CHROM. 10,851

PAPER CHROMATOGRAPHY OF N-MONO- AND N,N-DI-SUBSTITUTED 2,4-DINITRO-, 2,6-DINITRO- AND 2,4,6-TRINITROANILINES

EVA ZEMANOVÁ and SVATOPLUK ZEMAN

Research Centre, Chemko n. p., 072 22 Strážske (Czechoslovakia)

(Received October 18th, 1977)

SUMMARY

A study is presented of the chromatographic behaviour of 38 compounds (mostly N-mono- and N,N-dialkyl-substituted 2,4- and 2,6-dinitro- and 2,4,6-trinitro-anilines) on Whatman No. 2 paper impregnated with formamide and with cyclohexane as mobile phase. It is shown that the relationship between the R_F values and the melting-points permits division of the compounds into four groups, for each of which m.p. $= bR_F + a$. This interdependence is accounted for by the combined influences of electronic and steric factors on the amine-N and its interaction with the stationary phase. It is also shown that there is a linear relationship between the R_M values of the N-mono-n-alkyl-2,4- and -2,6-dinitro- and -2,4,6-trinitroanilines and the number of carbon atoms in the alkyl chain (N_c); this relationship is expressed by $R_M = b_1 \cdot \log N_c + a_1$. By analogy, the relationship $R_M = b_2 \cdot \log (\log 2N_c) + a_2$ exists for N,N-di-n-alkyl derivatives. The R_M values of the compounds show that introduction of another nitro-group into a dinitroaniline derivative, as well as introduction of a first or second substituent into the amine-group of a polynitroaniline, is not incrementally additive.

INTRODUCTION

The molecular structures of polynitroanilines and their N-alkyl and N,N-dialkyl derivatives have been studied fairly well. Aspects of the molecular conformation of these compounds were dealt with by Kamlet and co-workers[1–4], who used UV spectroscopy, and by Heidberg and von Jouanne[5–7] and Lamm and co-workers[8–10], who used NMR spectroscopy.

Kamlet and co-workers[1] state that introduction of an alkyl group into the amino-group of 2-nitro- or 2,6-dinitro-aniline will cause rotation of the 2-nitro (or 6-nitro) group out of coplanarity with the benzene nucleus and simultaneous deformation of the bond angle between the amin-N and the carbon of the nucleus; alternatively, the amin function can even rotate out of coplanarity with the nucleus. The introduction of a nitro-group in position 4 in N-alkyl-2-nitro- or N-alkyl-2,6-dinitro-aniline may (and with 2,4-dinitroaniline derivatives does) induce return of the amine-

nitrogen to coplanarity with the nucleus[1,2]; this phenomenon is defined by Kamlet as "steric enhancement of resonance". In 2,4,6-trinitroaniline, a more powerful substituent on the amine-N may cause not only rotation of the 2-nitro (or 6-nitro) group and the amine-N out of coplanarity with the nucleus, but also deformation of the bond angles in the benzene nucleus[2]. The conclusions of Kamlet *et al.* are essentially in good agreement with the results obtained by von Jouanne and Heidberg[7].

In our present research on the molecular structure of N-mono- and N,N-di-alkyl-2,4- and -2,6-dinitro- and -2,4,6-trinitro-anilines, paper chromatography was used. The results published here have also been applied in our studies[11,12] on the thermal stability of polynitroaniline derivatives by differential thermal analysis.

EXPERIMENTAL

N-Alkyl- and N,N-dialkyl-polynitroanilines were prepared by boiling 2,4- or 2,6-dinitrochlorobenzene, or 2,4,6-trinitrochlorobenzene, with the corresponding amine in methanol or ethanol in the presence of potassium acetate (as hydrogen chloride acceptor). Similarly, *i.e.*, by reaction of polynitrochlorobenzenes with ammonia, 2,4- and 2,6-dinitro- and 2,4,6-trinitro-aniline were synthesized. Compounds so obtained were purified by crystallization from methanol, ethanol, acetone or a acetone–methanol mixture.

