INFRARED SPECTRA AND THE STRUCTURE OF SALTS OF IMIDAZOLES

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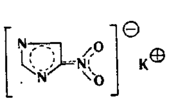
The IR spectra of nitro- and polynitroimidazoles, and their salts are investigated. Salt formation with nitroimidazoles is shown to involve one nitro group, with conversion of the imidazole ring to an isoimidazole one. Assignment of frequencies to valence vibrations of NO in charged and uncharged NO_2 groups, and to skeleton vibrations of the ring, is made for nitroimidazoles, so that these data can be used to identify newly synthesized compounds.

The IR spectra of imidazole, some derivatives of it [1–4], benzimidazoles [5, 6], and heteroaromatic systems resembling them [7], have been described in the literature. Regarding the IR spectra of nitro derivatives of imidazole, the literature records only the spectra of 2-nitro- and 4(5)-nitroimidazoles [8].

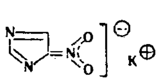
The present work is devoted to a study of the spectra of nitroimidazoles and the occurrence of regularities which can be used to identify nitro compounds of the imidazole series. In addition, work on the foundations of the particular IR spectra considers the structure of salts of mono- and polynitroimidazoles.

It is known that when anions of imidazoles are formed, the negative charge does not remain on the nitrogen atom from which the proton disengages, but is distributed over the entire ring, due to the aromaticity of the anion. In imidazole nitro derivatives, nitro groups can also participate in distribution of the anion's negative charge, e.g:



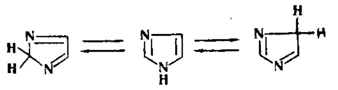
However the imidazole ring and the nitro group can participate to a greater or lesser extent in this delocalization. Then the structure of the salt will approximate one of the following structures:


II


III

In the case of salt formation by the ring (II), only an insignificant shift of the N—O valence vibrations band would be expected, as for any conjugation with an uncharged nitro group [9]. The actual formation of salts by the nitro group* (III) must result in the appearance in the spectra of absorption bands characteristic of the charged NO_2 group (region ~1180 and 950 cm^{-1})* [13, 14], and disappearance of N—O valence vibrations absorption bands in the uncharged nitro group.

Furthermore, formation of a salt by the nitro group is connected with conversion of the imidazole ring to an isoimidazole one, which can give rise to changes in the IR spectra.



Bands characteristic of the imidazole and isoimidazole rings are reported in [6]. The authors assign the band in the 1502 cm^{-1} region to imidazole ring skeleton vibrations, and bands in the 1485 cm^{-1} region and 1594 and 1563 cm^{-1} regions can be assigned to vibrations of 2N- and 4N-isoimdiazole rings respectively.

It is difficult to assign frequencies in the imidazole series, due to the powerful effect of substituents in the imidazole ring on the positions and intensities of many absorption bands. Obviously this indicates that imidazole derivatives are not very much characterized by absorption band frequencies.

Careful analysis of the spectra of a large number of nitro derivatives of imidazole, as well as of literature data, made it possible to assign frequencies to NO valence vibrations in the charged and uncharged nitro group, and to skeleton vibrations of the imidazole ring. Assignment of frequencies to NO valence vibrations in the uncharged NO group is aided by the fact that these vibrations are rather intense. In addition, the antisymmetric valence vibration lies in the 1520–1650 cm^{-1} region, where there are no other sufficiently intense absorption bands. The table gives frequency assignment data.

Assignment of absorption bands to NO valence vibrations in mononitroimidazoles (compounds nos. 2–12) proceeded on the basis of comparison of spectra of free nitroimidazoles and their salts. It can be seen from the figure that in the case of 4(5)-nitroimidazole and tabulated data for its derivatives, on passing from free nitroimidazoles to their salts, the NO valence vibration bands in the uncharged NO_2 group (regions

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*A similar structure is put forward for salts of nitropyrroles [10, 11].

*The regions given are characteristic of saturated aliphatic compounds. However, as was shown in a paper [12], conjugation is practically without effect on the positions of bands due to N—O vibrations in the charged nitro group.

