INFRARED SPECTRA AND THERMAL STABILITIES OF NITRO-ANILINES

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Decomposition temperatures were correlated with frequencies of valence and deformation bond vibrations in a series of N-substituted derivatives of 2,4- and 2,6-dinitroanilines (DNA). These vibrations are directly influenced by the nitro group structure and by its resonance and inductive interaction with the benzene ring. Analysis of the infrared spectra reveals a great sensitivity of the frequency and hence the $C_{Ar}-NO_2$ bond order on the substitution character of the amino group, whereas the frequencies of the valence vibrations of the *o*-nitro group are influenced to a small extent only. However, at the same time the valence vibration of $C_{Ar}-NO_2$ is a sensitive indicator of the thermal stabilities of 2,4-DNA and 2,6-DNA.

On the basis of detailed spectral studies of N-substituted derivatives of 2,4- and 2,6-DNA in the IR [1, 2] and UV [2, 3] regions, we decided to attempt to correlate the decomposition temperatures with those spectral frequencies which are closely related to the structure of the nitro group and its resonance and inductive interaction with the benzene ring. A linear correlation was demonstrated between the decomposition temperatures and some particular frequencies of valence vibrations in the IR region. The experiment to correlate UV spectral data, especially shifts of absorption maxima, with decomposition temperatures was not successful [2]. We see the probable reason for this in the fact that the electronic absorption spectra more or less represent the behavior of the molecular π-electronic system, and the σ-molecular system is better manifested as a higher-order perturbation. The destruction of the molecules begins by the breaking of the π- and σ-bonding system; the σ-bonds have the lower energy requirements for breaking and therefore play the more important role in the early stages of thermolysis. The study of nitro compounds in different phases [4—9] has shown that the first stage of thermo-lytic decomposition proceeds via homolytic fission, according to scheme (1)

$$Ar-NO_2 \rightarrow Ar \cdot + \cdot NO_2 \tag{1}$$

From a theoretical point of view, the ease of primary bond splitting in a molecule of an aromatic nitro compound is defined by the bond dissociation energy and resonance stabilization of the molecule [10, 11]. However, the bond strength and resonance stabilization of a compound need not always be the limiting factors for thermal stability: the thermolysis of many compounds occurs via sterically actived

complexes with lower activation energies than the dissociation energy of the weakest molecular bond [4].

The frequencies closely related to the structure of the nitro group and its resonance interaction with the benzene ring were correlated with the decomposition temperatures of N-substituted derivatives of 2,4- and 2,6-DNA.

Experimental

N-substituted derivatives of 2,4- and 2,6-dinitroanilines were prepared according to [12]. The purities of the compounds were checked by paper-chromatography, thin-layer chromatography on silica gel, and by comparing their melting points with the published data [12]. The infra-red absorption spectra were recorded on a Perkin−Elmer 621 spectrophotometer in KBr discs (2 mg/g KBr). The DTA measurements were carried out on the apparatus described earlier [12]. The compounds were tested in air with a heating rate of 4.5 deg · min^{-1} up to 400°. The sample weight was 50 mg, diluted by the same amount of glass powder, which was also used as reference material.

Results and discussion

Results on the thermal stabilities of N-substituted derivatives of 2,4- and 2,6-dinitroaniline and correlated frequencies of valence vibrations are given in Table 1−3. The linear regressions for the studied nitroanilines and graphical plots are given in Table 3 and Figs 1−3, respectively.
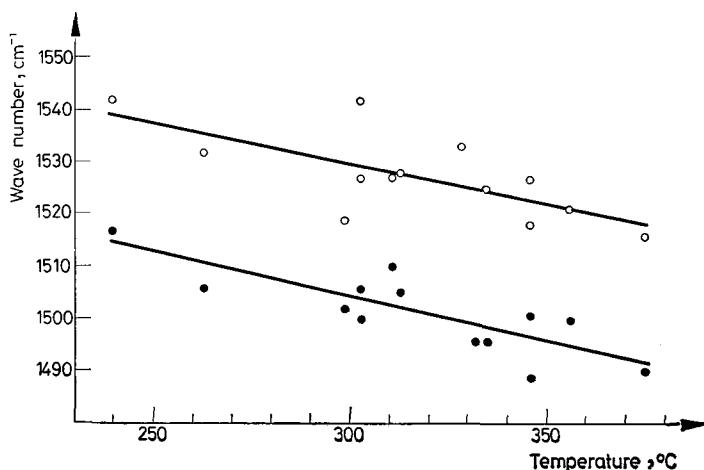