For the paper chromatography, we used as stationary phase Whatman No. 2 paper impregnated with formamide–methanol (5:2, v/v); descending development with cyclohexane was carried out for 300 min at $21.0 \pm 0.3°$, and the spots were identified from their colours in daylight and under UV radiation. The R_F values reported are averages from five measurements.

The m.p. were determined on a Boëtius micro-heating table equipped with a special microscope (VEB Analytik, Dresden, G.D.R.). To determine the corresponding relationships, the upper limits of the m.p. range were used.

RESULTS AND DISCUSSION

An analysis of measured R_F values and m.p. (see Table I) revealed that the compounds could be divided into four groups, in which the R_F and m.p. were related by a linear equation of the type:

$$\text{m.p.} = bR_F + a \tag{1}$$

The coefficients of eqn. 1 (obtained on the basis of linear regression) and the corresponding correlation coefficients (r) are summarized for the individual groups (A, B, C and D) of polynitroaniline derivatives in Table II. The mathematical treatment excluded compounds with $R_F = 0$ (*i.e.*, compounds 1 and 27) and compound 35, all of which, however, approximated to the relation for compounds in group A.

An analogous, but unambiguous dependence, was observed for several groups of sugars by Jermyn and Isherwood[13,14], whose work was cited by Tockstein *et al.*[15] when establishing that the relationship between R_F values and m.p. could be explained by mutual cohesion of the molecules.

TABLE I

MELTING-POINTS AND R_F AND R_M VALUES OF THE POLYNITROANILINE DERIVATIVES

Compound No.	Compound	Melting-point, °C	R_F	R_M
1	2,4-Dinitroaniline	187.5	0.000	∞
2	N-Methyl-2,4-dinitroaniline	178.0	0.040	1.380
3	N-Ethyl-2,4-dinitroaniline	114.0	0.208	0.588
4	N-n-Propyl-2,4-dinitroaniline	95.0	0.500	0.158
5	N-n-Butyl-2,4-dinitroaniline	90.0	0.600	−0.176
6	N-Isopropyl-2,4-dinitroaniline	94.0	0.495	0.000
7	N-Isobutyl-2,4-dinitroaniline	80.0	0.605	−0.194
8	N-Cyclohexyl-2,4-dinitroaniline	155.0	0.640	−0.250
9	N-Allyl-2,4-dinitroaniline	75.5	0.240	0.501
10	N-Phenyl-2,4-dinitroaniline	160.0	0.524	−0.042
11	N,N-Dimethyl-2,4-dinitroaniline	87.0	0.150	0.750
12	N,N-Diethyl-2,4-dinitroaniline	80.0	0.640	−0.250
13	N,N-Di-n-propyl-2,4-dinitroaniline	95.0	0.810	−0.631
14	N,N-Di-isopropyl-2,4-dinitroaniline	94.5	0.070	1.123
15	N-(2,4-Dinitrophenyl)piperidine	93.0	0.640	−0.250
16	2,6-Dinitroaniline	138.0	0.149	0.759
17	N-Methyl-2,6-dinitroaniline	106.0	0.321	0.329
18	N-Ethyl-2,6-dinitroaniline	86.0	0.682	−0.329
19	N-n-Propyl-2,6-dinitroaniline	81.0	0.803	−0.611
20	N-n-Butyl-2,6-dinitroaniline	41.0	0.873	−0.839
21	N-Cyclohexyl-2,6-dinitroaniline	76.5	0.875	−0.844
22	N-Allyl-2,6-dinitroaniline	65.5	0.750	−0.477
23	N,N-Dimethyl-2,6-dinitroaniline	78.0	0.744	−0.464
24	N,N-Diethyl-2,6-dinitroaniline	49.0	0.836	−0.708
25	N,N-Di-n-propyl-2,6-dinitroaniline	86.0	0.335	−0.819
26	N-(2,6-Dinitrophenyl)piperidine	106.0	0.878	−0.788
27	2,4,6-Trinitroaniline	191.0	0.000	∞
28	N-Methyl-2,4,6-trinitroaniline	116.0	0.040	1.380
29	N-Ethyl-2,4,6-trinitroaniline	84.5	0.255	0.477
30	N-n-Propyl-2,4,6-trinitroaniline	60.0	0.540	−0.070
31	N-n-Butyl-2,4,6-trinitroaniline	78.0	0.720	−0.410
32	N-Cyclohexyl-2,4,6-trinitroaniline	102.0	0.870	−0.630
33	N-Allyl-2,4,6-trinitroaniline	80.0	0.330	0.327
34	N,N-Dimethyl-2,4,6-trinitroaniline	139.5	0.290	0.390
35	N,N-Diethyl-2,4,6-trinitroaniline	166.5	0.780	−0.550
36	N,N-Di-n-propyl-2,4,6-trinitroaniline	139.5	0.910	−1.004
37	N,N-Di-n-butyl-2,4,6-trinitroaniline	94.0	0.920	−1.061
38	N-(2,4,6-Trinitrophenyl)piperidine	98.0	0.812	−0.631