Table

Absorption Bands of N – O on the NO_2 Group, and Bands of Imidazole Ring Skeleton Vibrations

Experiment no.	Compound	Mp, °C (literature values)	Absorption bands cm^{-1}				
			N–O in the group NO_2				Imidazole ring, skeletal
			Uncharged NO_2		Charged NO_2		
			Anti-symmetric	Symmetric	Anti-symmetric	Symmetric	
1	2	3	4	5	6	7	
1	Imidazole	88–90 (88–90[15])					1584 medium, 1550 strong, 1502 strong, 1485 strong 1454 very strong, 1332 very strong
2	4(5)-Nitroimidazole	308–310 (313[16]; 308[17])	1561 strong	1344 strong			1516 very strong, 1504 very strong, 1448 very strong
3	1-Methyl-4-nitroimidazole	133–134 (135[18])	1556 strong 1539 strong	1333 strong			1494 strong, 1484 dense, 1435 strong
4	1-Methyl-5-nitroimidazole	54–55 (55[19])	1545 strong 1529 strong	1365 strong			1491 strong, 1478 weak, 1448 medium
5	Na salt of 4(5)nitroimidazole	*			1173 very strong 1160 very strong	950 medium	1550 weak, 1502 dense, 1490 very strong, 1440 very strong
6	2-Iodo-4(5)-nitroimidazole	277–280*	1544 strong 1526 strong	1366 very strong			1488 very strong, 1420 medium
7	2,4(5)-Di-iodo-5(4)nitroimidazole	225–226.5*	1545 very strong	1354 very strong			1504 very strong, 1456 very strong
8	1-Methyl-2,3-di-iodo-5-nitroimidazole	205–207*	1526 strong	1334 strong			1448 strong
9	K salt of 2,4(5)-di-iodo-5(4)nitroimidazole**	231.5–232.5*			1173 very strong	973 medium	1469 strong
10	2-Nitroimidazole	281–283* (287[21]; 284[8, 22])	1540 medium 1518 medium	1362 very strong			1492 very strong, 1423 medium

Table (cont'd)

1	2	3	4	5	6	7	8
11	1-Methyl-2-nitroimidazole	102—103* (100—102[17])	1538 medium	1357 very strong	—	—	1504 very strong 1486 very strong
12	Na salt of 2-nitroimidazole	71—72*	—	—	1197 medium	1062 very strong	1472 medium, 1448 strong
13	4,5-Dinitroimidazole	185—188*	1548 strong 1532 strong	1358 very strong 1326 very strong	—	—	1572 dense, 1499 strong 1458 strong
14	1-Methyl-4,5-dinitroimidazole	73—75*	1541 strong	1356 strong 1328 strong	—	—	1506 strong, 1468 strong 1426 medium
15	K salt of 4,5-dinitroimidazole	255—258*	1528 medium	1366 strong	1187 strong	960 medium (?)	1550 dense, 1498 strong 1478 strong, 1458 very strong
16	2-Methyl-4,5-dinitroimidazole	207—208*	1554 dense 1523 very strong	1334 strong	—	—	1405 medium
17	1,2-Dimethyl-4,5-dinitroimidazole	49—50*	1536 very strong	1346 medium 1320 medium	—	—	1476 medium, 1435 medium,
18	K salt of 2-methyl-4,5-dinitroimidazole	*	1530 strong	1341 strong	1197 very strong	1108 medium	1494 dense 1479 very strong 1459 medium 1440 medium
19	2,4(5)-Dinitroimidazole	273—274* (266—268[17])	1554 very strong 1517 very strong	1350 very strong	—	—	1435 medium
20	1-Methyl-2,5-dinitro-4-iodoimidazole	111—113*	1586 medium 1544 strong	1325 very strong	—	—	1498 strong 1466 weak
21	1-Methyl-2,4,5-trinitroimidazole	81.5—82.5*	1582 very strong 1554 very strong	1368 strong 1336 very strong	—	—	1508 very strong
22	K salt of 2,4,5-trinitroimidazole	240 (decomp.)*	1541 very strong 1521 dense		1120 medium (?)	— (?)	1476 very strong 1435 medium
23	1-Methyl-5-nitro-4-trinitromethylimidazole	128—130*	1624 very strong 1614 very strong 1600 very strong *** 1524 very strong	1354 strong 1354 strong 1350 strong	—	—	1475 medium

Table (cont'd)