Fig. 1. Correlation of frequencies of valence vibrations of nitro groups with decomposition temperatures of 2,4-dinitroanilines: ○ ν_{as} (ortho-NO$_2$); ● ν_{as}(para-NO$_2$)

In accordance with [13, 14], the absorption bands with wave numbers 1542—1516 cm^{-1} and 1517—1489 cm^{-1}, respectively, were attributed to the antisymmetric vibrations of the o- and p-nitro groups in the 2,4-dinitroanilines. The frequencies of the antisymmetric valence vibrations $\nu_{as}NO_2$ for both o- and p-nitro groups in derivatives of 2,4-dinitroanilines display a good linear dependence on the decomposition temperatures. The slope ($B_1 = -0.153$ or -0.169, respectively) is
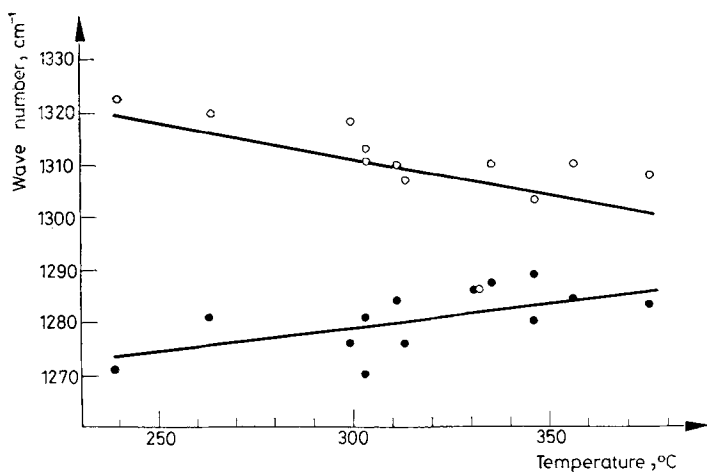

Fig. 2. Correlation of frequencies of valence vibrations of para-NO_2 groups and C_{Ar}—NH_2 bonds with decomposition temperatures of 2,4- and 2,6-dinitroanilines: ○ ν_s(para-NO_2); ● $\nu_{C_{Ar}}$—NH_2

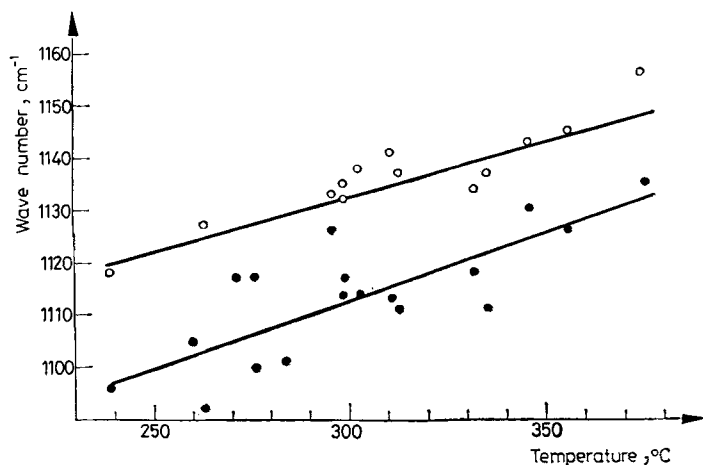Fig. 3. Correlation of frequencies of valence vibrations of C_{Ar}—NO_2 bonds with decomposition temperatures of 2,4- and 2,6-dinitroanilines: ○ ν_{Ar}—NO_2(ortho) (compounds 1—13); ● $\nu_{C_{Ar}}$—NO_2(ortho) (compounds) 1—13, 14—18)

Table 1

Decomposition temperatures and frequencies of valence vibrations of nitro groups of $N(R^1, R^2)$-2,4-dinitroanilines

Com-pound	Substituent		DTA peak temperature °, (exothermic)	$\nu_{(NO_2)}$ cm^{-1}		
	R^1	R^2		ν_{as}(ortho-NO$_2$)	ν_{as}(para-NO$_2$)	ν_s (para-NO$_2$)
1	H	H	346	1527	1501	1303
2	H	CH$_3$	335	1525	1496	1310
3	H	C$_2$H$_5$	313	1528	1505	1307
4	H	C$_4$H$_9$	303	1542	1500	1313
5	H	iso-C$_3$H$_7$	311	1527	1510	1310
6	H	iso-C$_4$H$_9$	303	1527	1506	1311
7	CH$_3$	CH$_3$	239	1542	1517	1323
8	C$_2$H$_5$	C$_2$H$_5$	263	1532	1506	1320
9	CH$_3$	C$_6$H$_5$	332	1533	1496	1286
10	H	2-NH$_2$C$_6$H$_4$	299	1519	1502	1308
11	H	C$_6$H$_5$	356	1521	1500	1310
12	H	1-C$_{10}$H$_7$	346	1518	1489	1304
13	C$_6$H$_5$	C$_6$H$_5$	375	1516	1490	1308

