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THE STRUCTURE OF THE DINITROMETHYL ANION IN AROMATIC AND HETEROCYCLIC COMPOUNDS

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It is shown experimentally that in salts of dinitromethyl derivatives of aromatic and heterocyclic compounds the nitro groups are equivalent, and participate equally in anion formation. It is shown that both in the free state, and as an anion, the dinitromethyl group in aromatic and heterocyclic compounds has just the same spectral characteristics as in aliphatic compounds. These characteristics can be utilized for analytical purposes. The IR spectra do not reveal conjugation between the mono- or dinitromethyl group and the benzene ring. Judging by the UV spectra the benzene ring is not conjugated with the dinitromethyl anion. It is found that in the solid state 2-dinitromethylpyridine is an internal salt.

This laboratory previously [1] investigated salts of aliphatic dinitromethyl compounds and showed that both nitro groups are equivalent and that they participate equally in anion formation. It was also shown that in IR spectra the charged dinitromethyl group is characterized by three absorption bands, which can be used to identify the compounds.

The present paper deals with a study of the interaction between dinitromethyl group and aromatic ring, determining the structure of salts, and the possibility of using spectra of aromatic and heterocyclic dinitromethyl derivatives for analytical purposes. IR and UV spectroscopy were used to solve these problems.

Study of the literature data shows that N—O valence vibration frequencies in the NO_2 group are almost unaffected by a benzene ring when the nitro group is in the side chain of aromatic compounds. This can be seen on comparing frequencies of N—O vibrations for aliphatic-aromatic nitro compounds with those for nitroalkanes (Table 1).

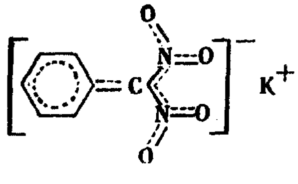
Table 1

Valence Vibrations of N—O in the NO_2 Group of Primary, Secondary, and Tertiary Nitro Compounds

Compound	NO_2 group position	Compound No.	Valence vibrations of NO in the group NO_2, cm^{-1}	
			Antisymmetric	Symmetric
Aliphatic-aromatic [2]	Primary	3	1557±2	1374±0
	Secondary	1	1548	1361
	Tertiary	2	1541±5	1346±6
Nitroalkanes [3]	Primary	—	1554±6	1382±6
	Secondary	—	1550.5±2.5	1360.5±3.5
	Tertiary	—	1538.5±4.5	1348±4.5

Had there been conjugation between nitro group and benzene ring, then the frequency of the N—O antisymmetric valence vibration in the NO_2 group of such compounds would have been in the region below 1535 cm^{-1} (characteristic of the conjugated nitro group when there are no steric effects). It would appear from their IR spectra that there is practically no conjugation between nitro group and benzene ring in the arylnitromethanes.

The problem of the effect of the benzene ring, (either as such or when it contains various constituents), on the frequencies of the dinitromethyl group, as well as of the interaction between dinitromethyl anion and benzene ring, has remained open. Any attempt at prediction regarding such interaction between anion and benzene ring is complicated by possible conjugation:



(1)

Frequencies Characteristic of the NO_2 Group and Anion of Dinitromethyl Aromatic and Heterocyclic Compounds

Experiment No.	Compound	Mp*, °C	Absorption frequencies, cm^{-1}							
			CH valence vibrations in the dinitromethyl group	NO_2 group valence vibrations				Dinitromethyl anion		
				In side chain		In ring				
				Antisymmetric	Symmetric	Antisymmetric	Symmetric			
1	Phenyldinitromethane		Unobserved	1587 s	1343 m	—	—	None	1198 m	None
2	K-salt of o-methoxyphenyldinitromethane		None	None	None	—	—	1480 s	1200 s, b	1115 m
3			Unobserved	1585 s	1348 Poor	1548 s	1362 s	None	None	None
4	K salt		None	None	None	1548 vs	1361 s	1488 s	1233 vs, b	1145 vs
5	1, 3-bis(dinitromethyl) benzene	97—98 (decomp)	3030 m 3040 cp	1580 vs, b	1330 s	—	—	None	None	None
6	Di-K salt	—	None	None	None	—	—	1478 s 1512 s	1222 vs, b	1128 s
7	p-Chlorophenyldinitromethane		3030 m	1580 vs	1330 s	—	—	None	None	None
8	K-salt		None	None	None	—	—	1486 m	1221 s	1138 m
9	K-salt of o-methoxyphenyldinitromethane	—	None	None	None	—	—	1483 m	1185 s	1105 vs
10	2-Nitro-5-dinitromethylfuran	53—54 (decomp)	3030 s	1587 vs	1327 s	1517 s 1552 s	1367 vs	None	None	None
11	K salt	—	None	None	None	1527 s	1362 s	1488 m	1215 s	1145 m
12	2-Nitro-5-dinitromethylthiophene	71—72 (decomp)	3010 s	1585 vs	1327 m	1550 m	1350 vs	None	1210 s	None
13	K salt	—	None	None	None	1562 m	1350 m	1462 w 1498 vs 1500 s	1220 vs, b	1150 s
14	2-Dinitromethylpyridine	115—115.5 (decomp)	None	None	None	—	—		1235 vs, b	1130 s
15	K salt	—	None	None	None	—	—	1502 s 1478 m	1250 s, b	1137 s
16	1, 1-Dinitroalkanes [3]		—	1575±12	1333,5±3,5	—	—	None	None	None
17	Salts of 1, 1-dinitroalkanes [1]		—	None	None	—	—	1480 m	1210 s, b	1120 s

