

IR SPECTRA OF ETHYL ARYLHYDRAZONOCYANOACETYL
CARBAMATES AND OF PHENYLHYDRAZONO-
-2-CYANOMETHYLBENZIMIDAZOLE

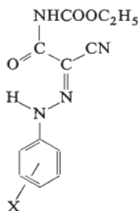
V. BEKÁREK and J. SLOUKA

Faculty of Natural Sciences, Palacký University, 771 46 Olomouc

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The IR spectra ($4000-400\text{ cm}^{-1}$) of 15 substituted ethyl arylhydrazonocycanoacetylcarbamates (Nujol, chloroform) and of phenylhydrazono-2-cyanomethylbenzimidazole (Nujol) were measured. The absorption bands were assigned with the aid of ^{15}N -isotopomers. Influence of the substituted aromatic ring on the pattern of spectra and on tautomerism in these compounds is considered.

In the earlier work¹, substituted ethyl arylhydrazonocycanoacetylcarbamates (*I-XV*) were studied by $^1\text{H-NMR}$ spectroscopy. Influence of the substituents of the aromatic ring on proton chemical shifts of the two NH groups bonded by intra- and intermolecular hydrogen bonds was examined. Moreover, the $^1\text{H-NMR}$ spectra of ^{15}N -isotopomers proved that ethyl phenylhydrazonocycanoacetylcarbamate dissolved in dimethylsulphoxide exists in the hydrazo-form, in the case of phenylhydrazono-2-cyanomethylbenzimidazole dissolved in dimethylformamide a mixture of the two tautomers (*A, B*) was detected.



I-XV

- I*, X = H
II, X = *p*-COCH₃
III, X = *p*-NO₂
IV, X = *m*-NO₂
V, X = *p*-COOH
VI, X = *p*-COOC₂H₅
VII, X = *p*-COOC₂H₅
VIII, X = *p*-CHO
VIII, X = *p*-F

- IX*, X = *p*-Cl
X, X = *p*-Br
XI, X = *p*-I
XII, X = *m*-Br
XIII, X = *m*-OCH₃
XIV, X = *p*-OCH₃
XV, X = *p*-OC₂H₅

In the last few years, a considerable attention has been focused on studies of substituent effects in the IR spectra²⁻⁴. In some cases, however, the sign of the reaction constant remains questionable². Studying substituent effects in the systems with hydrogen bond, we found that the parity of the reaction constant is predictable on the basis of the effect of hydrogen bonding upon IR frequencies of the stretching and deformation vibrations^{5,6}.

The aim of this work was to evaluate the effect of substituents of aromatic ring on the parameters of the IR spectra of compounds *I-XV*, to solve the question of tautomerism in these compounds with the aid of IR spectroscopy, and finally, to assign some absorption bands of hydrazo-group with the aid of ¹⁵N-isotopomers.

EXPERIMENTAL AND RESULTS

The preparation and properties of compounds *I-XV* and of phenylhydrazono-2-cyanomethylbenzimidazole were reported earlier¹. The IR spectra were measured on a double-beam Zeiss (Jena) spectrometer, Model UR 20, in Nujol suspensions and in chloroform solutions (cell thickness 0.1 cm).

The wavenumbers of maxima (in cm^{-1}) of *I-XV* in Nujol suspensions are listed below, the data in parenthesis refer to chloroform solutions.

I. 435 w, 503 m, 575 m, 587 m, 617 w, 686 m, 812 sh, 721 s, 755 m, 785 m, 801 w, 824 w, 846 sh, 885 sh, 902 m, 927 w, 990 sh, 1012 s, 1087 s, 1119 m, 1162 m, 1186 s, 1216 s, 1223 sh, 1297 s, 1335 m, 1365 sh, 1448 m, 1549 sh, 1556 m, 1610 s, 1679 s, 1734 sh, 1762 s, 2225 m, 3022 m, 3046 w, 3076 m, 3144 m, 3200 m, 3234 m, 3285 m, 3416 w (1720 m, 1739 sh, 1785 s, 3290 m, 3416 m).

II. 438 w, 501 w, 576 m, 589 m, 693 m, 722 m, 734 m, 755 w, 781 s, 821 sh, 845 s, 893 m, 921 m, 957 m, 979 w, 1010 sh, 1039 m, 1071 w, 1110 sh, 1127 m, 1164 sh, 1180 m, 1207 w, 1265 s, 1286 w, 1299 s, 1360 w, 1375 s, 1395 m, 1415 m, 1456 sh, 1537 sh, 1550 s, 1602 s, 1681 s, 1691 sh, 1697 sh, 1704 s, 1725 sh, 2232 m, 2988 m, 3065 w, 3117 m, 3194 m, 3227 m, 3270 m, 3406 m (1721 m, 1740 sh, 1787 s, 3293 m, 3416 m).