Table 2

Decomposition temperatures and frequencies of valence vibration bands of C_{Ar}-NO$_2$ and C_{Ar}-NH$_2$ of $N(R^1,R^2)$-derivatives of 2,4- and 2,6-dinitroanilines

Com-pound	Substituent		DTA peak tempera-ture °, (exother-mic)	Frequency cm^{-1}			
	R^1	R^2		$\nu C_{Ar}-NO_2$ (para)	$\nu C_{Ar}-NO_2$ (ortho)	$\nu C_{Ar}-NO_2$ (ortho)	$\nu C_{Ar}-NH_2$
1	H	H	346	1133	1126	1126	1289
2	H	CH$_3$	335	1137	1111	1111	1287
3	H	C$_2$H$_7$	313	1137	1111	1111	1276
4	H	C$_4$H$_9$	303	1138	1114	1114	1281
5	H	iso-C$_3$H$_7$	311	1141	1113	1113	1284
6	H	iso-C$_4$H$_9$	303	1135	1114	1114	1270
7	CH$_3$	CH$_3$	239	1118	1096	1096	1271
8	C$_2$H$_5$	C$_2$H$_5$	263	1127	1092	1092	1281
9	CH$_3$	C$_6$H$_5$	332	1134	1118	1118	1286
10	H	2-NH$_2$C$_6$H$_4$	299	1132	1117	1117	1276
11	H	C$_6$H$_5$	356	1145	1126	1126	1284
12	H	1-C$_{10}$H$_7$	346	1143	1130	1130	1280
13	C$_6$H$_5$	C$_6$H$_5$	375	1156	1135	1135	1283
14	H	CH$_3$	284	—	—	1111	—
15	C$_2$H$_5$	H	271	—	—	1117	—
16	CH$_3$	CH$_3$	276	—	—	1100	—
17	C$_2$H$_5$	C$_2$H$_5$	276	—	—	1117	—
18	H	C$_6$H$_{11}$	260	—	—	1105	—

Compounds 14−18 are N-substituted 2,6-dinitroaniline derivatives.

Table 3

Linear regression for N-substituted derivatives of 2,4- and 2,6-dinitroanilines according to the equation $Y = B_1X + B_0$

Compound	Vibration	B_0^a	B_1^a	r^a	n^a	Confidence interval (95%)		Standard deviation
1—13	ν_{as} (ortho-NO$_2$)	1576	−0.153	−0.699	13	−0.258;	−0.048	0.048
1—13	ν_{as} (para-NO$_2$)	1555	−0.169	−0.818	13	−0.248;	−0.090	0.036
1—13	ν_s (ortho-NO$_2$)	1337	−0.008	−0.063	13	−0.086;	−0.071	0.036
1—13	ν_s (para-NO$_2$)	1354	−0.143	−0.608	13	−0.267;	−0.019	0.056
1—13	$\nu_{C_{Ar}-NO_2}$ (para)	1070	0.209	0.861	13	0.127;	0.290	0.037
1—13	$\nu_{C_{Ar}-NO_2}$ (ortho)	1021	0.300	0.917	13	0.213;	0.386	0.039
1—13, 14—18	$\nu_{C_{Ar}-NO_2}$ (ortho)	1038	0.250	0.836	18	0.163;	0.336	0.041
1—13	$\nu_{C_{Ar}-NH_2}$	1250	0.097	0.619	13	0.016;	0.179	0.097

[a] B_0 regression constant; [a]B_1 regression coefficient; [a]r correlation coefficient; [a]n number of members for correlation; chart values of correlation coefficients (confidence interval 95%) 0.55 ($n = 11$), 0.47 ($n = 16$); X decomposition temperature, °C; Y valence vibration.
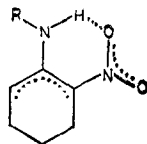
about the same for the two nitro groups. This leads to the idea that the mesomeric interaction of the nitro groups with the benzene ring, which is the decisive factor for their vibration and the thermal stability of the molecule, is nearly equally changed for both types of nitro group upon amino group steric distortion and other effects.