vs — very strong; s — strong; w — weak; b — broad.

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*Melting points given for compounds not previously described. These compounds were prepared from the aldoximes and N_2O_4.

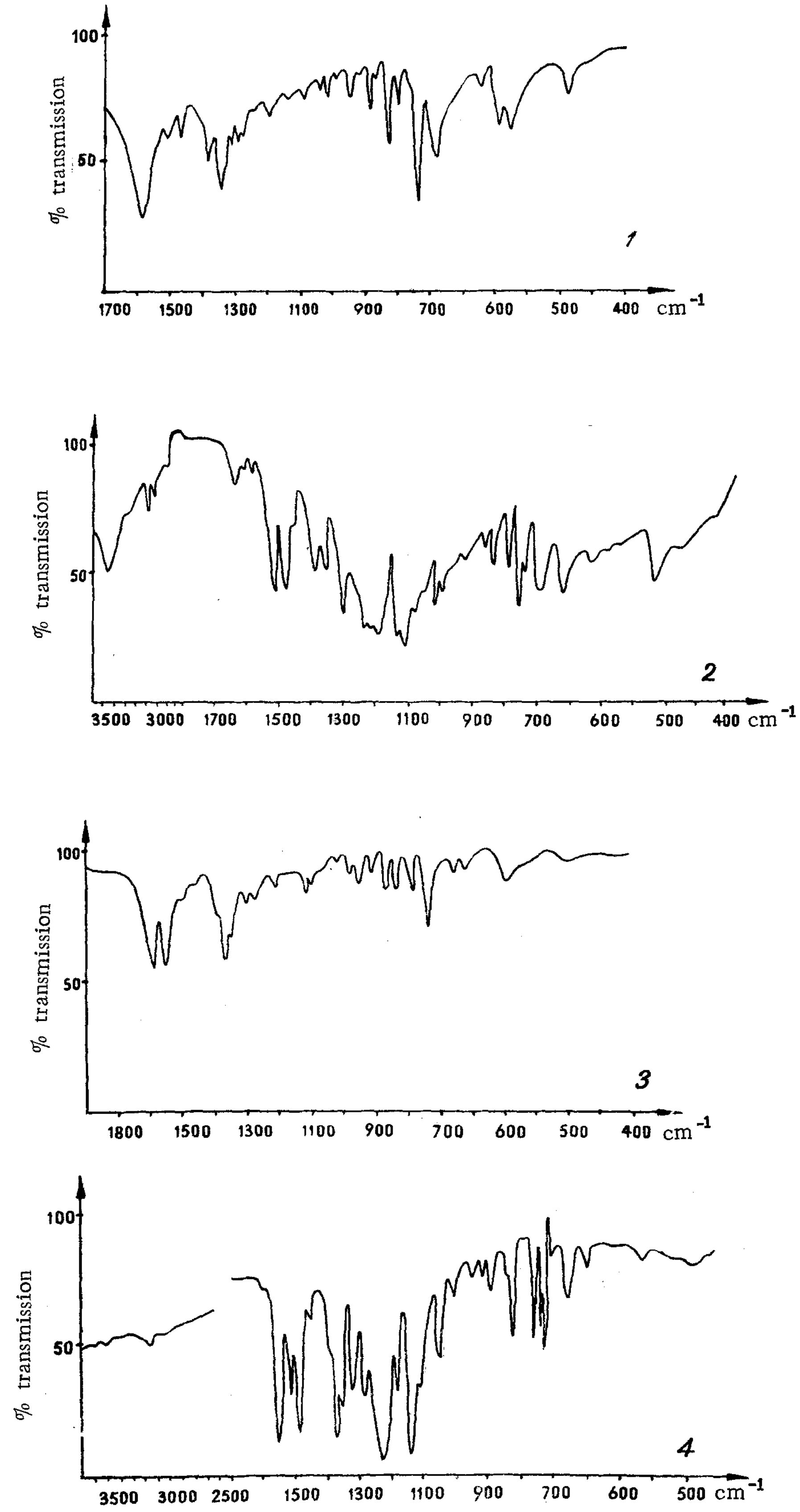
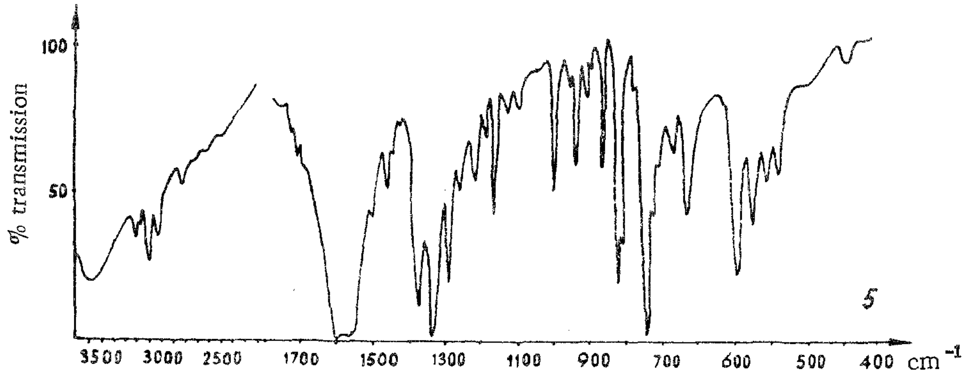