Among the general molecular-structural aspects of physical stability[11,16], we must consider the manner and intensity of interaction between the amine-N of the compounds and the stationary phase of our chromatographic system; this interaction is analogous to the solvation of anilines by protic solvents. Eastes and co-workers expressed the opinion[17] that solvation of aniline derivatives depended both on hybridization at the amine-N and on the steric environment of this atom. From studies on the conformation of polynitroaniline derivatives[1-4,6,7], and on analogous poly-nitro-m-phenylenediamine derivatives[18], the combined influence of the electronic and steric factors on the amine-N can be assumed to be responsible for the division of

TABLE II

COEFFICIENTS OF EQN. 1 FOR INDIVIDUAL GROUPS OF THE POLYNITROANILINE DERIVATIVES

Group	Structure of group*	Value of coefficient		
		b	a	r
A	2, 8, 10, 36	−43.293	181.005	0.9921
B	13, 16, 26, 32, 34, 37, 38	−59.964	150.867	0.9573
C	3, 4, 5, 6, 7, 12, 15, 17, 18, 19, 21, 23, 28, 31	−54.270	121.055	0.9479
D	9, 11, 14, 20, 22, 24, 25, 29, 30, 33	−56.949	97.238	0.9377

* Compounds numbered as in Table I.

the chromatographed compounds into four groups in the sense of the mutual relationship between R_F values and m.p. Also, the fact that the separate groups do not represent homologous (or any other) series can be similarly accounted for.

By analysing the relationship between the R_M values of N-mono-n-alkyl- and N,N-di-n-alkyl-polynitroanilines and the number (N_c) of carbon atoms in the alkyl chains, linear relationships were found for the separate groups of polynitroanilines, i.e., the 2,4- and 2,6-dinitro- and 2,4,6-trinitro-anilines. For N-mono-n-alkyl substitution, the relationship was of the form

$$R_M = b_1 \cdot \log N_c + a_1 \qquad (2)$$

For N,N-di-n-alkyl substitution, the form was

$$R_M = b_2 \cdot \log (\log 2N_c) + a_2 \qquad (3)$$

The values of the coefficients of eqns. 2 and 3, with the corresponding correlation coefficients, are summarized in Tables III and IV, respectively.

