IR SPECTRA AND STRUCTURE OF 2-IMINO-1,3-DIMETHYLBENZIMIDAZOLINES

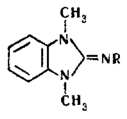
O. E. Shelepin, V. G. Sayapin, N. K. Chub,
and A. M. Simonov

UDC 547.785.5:543.422.4

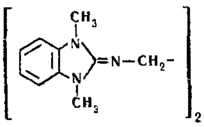
The fine structure of some N-substituted 2-imino-1,3-dimethyl-benzimidazolines is examined with the aid of IR spectroscopy. It is shown that the introduction of an alkyl or phenyl group into the imino group does not affect the C=N group or the imidazoline ring structure. In salts of 2-imino-1,3-dimethylbenzimidazoline and its N-substituted derivatives, the heterocyclic system has the benzimidazolium structure. The structure of 2-imino-1,3-dimethylbenzimidazolines in which the exocyclic nitrogen atom has electrophilic substituents which are conjugated with the heterocycle is characterized by a considerable contribution from dipolar forms, with the imidazole ring bearing a positive charge.

Continuing our investigations into the structure of 2-amino-benzimidazole and 2-iminobenzimidazoline, we investigated the structure of the conjugated guanidine system in various N-substituted 2-imino-1,3-dimethylbenzimidazolines (I). IR spectroscopy was an attractive method, since changes in the spectral characteristics in the regions of stretching and deformational vibrations depend on the electronic influence of the substituents [1] on the nature of the bonds in such systems.

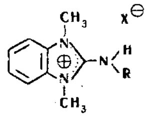
Differences in the structure of derivatives of 2-imino-1,3-dimethyl-benzimidazolines are seen in the IR spectra in the 1670-1200-cm^{-1} region. The spectrum of 1,2-ethylenedi-N,N'-(2-imino-1,3-dimethylbenzimidazoline) (II)* as well as that of 2-imino-1,3-dimethylbenzimidazoline [5] were characterized by the presence in this region of wide, intense bands corresponding to the stretching of the exocyclic C=N bond (1655-1638 cm^{-1}, and of strong stretching bands due to the orthodisubstituted benzene ring at 1602 and 1497 cm^{-1} (other bands were not considered, since they give little information concerning the structure of the heterocycle) (Fig. 1). Bands characteristic of the 2-iminobenzimidazoline structure are also present in the spectrum of 2-phenylimino-1,3-dimethylbenzimidazoline (I, R = C_6H_5) at 1658-1636 s, 1609 s, and 1500 cm^{-1} s (Fig. 1). The phenyl radical on the nitrogen of the imino group gives a sharp band at 1580 cm^{-1}.



I



II



III

Salt formation results in conversion of the guanidine fragment of structure I into the guanidium fragment. This results in the disappearance of the symmetrical and asymmetrical stretching frequencies of the guanidine C—N bond at 1250 and 1350 cm^{-1} (Fig. 1), which are present in the IR spectra of the imine I (R = H) [5], and of its N-alkyl and N-phenyl derivatives, and in the appearance of two bands at about 1410 and 1550 cm^{-1} (Fig. 2) due to symmetrical and asymmetrical stretching of the C—N bonds formed in the

---

* Since 2-methylimino-1,3-dimethylbenzimidazoline was extremely hygroscopic, [4], compound II was selected for the investigation of the structure of the alkyl derivatives of 2-imino-1,3-dimethylbenzimidazoline.

Rostov-on-Don State University. Translated from Khimiya Geterotskilicheskikh Soedinenii, Vol. 6, No. 5, pp. 674-678, May 1970. Original article submitted April 10, 1968.

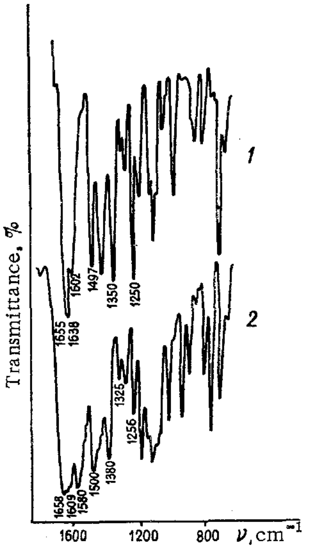


Fig. 1

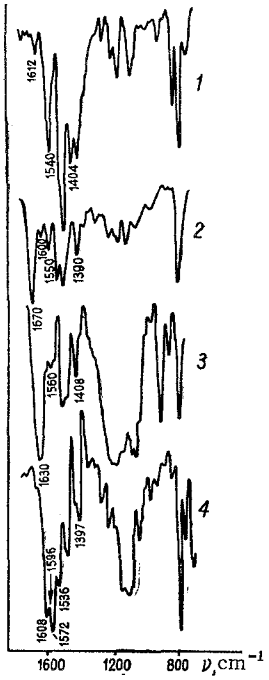


Fig. 2

Fig. 1. IR spectra: 1) 1,2-ethylenedi-N,N'-(2-imino-1,3-dimethylbenzimidazoline) and 2) 2-phenylimino-1,3-dimethylbenzimidazoline.