Fig. 1. IR spectra (Nos. 1-9) of aromatic dinitromethyl compounds and their salts. The numbers of the spectra correspond to the numbers in Table 2.



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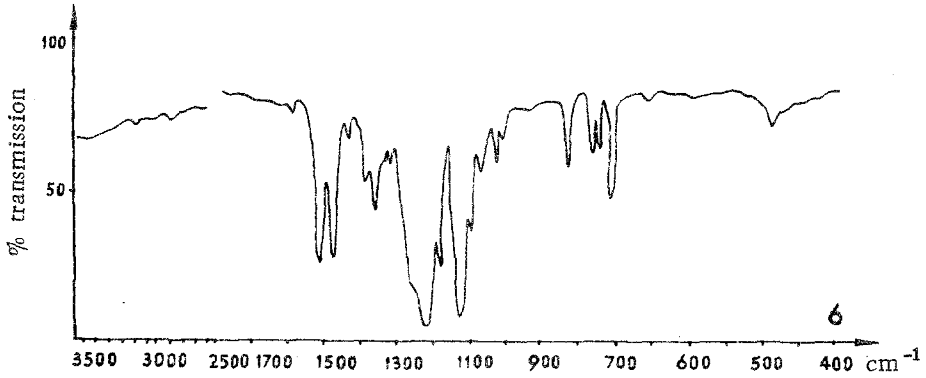

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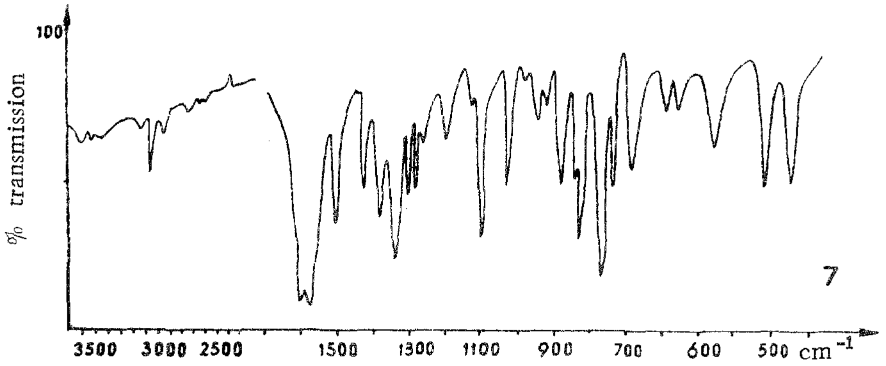

