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### Paper Chromatographic Behavior of Some Tertiary Amine Pollutants and an Attempt at Structure-Activity-Correlation

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PAPER CHROMATOGRAPHIC BEHAVIOR OF SOME TERTIARY  
AMINE POLLUTANTS AND AN ATTEMPT AT  
STRUCTURE-ACTIVITY-CORRELATION

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ABSTRACT

Ascending paper chromatography of some pesticides and toxicants containing a tertiary amino group has been performed to record their mobilities in acidic, basic and saline waters and some common organic solvents. Several binary separations of these pollutants have been achieved. The important separations are summarized below:

Amitrole from azobenzene, bavistin, calixin, 2,4-Lutidine, 2,6-Lutidine, N-ethylmorpholine,  $\beta$ -picoline,  $\gamma$ -picoline and quinoline; Azobenzene from bavistin, calixin, 2,4-Lutidine, 2,6-Lutidine,  $\beta$ -picoline,  $\gamma$ -picoline, pyridine and quinoline; Bavistin from 2,4-Lutidine, 2,6-Lutidine,  $\beta$ -picoline,  $\gamma$ -picoline and quinoline; and Quinoline from 2,4-Lutidine, 2,6-Lutidine,  $\beta$ -picoline,  $\gamma$ -picoline and N-ethylmorpholine from binary mixtures. An attempt at structure-activity-correlation reveals that the physical forces responsible for both the chromatographic

behaviour as well as the toxicity are almost identical and the most important common physical interaction seems to be the hydrogen-bonding.

### INTRODUCTION

Tertiary amine pollutants are found in varying quantities in samples of air, water and soil. One of their important characteristics is their carcinogenicity. Though the literature is replete with analytical, physico-chemical and chemical data on polycyclic aromatic hydrocarbons (PAH)(1) comparatively little progress has been made with tertiary amine pollutants and as far as we are aware there has been negligible attempt at structure-activity-correlations for this class of compounds. In primary attempts in this direction from our laboratories, a simple and inexpensive spot-test (2) was developed for the detection of these compounds in neutral, saline acidic and basic waters and a spectrophotometric method has been developed for the near-specific analysis of 2,6-Lutidine - an important member of this class (3).

The classical technique of chromatography i.e., column, paper and thin layer though on the decline due to the development of more powerful and sophisticated techniques i.e., HPLC and GC, certainly offer certain unique advantages as they can be used to separate complex mixtures into simpler fractions prior to further separation by high resolution techniques and identification of mixture constituents (4). Paper chromatography is a versatile technique due to its inherent simplicity and gives better resolution than column chromatography (5). Separations difficult in columns can be carried on papers often with success. A further advantage stems from the fact that paper techniques can often separate compounds with identical uv-absorption spectra (6). The disadvantages of paper chromatography are irreproducible papers,

often inadequate resolution and poor quantification (7). However, the disadvantages are not applicable to the development of structure-activity-correlations where only broad trends of various members of a family are considered. Furthermore the extreme simplicity and very modest cost makes it an ideal technique for routine analysis especially in third world countries.

The present communication summarises the separations and mobilities of tertiary amine pollutants by paper chromatography and an attempt has been made at a structure-activity-correlation.

### EXPERIMENTAL

#### Reagents

Prepare aqueous or ethanolic solutions of the test substances (1M). When it is not possible to prepare 1M solution, prepare saturated solution. Prepare also aqueous saturated solution of phosphomolybdic acid, sodium carbonate and saturated solution of copper iodide in acetonitrile. All chemicals and reagents were of ANALAR grade obtained from BDH (England) and SIGMA (USA) except: bavistin [2-(methoxycarbonyl) benzimidazole 50% W/W; adjuvants add 100% W/W], and calixin (N-tridecyl-2,6-dimethylmorpholine 80% W/W; adjuvants 20% W/W), BASF, Aktiengesellschaft, West Germany. Whatman No. 1 filter papers.

#### Apparatus

Ordinary 20 x 5 cm, glass jars were used to develop the paper 14 x 3 cm strips. UV-lamp was used for irradiating the spot to detect the fluorescent spot.

### PROCEDURE

The ascending technique was applied in these studies. The papers were spotted for the pollutants, hung in the

glass jars and developed in the various types of waters and organic solvents. The pollutants were detected as yellow spots by dipping the strip in the solution of phosphomolybdic acid or by dipping in the solutions of copper iodide and sodium carbonate respectively followed by irradiation with uv-light.

### RESULTS

The chromatographic behaviour of the following 12 pesticides (P) and toxicants (T) have been studied.