In the homologous series of N-mono-n-alkyl- and N,N-di-n-alkyl-polynitroaniline we found no constant increment, $\Delta R_{M(CH_2)}$, for a methylene group; this is confirmed by eqns. 2 and 3. Similarly, there was no constant increment, $\Delta R_{M(NO_2)}$, for a 6- (or 2-) and a 4-nitro-group. This is in agreement with conclusions from conformational studies on the compounds[1-4,6,7,18] and with those from the chromatographic structural analysis of alkylaromatics[19]. We have confirmed that introduction of a nitro-group into a dinitroaniline, or substitution on the amine-N, is not incrementally additive. Depending on the type and intensity of the interaction between

TABLE III

COEFFICIENTS OF EQN. 2 FOR N-MONO-n-ALKYL DERIVATIVES

N-Mono-n-alkylaniline	Value of coefficient		
	b_1	a_1	r
2,4-Dinitro	−2.597	1.379	0.9998
2,6-Dinitro	−1.933	0.304	0.9975
2,4,6-Trinitro	−2.991	1.376	0.9998

TABLE IV

COEFFICIENTS OF EQN. 3 FOR N,N-DI-n-ALKYL DERIVATIVES

N,N-Di-n-alkylaniline	Value of coefficient		
	b_2	a_2	r
2,4-Dinitro	−3.342	−0.991	0.9999
2,6-Dinitro	−0.850	−0.904	0.9989
2,4,6-Trinitro	−3.140	−1.251	0.9973

the given nitro-group, or on the substituent with the rest of the molecule (particularly in the highly crowded polynitroaniline derivatives), the corresponding substitution is always associated with a redistribution of electron density in the molecule, which is specific for a given compound[11]. A similar conclusion holds for, e.g., the contribution of a nitro-group or of intra- or inter-molecular hydrogen bonds to the heat of sublimation[11,16,20].

REFERENCES

1 M. J. Kamlet, H. G. Adolph and J. C. Hoffsommer, J. Amer. Chem. Soc., 86 (1964) 4018.
2 M. J. Kamlet, J. C. Hoffsommer, R. R. Minesinger and H. G. Adolph, J. Org. Chem., 33 (1968) 3070.
3 M. J. Kamlet, R. R. Minesinger, J. C. Hoffsommer, J. C. Dacons and H. G. Adolph, J. Chem. Soc., B, (1968) 1147.
4 C. Dickinson, J. R. Holden and M. J. Kamlet, Proc. Chem. Soc., (1964) 233.
5 J. Heidberg, J. A. Weil, G. A. Janusonis and J. K. Anderson, J. Chem. Phys., 41 (1964) 1033.
6 J. von Jouanne and J. Heidberg, Ber. Bunsenges. Phys. Chem., 75 (1971) 261.
7 J. von Jouanne and J. Heidberg, J. Amer. Chem. Soc., 95 (1973) 487.
8 B. Lamm, Acta Chem. Scand., 19 (1965) 2316.
9 B. Lamm and K. Nordfält, Acta Chem. Scand., 20 (1966) 1208.
10 B. Lamm and K. Nordfält, Acta Chem. Scand., 20 (1966) 1221.
11 S. Zeman, Thermostable Polynitroaromatic Compounds, Part I, Ph.D. Thesis, Univ. Chem. Technol., Pardubice, June 1973.
12 S. Zeman and E. Zemanová, J. Thermal Anal., in preparation.
13 M. A. Jermyn and F. A. Isherwood, Biochem. J., 44 (1949) 402.
14 F. A. Isherwood and M. A. Jermyn, Biochem. J., 48 (1951) 515.
15 A. Tockstein, J. Dvořák and I. M. Hais, in I. M. Hais (Editor), Papírová Chromatografie, ČSAV, Prague, 1959, p. 88.
16 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
17 J. W. Eastes, M. H. Aldridge and M. J. Kamlet, J. Chem. Soc., B, (1969) 922.
18 R. R. Minesinger and M. J. Kamlet, J. Amer. Chem. Soc., 91 (1969) 4155.
19 L. S. Bark, Progr. Thin-Layer Chromatogr. Relat. Methods, 1 (1972) 1.
20 C. Lenchitz and R. W. Velicky, J. Chem. Eng. Data, 15 (1970) 401.