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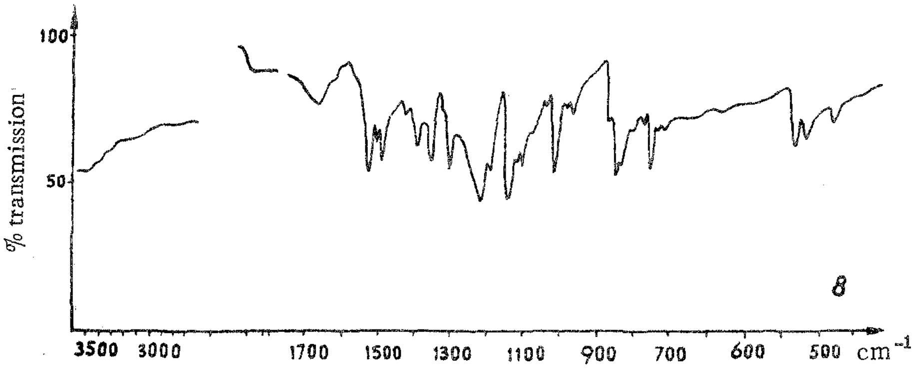

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Fig. 1 (cont'd)

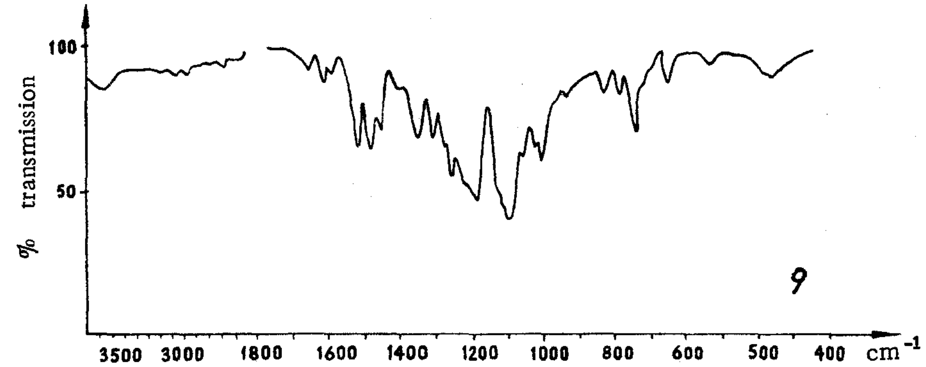

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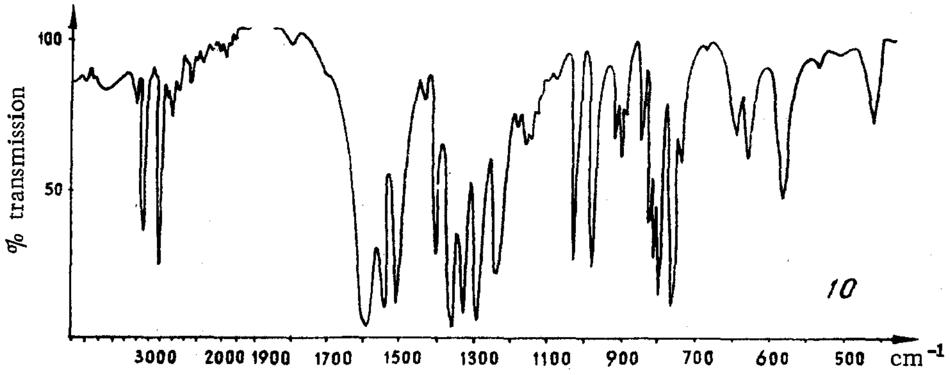
Fig. 1 (cont'd)

The only paper dealing with the cause of the presence or absence of conjugation between the dinitromethyl anion and the benzene ring is by Kamlet and Glover [4], who concluded, from the existence of a relationship between λ_{max} and σ^* for the potassium salt of phenyldinitromethane, that there is no conjugated effect in the phenyldinitromethane salt, and hence that the angle between the plane of the benzene ring and the N–C–N plane is about 90°.