1. <sup>(P)</sup> Amitrol (3-Amino-1,2,4-triazole), 2. <sup>(P)</sup> Azobenzene (Diphenyldiazene), 3. <sup>(P)</sup> Bavistin (2-methoxy-carbamoyl benzimidazole), 4. <sup>(P)</sup> Calixin (N-tridecyl-2,6-dimethyl morpholine), 5. <sup>(T)</sup> 2,4-Lutidine (2,4-dimethyl pyridine), 6. <sup>(T)</sup> 2,6-Lutidine (2,6-dimethyl pyridine), 7. <sup>(T)</sup> N-Ethyl-morpholine, 8. <sup>(T)</sup>  $\beta$ -Picoline (3-methyl pyridine), 9. <sup>(T)</sup>  $\gamma$ -Picoline (4-methyl pyridine), 10. <sup>(T)</sup> Pyridine, 11. <sup>(T)</sup> quinoline and 12. <sup>(T)</sup> Trimethylamine. The solvent systems used were: 1. Distilled water, 2. 2%, 1% and 0.1% HCl, 3. 2%, 1% and 0.1% HNO<sub>3</sub>, 4. 2%, 1% and 0.1% NaOH, 5. 2%, 1% and 0.1% NaCl, 6. 2% NaH<sub>2</sub>PO<sub>4</sub>, 7. 2% KHSO<sub>4</sub>, 8. 2% Na<sub>2</sub>CO<sub>3</sub>, 9. 2% NaNO<sub>2</sub>, 10. 2% NaNO<sub>3</sub>, 11. 2% Pb(NO<sub>3</sub>)<sub>2</sub>, 12. Chloroform, 13. Carbontetrachloride, 14. Benzene, 15. Chlorobenzene and 16. Butyl alcohol.

The chromatographic behaviour of these compounds is illustrated in figure 1 by plotting R<sub>F</sub> values against the solvents used. On the basis of the R<sub>F</sub> values, several separations have been achieved.

### DISCUSSION

Application of paper chromatography for the separation of organics containing a tertiary amino group using phosphomolybdic acid as a detector is documented in the Lederer's book of "Chromatography" (8) and the "Analytical Chemistry of Nitrogen and its Compounds" (9). Wagner and