Fig. 2. IR spectra: 1) 1,2,3-trimethylbenzimidazolium iodide, 2) 2-imino-1,3-dimethylbenzimidazoline hydriodide, 3) 2-methylimino-1,3-dimethylbenzimidazoline sulfate, and 4) 2-phenylimino-1,3-dimethylbenzimidazoline hydriodide.

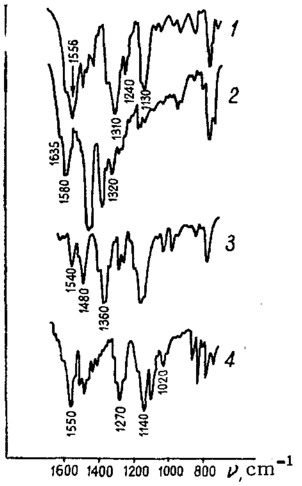


Fig. 3. IR Spectra: 1) N-2,4-dinitrophenyl-, 2) N-picryl-, 3) N-nitroso-, and 4) N-benzenesulfonyl-2-imino-1,3-dimethylbenzimidazoline.

benzimidazolium structure. These bands are also present in the spectrum of 1,2,3-trimethylbenzimidazolium iodide (Fig. 2). The increase in the frequency of the deformation vibration of the NH_2 group to 1670 cm^{-1} in the spectrum of 2-imino-1,3-dimethylbenzimidazoline hydriodide [III, R = H, X = I (Fig. 2)] indicates that its structure is more planar in comparison with the normal amino group as a result of conjugation with the ring. (The δ_{NH_2} band in the spectra of aliphatic and aromatic amines [6] lies in the 1560-1640-cm^{-1} region.) The intense band at 1630 cm^{-1} in the spectrum of 2-methylimino-1,3-dimethylbenzimidazoline sulfate [III, R = CH_3, X = HSO_4 (Fig. 2)] is due to the deformation vibrations of the NH group in the C=$NHCH_3$ fragment. In the spectrum of 2-phenylimino-1,3-dimethylbenzimidazoline hydriodide (III, R = C_6H_5, X = I), the intense bands at 1608, 1596, and 1572 cm^{-1} are due to vibrations of the o-phenylene radical, the NH group, and the phenyl radical, respectively.

The IR spectrum of 2-picrylimino-1,3-dimethylbenzimidazoline (I, R = picryl) shows two intense bands at 1580 and 1320 cm^{-1} (Fig. 3), corresponding to the asymmetrical and symmetrical stretching of the nonionized nitro groups [7]. The band at 1635 cm^{-1} is due to the vibration of the exocyclic C=N bond. However, in the spectrum of the 2,4-dinitrophenyl derivative (Fig. 3), in addition to the bands due the nonexcited nitro group at 1310 and 1556 cm^{-1}, strong bands occurs at 1130 and 1240 cm^{-1}, corresponding to the symmetrical and asymmetrical stretching vibrations of the ionized nitro group [8]. In addition, above 1585 cm^{-1} the spectrum of this compound contains no bands whatsoever. These results contraindicate the imino structure for this compound, whose molecule apparently has a betaine-like structure (IV), the heterocycle having the benzimidazolium structure. This is also shown by its

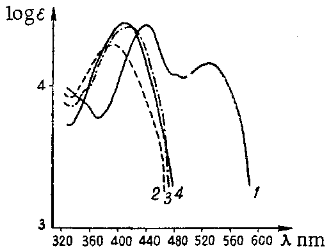
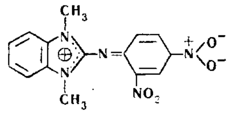
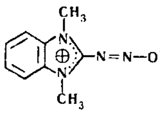


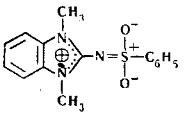
Fig. 4. UV spectra of 2-picrylamino-1,3-dimethylbenzimidazoline in: 1) an acetone solution of NaOH and 2) acetone; and of 2-(2,4-dinitrophenyl)imino-1,3-dimethylbenzimidazoline in: 3) acetone and 4) an acetone solution of NaOH.

behavior toward alkali. There is no deepening of its color in alkaline acetone solution [the UV spectra of the neutral and alkaline solutions are identical (Fig. 4)], while the action of alkali on acetone solutions of the picryl derivative results in a deep coloration, attributable to the ionized molecule of the sodium salt (the UV spectra of alkaline solutions show a strong bathochromic shift in comparison with neutral solutions).