First IR spectrum data of aromatic and heterocyclic compounds and their salts will be reviewed. Table 2 gives characteristic valence vibration frequencies of NO in NO_2, and of the dinitromethyl anion. There was practically never any difficulty about assigning IR spectrum frequencies to valence vibrations of NO in NO_2 of aromatic compounds. Review of Table 2 data shows that the NO valence vibration absorption bands of the NO_2 groups in free dinitromethyl compounds are situated in the same regions as those of saturated aliphatic dinitromethyl derivatives [3] (see columns 5 and 6 in Table 2). These results indicate the absence of conjugation between the dinitromethyl group and the benzene ring



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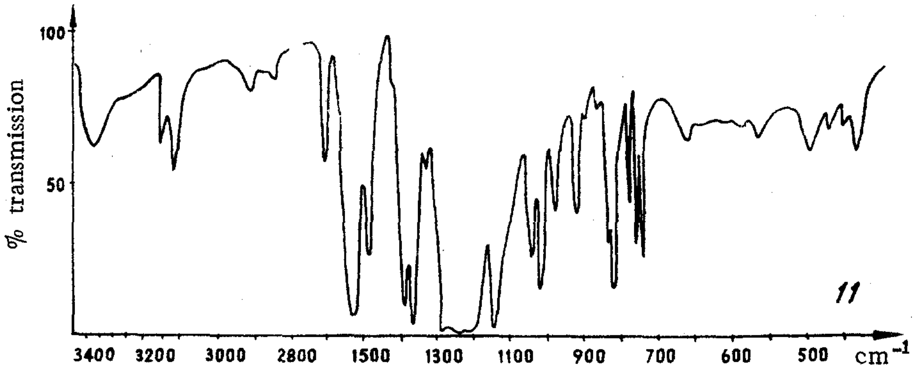

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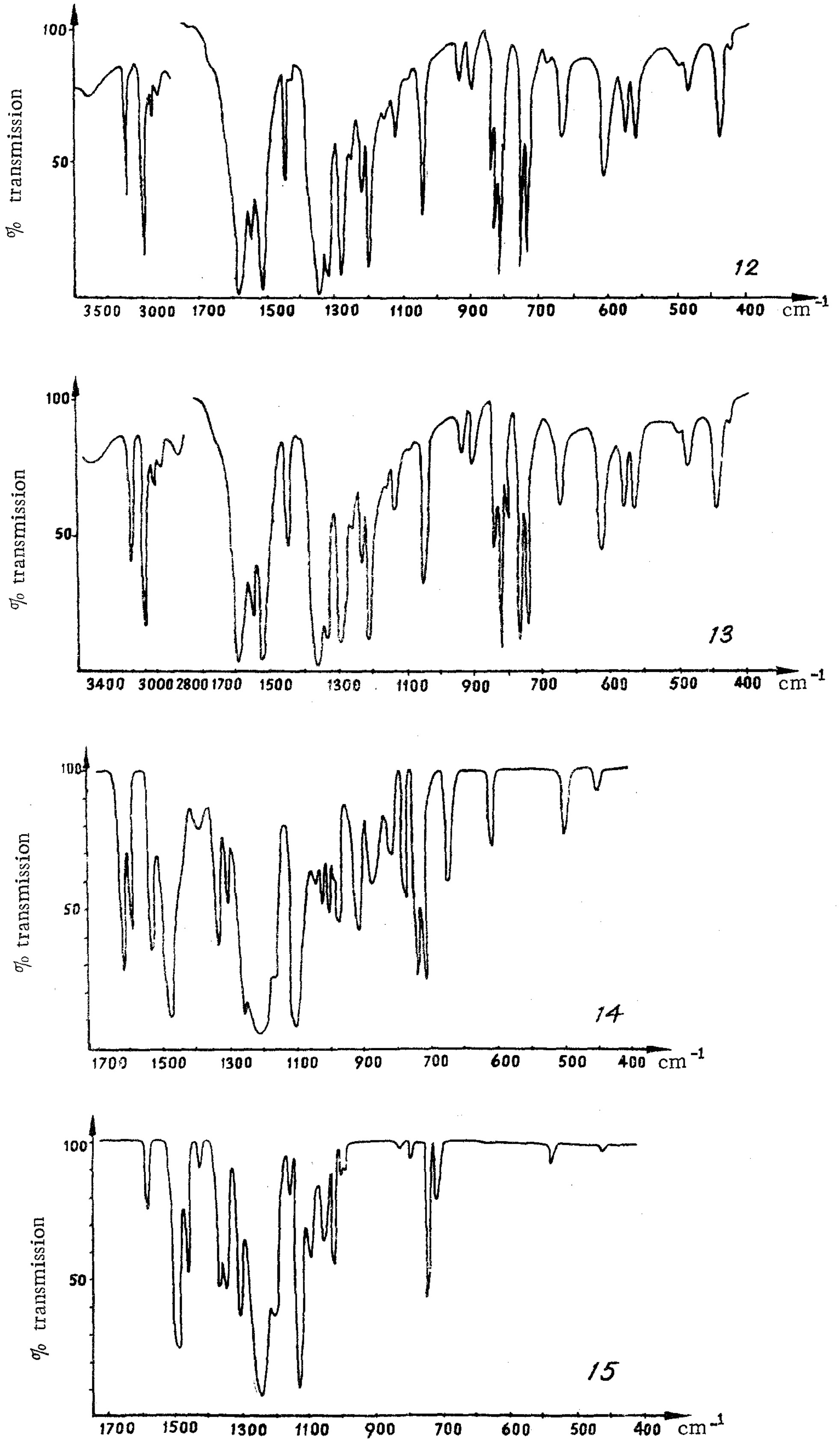
Fig. 2. IR spectra (Nos. 10-15) of heterocyclic dinitromethyl derivatives and their salts. The spectrum numbers correspond to those in Table 2.