1	2	3	4	5	6	7	8
24	1,5-Dimethyl-2-nitro-4-trinitromethylimidazole	110—111.5*	1626 very strong *** 1606 strong 1596 very strong 1556 strong	1340 very strong 1308 very strong	—	—	1507 strong, 1445 medium 1418 medium
25	2-Nitro-4(5)-methyl-5(4)-trinitromethylimidazole	112 (medium)*	1636 very strong *** 1618 dense 1608 very strong 1558 very strong	1335 strong 1292 strong	—	—	1515 strong, 1488 dense 1440 medium
26	1-Methyl-2,5-dinitro-4-trinitromethylimidazole	136—137*	1633 very strong *** 1621 very strong 1598 very strong 1581 very strong 1538 very strong	1380 medium 1326 very strong 1298 strong	—	—	1501 very strong
27	K salt of 2,5(4)-dinitro-4(5)trinitromethylimidazole	142 (medium)*	1631 very strong *** 1619 very strong 1598 very strong 1548 strong	1354 strong 1320 very strong 1299 strong	1200 medium	854 medium	1494 very strong 1424 medium 1480 very strong
28	Ammonium salt of 2,5(4)-dinitro-4(5)-trinitromethylimidazole	135 (decomp.)*	1633 very strong *** 1617 very strong 1601 very strong 1552 strong	1358 strong 1322 very strong 1300 medium	1198 medium	846 medium	1494 very strong 1417 very strong 1480 very strong
29	1,4(5?)-Dinitroimidazole	91.5—92.5*	1642 very strong (N–NO_2) 1554 strong (C–NO_2)	1332 very strong 1286 very strong (N–NO_2) 1354 medium (C–NO_2)	—	—	1519 very strong, 1483 strong
30	1,4(5?)-Dinitro-2-methylimidazole	121.5—122*	1647 very strong (N–NO_2) 1567 very strong 1548 dense (C–NO_2)	1316 very strong 1286 very strong (N–NO_2) 1356 medium (C–NO_2)	—	—	1518 very strong, 1434 medium

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*The method of preparation will be described in a later paper, being prepared for publication.

**The spectrum has a band at 1640 cm^{-1}, ascribed to absorbing water.

***All 3 bands are assigned to N–O antisymmetric valence vibrations in the trinitromethyl group.

~1550 and ~1350 cm^{-1}) vanish, and NO vibration absorption bands in the charged NO_2 group (about 1180 and 950 cm^{-1}) appear.

It should be noted that with salts of mononitroimidazoles, any selective absorption is absent from the 1550 and 1350 cm^{-1} regions, which at about 1180 and 950 cm^{-1}, weak and medium intensity absorption bands are sometimes seen even with the free compounds, these being considerably strengthened on passing to the spectra of the salts.

Differences found for imidazole and isoimidazole rings in the IR spectra of arylimidazoles [6] did not appear in the case of mononitroimidazoles. Regarding the analytical features of derivatives of mononitroimidazoles and their salts, it is to be mentioned that they show a strong stable band in the 1000 cm^{-1} region, lacking with all polynitro- and 2-nitroimidazoles. Furthermore, in the 400–700 cm^{-1} region (KBr prism), mononitroimidazoles have two stable bands in the 655 (strong) and 610 (medium) cm^{-1} regions, which are lacking with the rest of the derivatives.*

N-Nitroimidazoles (compounds nos. 29 and 30), can be identified by the NO antisymmetric vibrations band in the nitroamino group (region 1640 cm^{-1}). In the regions ~1330 and 1280 cm^{-1}, the band of symmetric vibrations is split into two.

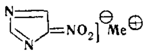
Assigning absorption bands in IR spectra of polynitroimidazoles (2 or more nitro groups) was also carried out by comparing the spectra of the free nitro compounds with those of their salts. On passing to the salts, one absorption band vanishes in each of the 1550 and 1360 cm^{-1} regions, and bands appear in the same region as in mononitro derivatives (compound 15), or are somewhat displaced (compounds nos. 18, 22, 27, 28).

In the case of salts of dinitroimidazoles, it was also impossible to find spectrum indications of the isoimidazole ring [6]. Absorption bands characteristic of the isoimidazole ring, were found only with salts of dinitrotrinitromethylimidazole (compounds nos. 27, 28), and salts of trinitroimidazole (compound no. 22). Free polynitroimidazoles with the ordinary imidazole ring have a strong absorption band of ring skeletal vibration somewhat above 1500 cm^{-1}, their salts below 1500 cm^{-1}, sometimes splitting into 2 bands.