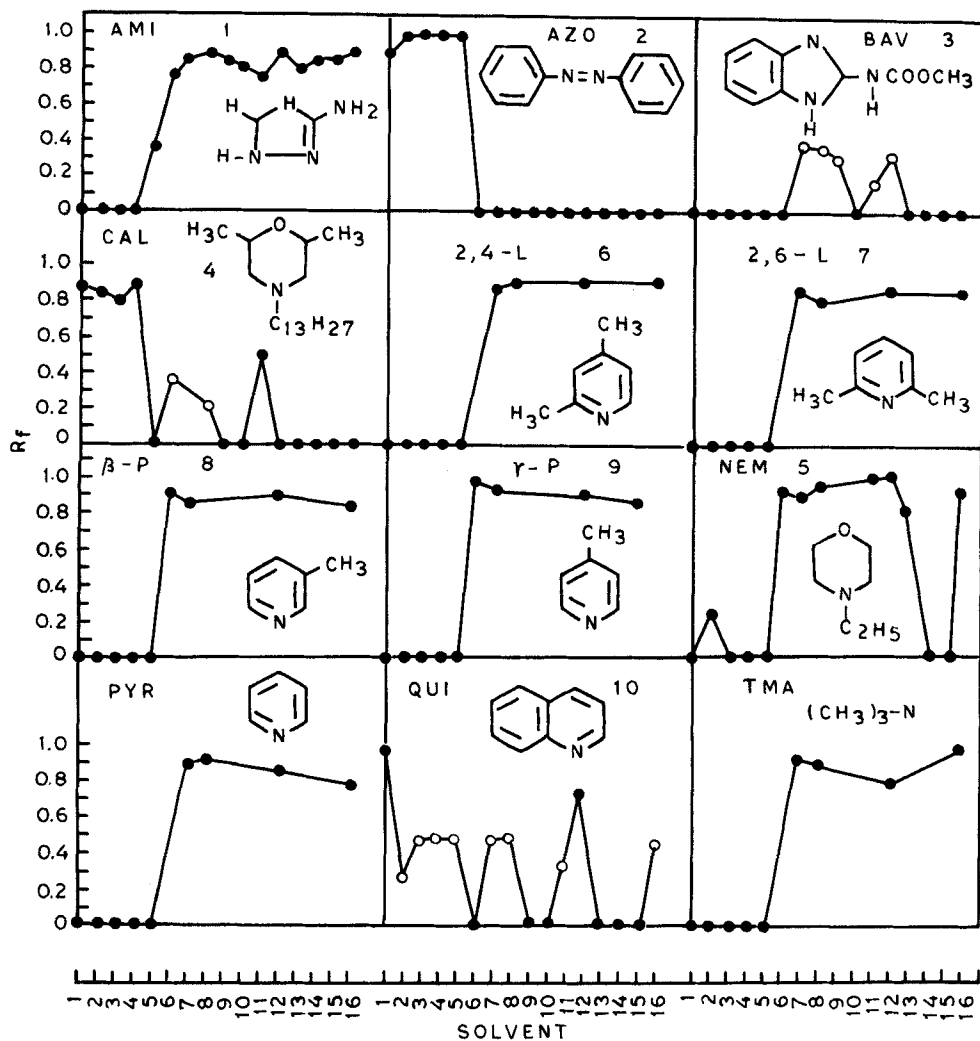


FIG. 1

ABBREVIATIONS: - 1 = CHCl<sub>3</sub>, 2 = CCl<sub>4</sub>, 3 = C<sub>6</sub>H<sub>6</sub>, 4 = C<sub>6</sub>H<sub>5</sub>Cl, 5 = (CH<sub>3</sub>)<sub>3</sub>C-OH  
 6 = DISTILLED WATER 7 = HCl, 8 = HNO<sub>3</sub> 9 = NaOH, 10 = NaCl, 11 = NaH<sub>2</sub>PO<sub>4</sub>  
 12 = KHSO<sub>4</sub>, 13 = Na<sub>2</sub>CO<sub>3</sub>, 14 = NaNO<sub>3</sub> 15 = NaNO<sub>2</sub> 16 = Pb(NO<sub>3</sub>)<sub>2</sub>  
 AMI = AMITROL, AZO = AZOBENZENE, BAV = BAVISTIN, CAL = CALIXIN,  
 2,4-L = 2,4-LUTIDINE, 2,6-L = 2,6-LUTIDINE, NEM = N-ETHYLMORPHOLINE  
 $\beta$ -P =  $\beta$ -PICOLINE,  $\gamma$ -P =  $\gamma$ -PICOLINE, PYR = PYRIDINE, QUI = QUINOLINE  
 TMA = TRIMETHYLAMINE

● = R<sub>f</sub> ○ = R<sub>f</sub> OF TAILING COMPOUNDS

Lehmann have used saturated solution of copper iodide in acetonitrile, saturated solution of sodium carbonate in water followed by uv radiation for the detection of heterocyclic nitrogen compounds by fluorescence (10). These two detectors proved to be complementary for the pollutants under study as they give bright yellow colour and fluorescence respectively. The chromatographic data given in figure 1 shows that as the pH of the water decreases, detection and separation becomes easier. For example 27 separations can be achieved in strongly acidic solutions of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{Pb}(\text{NO}_3)_2$  while only two separations can be achieved in strongly alkaline solution of  $\text{NaOH}$ . This aspect is further discussed below.

Figure 1 also indicates that the mobility of organics under study except azobenzene, calixin and quinoline is very low in organic solvents. The mobility of these compounds is high in acidic waters, medium in neutral waters and low in alkaline waters. The results give the relevant information about several binary separations.

The next and perhaps the more important aspect of this work was to attempt a structure-activity-correlation. This attempt was due to the fact (figure 1) that trimethylamine, pyridine and its derivatives: 2,4-Lutidine, 2,6-Lutidine,  $\beta$ -picoline and  $\gamma$ -picoline give almost identical chromatographic behaviour and this made us suspect that the toxic/carcinogenic behaviour of these compounds is in some way localised on the lone-pair on the Nitrogen atom for this class of compounds. It also became clear that hydrogen bonding seems to play a crucial role in the chromatographic behaviour of this class. For example, (figure 1) the mobility of anitrole is essentially zero in non-hydrogen bond or weak hydrogen bond donor solvents i.e.  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_5\text{Cl}$  while it has an intermediate value for  $(\text{CH}_3)_3\text{-COH}$  and a very high value for distilled water after which there is much less steep rise and levelling off as the pH of the media is decreased. These results are in consonance with the hydrogen-bond concept. It is

well known that hydrogen-bonding plays a crucial role in binding the carcinogen to nucleic acid analogue of DNA(11).