% transmission
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1700 1500 1300 1100 900 700 600 500 400 cm^{-1}

Fig. 2 (cont'd)

in aryl dinitromethanes. On passing from dinitromethyl derivatives to their salts, the frequencies of the N–O valence vibrations inherent in the unconjugated dinitromethyl group disappear, while in the spectra of the salts, in the regions characteristic of anions of aliphatic gem-dinitro compounds [1], rather intense absorption bands appear. The last line of Table 2 gives, for comparison, frequencies for anions of aliphatic gem-dinitro compounds. The comparison shows that dinitromethyl group salts of both aromatic and aliphatic groups of compounds, have absorption bands in the same regions, of about the same intensities (qualitatively), and very similar in shape (Fig. 1). Thus the IR spectra do not show an effect of the benzene ring on dinitromethyl anion frequencies. However, it is impossible to ignore the possibility of conjugation between dinitromethyl anion and benzene ring just for that reason, for it is not known how sensitive IR spectra are to such interaction, should it actually exist.

Table 3

UV Spectra of Dinitromethyl Derivatives and Their Salts

Compound	Medium	λ_{max} (lg ε)	λ_{min} (lg ε)
Phenyldinitromethane K salt	Water	245 (3.89) 375 (4.16)	230 (3.86) 315 (3.11)
	0.1 *N* HCl	265 (3.12)	
m-Nitrophenyldinitromethane K salt	Water	260 (4.12) 370 (4.18)	230 (4.01) 315 (3.46)
	0.1 *N* HCl	255 (3.87)	240 (3.82)
1, 3-Bis(dinitromethyl) benzene di-K salt	Water	230—250 Poor (4.19—4.18) 365 (4.44)	310 (3.52)
	0.8 *N* HCl	275 (3.22)	265 (3.19)
5-Nitro-2-dinitromethylfuran K salt	Water	230 (4.03) 350 (4.28)	280 (3.66)
	Conc. HCl (~10 *N*)	300 (4.01)	250 (3.50)
5-Nitro-2-dinitromethylthiophene K salt	Water	265 (3.98) 435 (4,30)	240 (3.90) 325 (3.44)
	Conc. HCl (~10 *N*)	310 (3.99)	250 (3.60)

It is important to note that, as a rule free dinitromethyl aromatic compounds do not have absorption bands in those regions. The actual frequencies of the N–O valence vibrations in the dinitromethyl group (see above) either coincide with, or are near the corresponding ones of gem-dinitroalkanes. So IR spectra are quite suitable for identifying aromatic dinitromethyl compounds and their salts.

The authors assumed that the regularities found would also hold for heterocyclic nitro derivatives. Actually, when investigating the structures of ring-nitrated dinitromethyl derivatives of furan and thiophene, their IR spectra were observed to have the very absorption bands mentioned above (Table 2 and Fig. 2). The free compounds have N–O valence vibration absorption bands in the NO_2 groups (~ 1585 and ~ 1330 cm^{-1}), but on passing to the salts, these bands vanish and new ones, characteristic of the dinitromethyl anion, appear (see Table 2, column 10).