The steric effect of a single nitro group situated in the position ortho to the nitrogen atom of the imino group is apparently insufficient for the complete departure of the dinitrophenyl radical from the plane of the heterocycle, while the two ortho-nitro groups of the picryl radical make this a possibility. A similar difference between the dinitrophenyl and picryl radicals has been mentioned earlier. Thus, the absorption band caused by the interaction of the NH group with the unsubstituted phenyl nucleus is present in the UV spectrum of 2,4-dinitrodiphenylamine [9], and absent in that of 2,4,6-trinitrodiphenylamine [10]. The plane of the benzene ring in the compound under consideration is inclined at an angle of 65° [11].


IV


V


VI

Thus in I (R = picryl) the radical is prevented from conjugating with the heterocycle and is able to influence it only by an inductive mechanism. The appearance of an intense blood-red color in the crystalline state (the color of the solution is yellow) is apparently due to the formation of a charge transfer complex.

The benzimidazoline structure may thus be converted into the benzimidazolium structure merely by the introduction of electron-accepting substituents on the exocyclic nitrogen atom in π, π-conjugation with the heterocycle. This condition is complied with in 2-nitroso- and 2-benzenesulfonylimino-1,3-dimethylbenzimidazoline, which may be described by the intraionic structures V and VI, respectively. The IR spectra of both these compounds (Fig. 3) do not show any significant absorption in the regions characteristic for the exocyclic C=N bond. In the spectrum of V, the N=O band is shifted to 1360 cm^{-1} compared with 1500-1430 cm^{-1} characteristic for the N=O bond in normal nitrosoamines [7]. The presence of structure VI is indicated by the long-wavelength shift of the bands due to asymmetrical (1271 cm^{-1}) and symmetrical (1140 cm^{-1}) vibrations of the SO_2 group in conjunction with the separate band due to stretching vibrations of the S=N at 1020 cm^{-1}, as opposed to 817 cm^{-1} for S–N [12].

In the IR spectra of the N-acetyl, N-benzoyl, and N-p-nitrobenzoyl derivatives of 2-imino-1,3-dimethylbenzimidazoline, the bands for the carbonyl group are shifted to much lower frequencies. The most intense band in the spectrum of the acetyl derivative (Fig. 5) in the solid phase occurs at 1526 cm^{-1}, while in solution its position is shifted to higher frequencies (1548 cm^{-1} in benzene, and 1550 cm^{-1} in chloroform). In benzene solution in the presence of acetic acid, it is shifted to 1566 cm^{-1}, i.e., in acid solution the double bond character of the C=O bond is increased. The absence of any clearly apparent absorption above 1600 cm^{-1} suggests that in this compound the degree of multiplicity of the exocyclic C=N bond is small. 2-Acetylimino-1,3-dimethylbenzimidazoline hydrochloride shows a normal amide spectrum (Fig. 5), having an electrophilic substituent on the nitrogen atom. The band at 1724 cm^{-1} corresponds to the stretching vibrations of the C=O group (am-

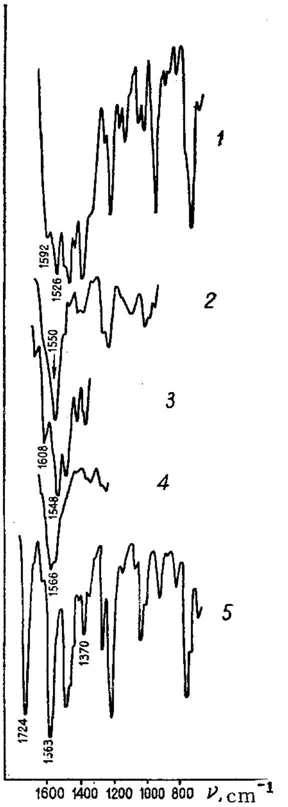
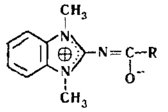
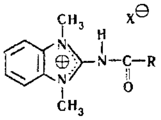