A characteristic peculiarity of the spectra of nitroimidazoles is splitting of the N—O antisymmetric valence vibrations absorption bands in the nitro group into 2, and sometimes 3 bands, independent of the number of nitro groups. Hence it is impossible to judge the number and positions of nitro groups in the imidazole ring from the IR spectra. Measurement of the total intensity of the NO antisymmetric valence vibrations would probably be an effective way of determining the number of nitro groups.

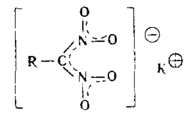
The presence of a trinitromethyl group in the imidazole ring leads to the appearance of 3 absorption bands in the 1600–1630 cm^{-1} region, and as a rule, two in the region 1300–1325 cm^{-1}, when the 1300 cm^{-1} band is considerably weaker than the 1325 cm^{-1} one. The presence of such splitting can be used to identify the trinitromethyl group, since imidazole ring absorption bands are absent in this region (1600–1630 cm^{-1}).

On the basis of the absence of frequencies characteristic of the uncharged NO_2 group and appearance of frequencies of the charged NO_2^- group in the spectra of salts of mononitroimidazoles, it can be inferred that the nitro group is involved in salt formation, e.g.:

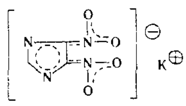


Hence salt formation must involve formation of an isoimidazole ring, though as has already been pointed out above, it did not prove possible to detect signs of the isoimidazole ring with mononitroimidazole salts.

By analogy with the structure of salts of gem-dinitro compounds [13, 23] (IV), it might have been expected that both nitro groups (V) would participate in salt formation with polynitroimidazoles, especially with 4, 5-dinitroimidazoles.

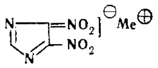


IV



V

In structure V, the equalization of the two nitro groups should proceed through the ring system of conjugated bonds, but actually that does not take place. On passing from polynitroimidazoles to their salts, the absorption bands of only 1 nitro group vanish, the bands of the other or others remain, and at the same time bands of the charged nitro group appear. Hence in salt formation with polynitroimidazoles, one nitro group is involved, e.g.:



Further, the IR spectra of salts of some polynitro compounds (compounds nos. 22, 27, and 28) show (see above) spectrum features of isoimidazoles.

Thus from a study of IR spectra of nitro derivatives of imidazoles, it is shown that salt formation with these compounds (at least in the crystalline state) always takes place at one of the nitro groups, when the imidazole ring changes to an isoimidazole one.

The IR spectra of compounds tabletted with KBr were recorded using a UR-10 spectrophotometer.

After securing constant melting point, all compounds for spectroscopic investigation were recrystallized repeatedly. Potassium salts (table, nos. 9, 15, 18, 22, 27) were prepared from the free compounds by dissolving in sodium carbonate solution, then saturating with potassium chloride. The potassium salts precipitated were separated off, and twice recrystallized from water.

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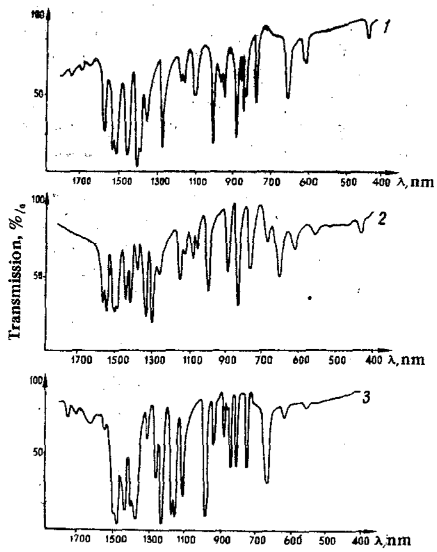
*In the case of 2-nitroimidazole, only 1 strong band, at 665 cm^{-1}, is found.



IR spectra:
1) 4(5)-Nitroimidazole; 2) 1-methyl-4-nitroimidazole;
3) Na salt of 4(5)-nitroimidazole.

The ammonium salt of 2,5(4)-dinitro-4(5)-trinitromethylimidazole (no. 28) was made by dissolving the free compound in aqueous ammonia, and purified by recrystallization from water.

Since the potassium and sodium salts of 2-nitroimidazole are readily soluble even in cold water, the sodium salt of that compound (no. 12) was made thus: 2-nitroimidazole was dissolved in an equimolecular amount of sodium ethoxide in solution, after which the solution was evaporated to dryness and dried over calcium chloride.

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