzenes are less retarded on TNP than they are on TTP, tertiary isomers are retarded more on the TNP phase than are secondary ones. Again this is probably the result of steric considerations, albeit somewhat unusual ones.

ACKNOWLEDGEMENTS

The authors are indebted to A. B. LITTLEWOOD and H. M. POWELL for helpful discussions, to Imperial Chemical Industries for the loan of a recorder, and to the Scientific Research Council for a maintenance grant (A.O.S.M.).

SUMMARY

Retention times measured on a column containing 2,4,6-trinitrophenetole show that this substrate possesses considerable aromatic selectivity. On 2,4,6-trinitrophenetole, benzene emerges between *n*-undecane and *n*-dodecane, and *m*-xylene precedes *p*-xylene, which is the reverse of the usual order. The major part of the difference in the retention of aliphatic and aromatic compounds appears to act by a mechanism which rejects aliphatics rather than one which preferentially retains aromatics. However, an analysis of the results using a ROHRSCHEIDER plot shows that this substrate is nevertheless specifically selective towards aromatic compounds. Moreover, compared with tritoyl phosphate, 2,4,6-trinitrophenetole strongly retards *o*- and *p*-xylene and retards methyl substituted aromatic hydrocarbons significantly more than it retards those substituted with more bulky groups.

REFERENCES

- 1 A. I. M. KEULEMANS, A. KWANTES AND P. ZAAL, *Anal. Chim. Acta*, 13 (1955) 357.
- 2 B. T. WHITMAN, in D. H. DESTY (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 194.
- 3 B. T. WHITMAN, in D. H. DESTY (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 395.
- 4 R. E. RIPPERE, in V. J. COATES, H. J. NOEBELS AND A. S. FAGERSON (Editors), *Gas Chromatography*, Academic Press, New York, 1958, p. 223.
- 5 G. Z. RAUPP, *Anal. Chem.*, 164 (1958) 135.
- 6 T. MAEDA AND M. FUJII, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 62 (1959) 649.
- 7 F. A. FABRIZIO, R. W. KING, C. C. CERATO AND J. W. LOVELAND, *Anal. Chem.*, 31 (1959) 2060.
- 8 B. SMITH, *Acta Chem. Scand.*, 13 (1959) 887.
- 9 J. PETRANEK AND J. SLOSAR, *Collection Czech. Chem. Commun.*, 26 (1961) 2667.
- 10 R. O. C. NORMAN, *Proc. Chem. Soc.*, (1958) 151.
- 11 H. J. ACHE, W. HERR AND A. THIEMANN, *Int. At. Energy Agency Symp., Vienna, 1961*, preprints paper TTS/10.
- 12 A. GOLDUP AND W. T. SWANTON, *Brit. Pat.*, 864611 (1961).
- 13 T. ARAKI AND R. GORO, *Bull. Chem. Soc. Japan*, 33 (1960) 115.
- 14 A. ZLATKIS, S. LING AND H. R. KAUFMAN, *Anal. Chem.*, 31 (1959) 945.
- 15 L. C. CASE, *J. Chromatog.*, 6 (1961) 381.
- 16 J. JANAK AND M. HRIVNAC, *J. Chromatog.*, 3 (1960) 297.
- 17 S. H. LANGER, C. ZAHN AND M. H. VIAL, *J. Org. Chem.*, 24 (1959) 423.
- 18 S. H. LANGER, C. ZAHN AND G. PANTAZOPOLOS, *J. Chromatog.*, 3 (1960) 154.
- 19 H. PINES AND C. T. CHEN, *J. Am. Chem. Soc.*, 82 (1960) 3562.
- 20 A. B. LITTLEWOOD, *J. Gas Chromatog.*, 1 (1963) 16.
- 21 H. KELKER, *Angew. Chem.*, 71 (1959) 128.
- 22 H. MCNAIR AND T. DEVRIES, *Anal. Chem.*, 33 (1961) 806.
- 23 A. B. LITTLEWOOD, *Gas Chromatography*, Academic Press, New York, London, 1962, p. 405.
- 24 L. ROHRSCHEIDER, *Z. Anal. Chem.*, 170 (1959) 256.
- 25 V. T. BROOKES AND G. A. COLLINS, *Chem. Ind. (London)*, (1959) 921.
- 26 H. M. TENNEY, *Anal. Chem.*, 30 (1958) 2.