Fig. 5. IR Spectra of 2-acetylimino-1,3-dimethylbenzimidazoline: 1) as a paste in Vaseline oil, 2) in chloroform, 3) in benzene, 4) in a mixture of benzene and acetic acid; and 5) its hydrochloride as a paste in Vaseline oil.

ide I), and the bands at 1563 and 1370 cm^{-1} are due to amide II and amide III, respectively. The band at 1550 cm^{-1}, which is characteristic of the benzimidazolium structure, is apparently included in the intense amide II band. A similar picture is also seen in the spectra of the N-benzoyl and N-p-nitrobenzoyl derivatives. Thus, N-acyl derivatives of 2-imino-1,3-dimethylbenzimidazoline must be assigned a structure with strong contributions by structure VII, and its hydrohalides, structure VIII.


VII


VIII

The authors thank Dr. Yu. N. Sheinker for valuable discussions and advice.

EXPERIMENTAL

2-Phenylimino-1,3-dimethylbenzimidazoline was obtained by fusing 2-anilinomethylbenzimidazole with methyl benzenesulfonate, followed by decomposition of the resulting benzenesulfonate with ammonia, mp 84° C. Found, %: C 75.9; H 6.3; N 18.0. Calculated for $C_{15}H_{15}N_3$, %: C 76.0; H 6.4; N 17.7. The hydriodide was obtained by adding a saturated solution of potassium iodide to an aqueous solution of the benzenesulfonate, mp 230° C. Found, %: N 11.4; I 35.2. Calculated for $C_{15}H_{15}N_3 \cdot HI$, %: N 11.5; I 34.7.

2-Imino-1,3-dimethylbenzimidazoline hydriodide was prepared by the reaction of 2-amino-1-methylbenzimidazole with methyl iodide, mp 254-255° C [2].

1,2,3-Trimethylbenzimidazolium iodide was synthesized by the reaction of methyl iodide with 1,2-dimethylbenzimidazole, mp 259° C [3].

2-Acetylimino-1,3-dimethylbenzimidazoline hydrochloride was prepared by passing dry HCl into a solution of 2-acetylimino-1,3-dimethylbenzimidazoline in dry benzene, mp 247° C. Found, %: N 17.6; Cl 15.0. Calculated for $C_{11}H_{13}N_3O \cdot HCl$, %: N 17.5; Cl 14.8.

The preparation of the remaining compounds has been described elsewhere [4].

The IR spectra were obtained using the compounds in the solid state (as pastes in Vaseline oil), and, in a few cases, using their solutions (as thin films). The measurements were carried out on UR-10 and IKS-14 spectrophotometers in the 400-4000-cm^{-1} region, using KBr, NaCl, and LiF prisms. The UV spectra were measured on an SF-4A spectrophotometer. Acetone and solutions of NaOH in acetone were used as solvents.

LITERATURE CITED

1. E. Wilson, G. Decius, and P. Cross, Molecular Vibrations: Theory of Infrared and Raman Vibrational Spectra [Russian translation], IL, 1960.
2. N. D. Vitkevich and A. M. Simonov, ZhOKh, 30, 2868, 1960.
3. N. A. Zakharova, B. A. Porai-Koshits, and L. S. Efros, ZhOKh, 23, 1225, 1953.
4. V. G. Sayapin and A. M. Simonov, KhGS [Chemistry of Heterocyclic Compounds], 1120, 1967.
5. Yu. N. Sheinker, A. M. Simonov, Yu. M. Yutilov, V. N. Sheinker, and E. I. Perel'shtein, ZhOrKh, 2, 917, 1966.
6. K. Nakanishi, Infrared Absorption Spectroscopy, Practical Holden-Day, San Francisco, 1957, p. 45.
7. K. Nakanishi, Infrared Absorption Spectroscopy, Practical Holden-Day, San Francisco, 1957, p. 61.
8. J. E. Brown, J. Am. Chem. Soc., 77, 6341, 1955; N. Jonatan, J. Mol. Spectr., 7, 105, 1961.
9. E. E. Milliaresi and V. A. Izmail'skii, DAN, 146, 1094, 1962; ZhOKh, 35, 776, 1965.
10. E. E. Milliaresi, ZhOKh, 36, 1034, 1966.
11. E. Grison, Acta Cryst., 2, 410, 1949 [cited in 10].
12. A. Kucsman, F. Ruff, J. Kapovits, and J. G. Fischer, Tetrah., 22, 1843, 1966.