The presence of a nitro group in the ring is confirmed by NO valence vibration absorption bands of NO_2 groups (1530 and 1350 cm^{-1} regions), which are non-conjugated and conjugated with the ring. This obtains in both free compounds and in their salts. The high intensity of the symmetric valence vibration of N–O in NO_2, characteristic of nitro group conjugation [5], speaks for the correctness of assigning these absorption bands to the nitro group [5].

Table 2 and Fig. 2 give experimental data for free 2-dinitromethylpyridine and its potassium salt. It is clear from these data that 2-dinitromethylpyridine exists as an internal salt.* The authors deduced internal salt formation from the occurrence of absorption bands, characteristic of the dinitromethyl anion (see Table 2, column 10), and the lack of absorption bands in the 3000, and 1575, 1330 cm^{-1} regions, (Table 2, columns 5-7), characteristic of valence vibrations of, respectively, C–N and N–O in the dinitromethyl group.

The results of the present work, and comparison of the data obtained with those in the literature indicate the equality of the two nitro groups in the dinitromethyl anions of aromatic and heterocyclic compounds. This is deduced from the spectra of salts containing frequencies characteristic of the anion of 1, 1-dinitroalkanes, and lacking

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*For example, Kamlet and Dacons [6] found such aliphatic internal salts to exist in the case of 2, 2-dinitroethylamine and its derivatives.