However, the correlation of the symmetric valence vibrations $\nu_s(NO_2)$ with exo peaks is not so satisfying. The frequency of the p-nitro group moves in a broader interval (1323 − 1303 cm^{-1}, excepting compound 9, with a frequency of 1286 cm^{-1}), than in the case of the o-nitro group, and there is no direct connection with conjugation and steric effects, respectively. A somewhat better dependence of the compared data is given by the frequency of the o-nitro group, which moves in a very narrow interval (1339 − 1331 cm^{-1}, again excepting compound 9), but the slope of the correlation line is low ($B_1 = 0.008$). The derivatives of 2,6-DNA were not taken into correlation because both the anti- and the symmetric valence vibrations of the nitro group give very poor correlation parameters.

The frequencies in the region of 1100 cm^{-1}, which according to [15, 16] belong to the valence vibration of the C_{Ar}-NO$_2$ bond, give very good correlations with the decomposition temperatures. The slopes are 0.210 and 0.300 for the p- and o-nitro groups, respectively. There was also a possibility to take into account the values for the o-nitro group in 2,6-DNA (compounds 14 − 18), without a greater influence on the correlation coefficient. This fact accentuates the importance of the correlation. From the values of the slopes it can be concluded that the order for the aromatic ring − nitro group bond is more sensitive to N-substitution than is the N − O bond, and for this reason the $C_{Ar} - NO_2$ frequency is the more sen-

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sitive indicator concerning the thermal stability of 2,4-DNA and to some extent of 2,6-DNA.

The frequencies in the region $1290 - 1270 \text{ cm}^{-1}$ give a linear dependence within the limits of reliability. This region of valence vibration bands (attributed to $C_{Ar} - NH_2$ valence vibration) for N-mono and N-unsubstituted derivatives is overlapped by the very broad absorption of the characteristic vibration of the poly-cyclic system involving a hydrogen-bond (structure 1). For this reason, the de-tection of single bands is very difficult and unreliable. The slope ($B_1 = 0.097$) indicates the direct relationship of the frequency and conjugation effect and the thermal stability expressed by the exo peaks.

As regards deformation vibrations (scissoring, rocking, wagging) and skeletal vibration of $C - C$ bonds (assigned 8a according to [17]) in relation to exo peaks, we did not find any linear dependence.

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RÉSUMÉ — On a établi des corrélations entre les températures de décomposition et les fréquences de valence ainsi que les vibrations de déformation des liaisons dans la série des dérivés N-substitués des 2.4- et 2.6-dinitroanilines (DNA). Ces vibrations sont directement influencées par la structure du groupe nitro et sa résonance ainsi que son interaction inductive avec le noyau benzènique. De l'analyse des spectres infra-rouges il ressort une haute sensibilité de la fréquence et, par conséquent, de l'ordre de la liaison C_{Ar}-No_2 dépendant du caractère de substitution du groupe aminé, tandis que la fréquence des vibrations de valence du groupe nitro n'est influencée que peu. Cependant, la vibration de valence de C_{Ar}-NO_2 est, en même temps, un indicateur sensible de la stabilité thermique de la 2.4-DNA et également de la 2.6-DNA.

ZUSAMMENFASSUNG — Zersetzungstemperaturen wurden mit Valenzfrequenzen und Deformationsbindungsvibrationen einer Reihe von N-substituierter Derivate von 2.4- und 2.6-Dinitroanilinen (DNA) korreliert. Diese Vibrationen werden unmittelbar von der Struktur der Nitrogruppe sowie seiner Resonanz und induktiven Wechselwirkung mit dem Benzolring beeinflußt. Aus der Analyse der Infrarotspektra geht eine große Empfindlichkeit der Frequenz und folglich der Bindungsordnung C_{Ar}-NO_2 in Abhängigkeit vom Substitutionscharakter der Aminogruppe hervor, während die Frequenzen der Valenzvibrationen der o-Nitrogruppe nur wenig beeinflußt werden. Jedoch ist die Valenzvibration von C_{Ar}-NO_2 gleichzeitig ein empfindlicher Indikator der thermischen Stabilität von 2.4-DNA wie auch von 2.6-DNA.

Резюме — В ряду N-замещенних 2,4- и 2,6-динитроанилинов (ДНА) температуры были скоррелированы с частотами валентных и деформационных колебаний связей. Эти колебания непосредственно связаны со структурой нитрогруппы и ее мезомерным и индуктивным взаимодействием с бензольным кольцом. Анализ инфракрасных спектров показал большую чувствительность частоты и, следовательно, порядка связи $C_{ар.}$— NO_2 от характера замещения аминогруппы. В то же самое время частота валентных колебаний о-нитрогруппы мало изменяется. Вместе с тем, валентное колебание $C_{ар.}$— NO_2 является чувствительным показателем термической устойчивости не только для 2,4-динитроанилинов, но также и для 2,6-динитроанилинов.