There was however no correlation between mobility in distilled water  $\left[ \rho_{H_2O} = R_f \right]$  and  $LD_{50}$  values and the scatter diagram is given in Figure 2.  $LD_{50}$  values are a measure of toxicity (12) and defined as:

Toxicity is expressed as the  $LD_{50}$  based on oral feeding of male rats. The figure given is number of milligrams of the compounds required per kilogram of animal weight to produce mortality in 50% of the test animals. Thus lower the figure, the higher the toxicity.

We next attacked the problem in two ways. The number of nitrogen atoms per molecule of the tertiary amine pollutant was taken as a rough structural measure and denoted by  $n$ . First a plot was constructed of  $LD_{50}$  vs.  $n$

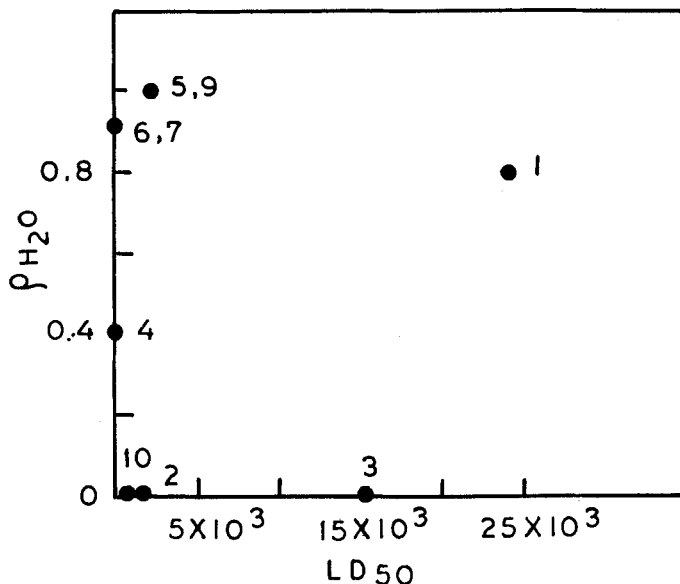
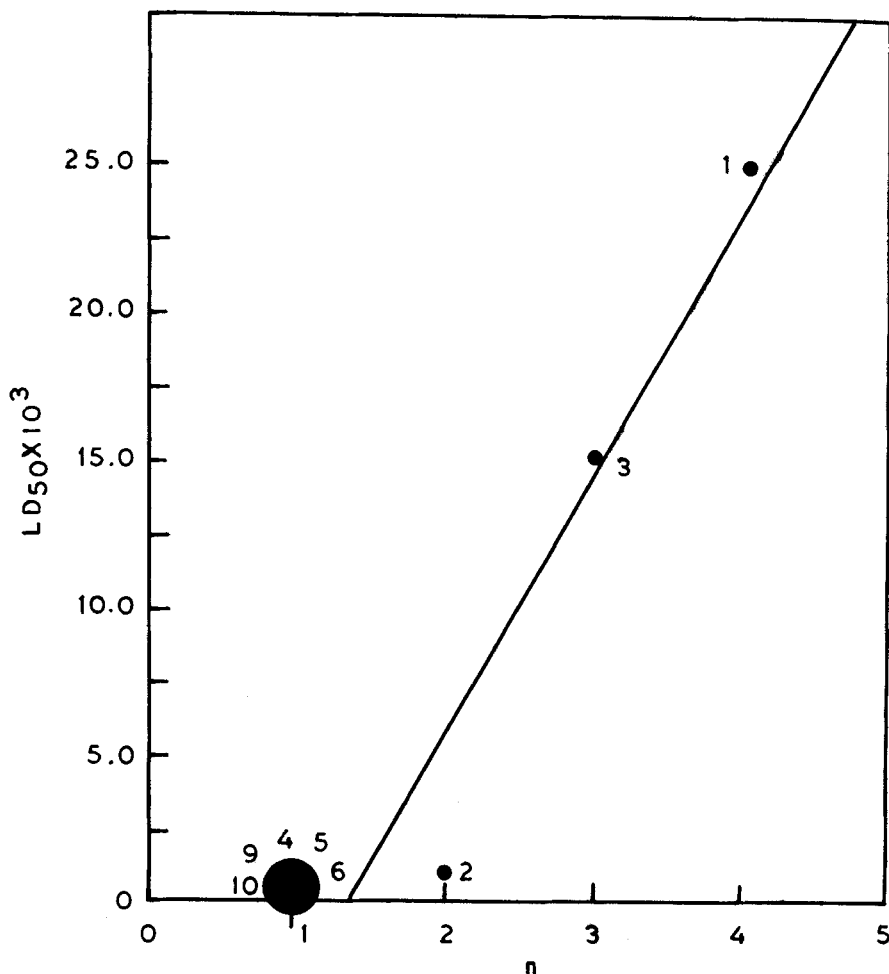