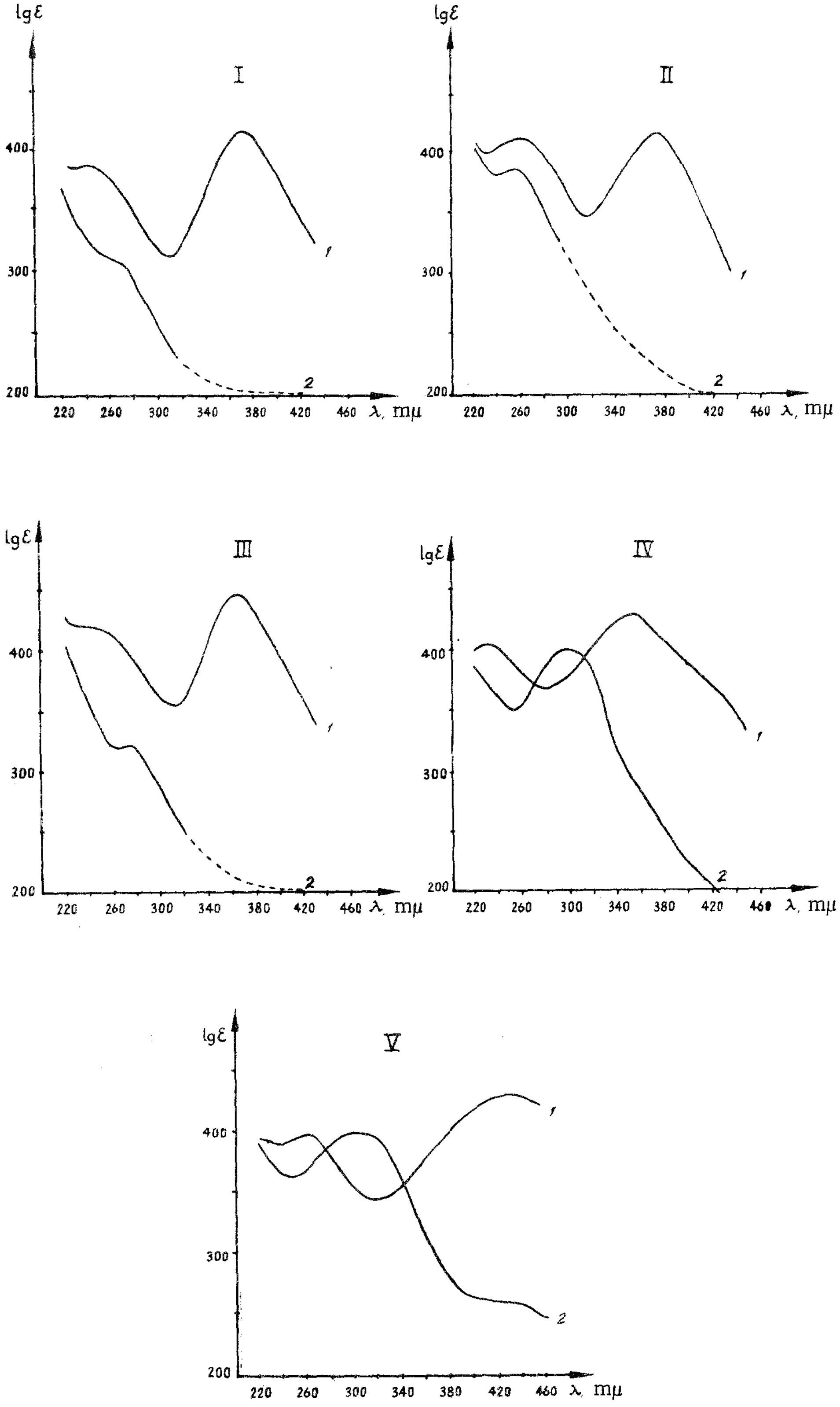

Fig. 3. UV spectra of dinitromethyl derivatives in aqueous solution: I) phenyldinitromethane; II) m-nitrophenyldinitromethane; III) 1, 3-bis(dinitromethyl) benzene; IV) 5-nitro-2-dinitromethylfuran; V) 5-nitro-2-dinitromethylthiophene; 1) anion spectrum; 2) spectrum of dinitromethyl derivative.

frequencies characteristic of valence vibrations of N–O, both in the non-conjugated NO_2 group, and in the charged mononitro group (NO_2^-) [7]. So both nitro groups participate in salt formation, just as obtains with aliphatic compounds [1].

It is important to note, that the C–H valence vibration frequency in the dinitromethyl group of aromatic and heterocyclic compounds shows up well in IR spectra, and is rather more intense than for aliphatic dinitromethyl derivatives.

The plotting was done with a UR-10 double-beam IR spectrophotometer. Spectra were observed for solids in KBr discs.

The UV spectra will now be dealt with. UV spectra of aqueous solutions of dinitromethyl compounds were measured over 220-400 mμ. First of all the spectra of the salts of these derivatives were determined in aqueous solution. Then the spectra of the dinitro derivatives were determined, after acidifying the solution with mineral acid, till dissociation of the free dinitro compound was suppressed. For benzene derivatives, 0.1-0.8 N mineral acid solution is acid enough, but for furan and thiophene derivatives 10 N hydrochloric acid is required, indicating the high acid strengths of these latter.

Table 3 and Fig. 3 give quantitative data for UV spectra of dinitromethyl compounds. A SF-4 spectrophotometer and a 1-cm cell was used for the plotting.

Table 3 shows that all salts of dinitromethyl derivatives have a longwave absorption maximum (λ = 350-375, 435 mμ, lg ε = 4.10-4.50). The appearance of this absorption band with such a high extinction coefficient can be ascribed to the presence of the dinitromethyl anion, the actual absorption being governed by Beer's law. So on the one hand this absorption band can be used to identify the dinitromethyl group anion, and on the other to determine quantitatively compounds containing that group.

If solutions of the salts are acidified enough, the longwave maximum vanishes, and this is regarded as full repression of dissociation of the dinitromethyl group. That the compounds under investigation are not decomposed under such conditions, can be inferred from the reversibility of the disappearance of the longwave absorption band, the band reappearing on decreasing solution acidity.

The new data obtained have been interpreted on a basis of Kamlet and Glover's results [4]. These latter authors showed that the UV spectra of 1, 1-dinitroalkanes have a maximum at 379+ 5 mμ (ε = 17 000 ± 1000). Introduction of an electronegative groups into these compounds at position 2 results in hypsochromic (shortwave) shift of the absorption maximum. At the same time salts of 3-substituted 1, 1-dinitro-2- propene have 2 maxima: 313-326 mμ (ε = 16 000-20 000) and 395-410 mμ (ε = 8400-10 000), or one longwave maximum of rather high intensity.

The data of Table 3 show that all aromatic dinitromethyl derivatives have an absorption maximum in the 365-375 mμ region. That is to say, salts of aromatic dinitromethyl derivatives do not exhibit spectral features characteristic of compounds where the dinitromethyl anion is conjugated with the double bond [4]. One such is the salt of 5-nitro-2-dinitromethylfuran.

The potassium salt of 5-nitro-2-dinitromethylthiophene is an interesting exception. It has an absorption maximum at 435 mμ, so, according to its UV spectrum, dinitromethyl anion and thiophene ring are conjugated. The nature of the conjugation in this and related compounds is at present under investigation.

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