FIG. 2 SCATTER DIAGRAM OF AN ATTEMPTED CORRELATION BETWEEN  $\rho_{H_2O}$  AND  $LD_{50}$



FIG. 3 CORRELATION FOR LD<sub>50</sub> AND n

(figure 3) and a near linear correlation obtained. Next a plot was constructed of  $\mathcal{P}_{H_2O}$  vs. n and a good parabolic relation analogous to equation 1 was obtained (figure 4)

$$\mathcal{P}_{H_2O} = n - c_1 + \frac{c_2}{n - c_1} \quad (1)$$

There is evidence to show that in many instances a parabolic relation is much more refined than a linear one.

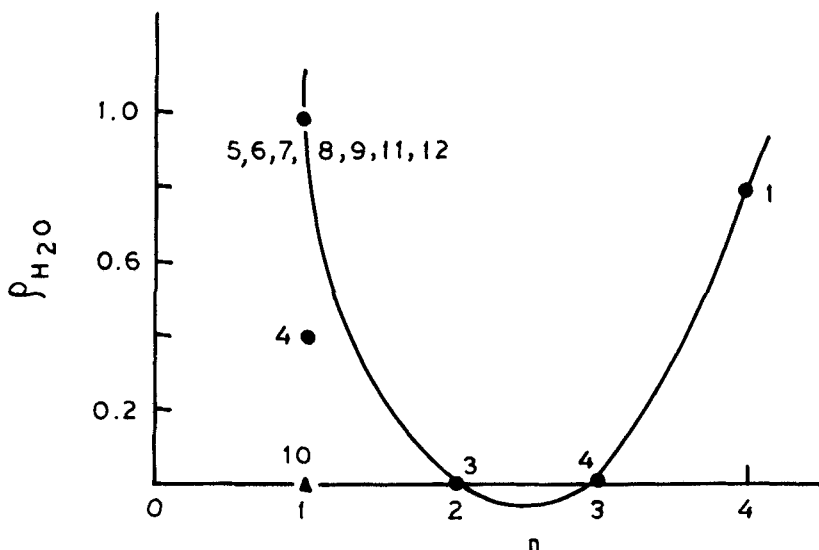


FIG. 4 CORRELATION FOR  $\rho_{H_2O}$  AND  $n$

For example the linear (13) and parabolic (14) relations of the energy of the highest intermolecular charge transfer band ( $h\nu_{CT}$ ) and ionisation potential of the donor ( $I^D$ ) though of course the theoretical considerations may be different. A characteristic common to both in the linear as well as the parabolic relationship is that compounds having one nitrogen atom per molecule have  $LD_{50}$  values closely spaced and  $\rho_{H_2O}$  almost identical, irrespective of the often severe structural modification of the molecule. The near-coincidence of  $\rho_{H_2O}$  values for  $n = 1$  (figure 4) as compared to the small scatter of  $LD_{50}$  values again for  $n = 1$  is surprising as the scale differs as 1 : 12,500 and hence a small deviation  $LD_{50}$  should not be apparent and hence the better coincidence of  $\rho_{H_2O}$  values as compared to  $LD_{50}$  values for  $n = 1$  vindicates our belief that the parabolic relations are more refined than linear relationships. A final significant support for the parabolic relationship being better comes from the fact that quinoline (compound 10, figure 1) is the only compound of

the series that have a fused ring system and hence its toxicity will have a very significant contribution from its polycyclic nature and hence should deviate considerably from both relations. However, figure 4 as compared to figure 3 reveals that the deviation is much more pronounced in the parabolic relation (figure 4) than the linear one (figure 3).

Hence though apparently we have failed in the first instance to correlate structure with activity — a very important conclusion emerges,  $n$  is related to  $LD_{50}$  values by a linear relationship and to  $\rho_{H_2O}$  values by perhaps a better parabolic relationship and for  $n = 1$  the  $\rho_{H_2O}$  values are effectively constant. Hence, it seems a common mode of mechanism is responsible for the chromatographic as well as the toxic behaviour of these compounds and this common mode most certainly appears to be hydrogen bonding between nitrogen lone-pair and a proton of nucleic acid analogue of DNA. Therefore, there is certainly a good relation between structure and activity though not as simple a one as attempted herein

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