III. 420 m, 450 m, 494 m, 512 w, 524 w, 553 m, 570 m, 635 w, 683 sh, 695 s, 750 n, 771 m, 840 sh, 852 s, 912 m, 1038 m, 1115 m, 1164 w, 1175 m, 1207 m, 1255 sh, 1268 m, 1285 w, 1312 s, 1348 m, 1452 m, 1519 s, 1564 m, 1600 m, 1620 m, 1670 sh, 1695 sh, 1705 s, 1720 sh, 2226 m, 3090 m, 3123 w, 3165 w, 3220 m, 3240 w, 3315 m, 3413 w.

IV. 431 w, 458 m, 530 w, 568 sh, 570 m, 680 w, 698 s, 721 m, 747 s, 779 s, 804 m, 837 m, 865 w, 888 m, 908 m, 934 w, 1040 m, 1121 m, 1160 w, 1172 w, 1204 w, 1274 m, 1313 m, 1358 m, 1378 m, 1450 m, 1502 w, 1530 m, 1558 m, 1605 m, 1668 sh, 1701 s, 1705 sh, 2230 m, 3080 w, 3113 w, 3142 w, 3202 w, 3223 sh, 3230 m, 3281 sh, 3289 m, 4405 w.

V. 417 m, 447 w, 462 w, 509 m, 536 m, 562 m, 577 w, 635 w, 646 w, 680 m, 700 m, 724 w, 755 w, 778 s, 808 m, 843 m, 864 m, 913 m, 968 w, 977 w, 1038 m, 1127 m, 1175 m, 1210 sh, 1258 s, 1290 s, 1308 sh, 1321 m, 1398 w, 1422 m, 1547 m, 1607 m, 1643 sh, 1680 s, 1706 s, 1722 sh, 2232 m, 3113 w, 3198 w, 3227 m, 3295 m, 3419 w.

VI. 418 w, 470 w, 496 m, 513 m, 550 w, 635 w, 682 m, 723 m, 770 m, 842 m, 861 m, 894 w, 913 m, 1021 w, 1043 m, 1100 sh, 1113 m, 1125 sh, 1173 m, 1207 w, 1259 s, 1287 m, 1310 w, 1400 m, 1419 w, 1548 m, 1607 m, 1650 sh, 1670 sh, 1703 s, 1720 sh, 1730 sh, 2232 m, 3108 m, 3130 w, 3194 m, 3222 m, 3303 m, 3405 w, (1716 m, 1740 sh, 1788 s, 3294 m, 3417 m).

VII. 424 w, 463 w, 519 m, 540 w, 581 m, 607 w, 622 w, 682 m, 705 w, 722 m, 754 w, 779 m, 822 m, 831 w, 848 m, 911 w, 1042 w, 1115 m, 1123 w, 1170 w, 1211 m, 1272 m, 1283 m, 1300 m, 1324 w, 1503 w, 1540 sh, 1555 m, 1590 sh, 1602 m, 1680 sh, 1700 m, 1722 sh, 1761 s, 1770 sh, 2224 m, 3125 m, 3195 m, 3223 m, 3305 m, 3353 w (1724 m, 1740 sh, 1789 s, 3294 m, 3415 m).

VIII. 406 w, 464 m, 514 m, 525 w, 553 m, 576 m, 640 w, 682 sh, 695 s, 710 m, 725 w, 738 m, 764 w, 780 m, 810 m, 836 s, 845 sh, 892 sh, 912 m, 1048 m, 1115 m, 1127 w, 1160 m, 1197 w, 1220 s, 1228 sh, 1265 sh, 1287 m, 1310 s, 1403 m, 1512 s, 1558 sh, 1562 m, 1620 m, 1648 sh, 1671 m, 1705 s, 2228 s, 3077 m, 3107 m, 3162 w, 3218 m, 3242 w, 3288 m, 3411 m (1720 m, 1740 sh, 1786 s, 3292 m, 3418 m).

IX. 424 w, 456 m, 471 w, 510 s, 547 m, 576 m, 667 sh, 692 m, 713 m, 750 m, 777 s, 818 m, 837 s, 890 m, 912 m, 940 w, 1013 w, 1045 m, 1090 m, 1120 sh, 1128 m, 1165 w, 1178 m, 1205 w, 1275 m, 1300 s, 1400 m, 1505 sh, 1552 m, 1600 sh, 1607 m, 1680 sh, 1705 s, 1723 sh, 2224 m, 3070 w, 3095 w, 3113 w, 3135 m, 3198 m, 3230 m, 3300 m, 3420 w (1720 m, 1738 sh, 1787 s, 3293 m, 3413 m).

X. 435 w, 453 w, 509 m, 544 w, 574 m, 690 m, 704 w, 722 w, 764 w, 773 m, 781 w, 822 m, 838 m, 890 w, 917 m, 1009 m, 1043 m, 1071 m, 1128 m, 1178 w, 1205 w, 1274 m, 1292 sh, 1296 s, 1400 m, 1552 s, 1590 w, 1604 m, 1675 sh, 1703 s, 1721 m, 1730 sh, 2232 m, 3068 w, 3090 w, 3110 w, 3130 w, 3188 sh, 3194 m, 3228 m, 3282 m, 3395 w, 3417 w, (1721 m, 1740 sh, 1786 s, 3290 m, 3413 m).

XI. 433 w, 462 w, 508 m, 543 w, 574 m, 686 m, 702 m, 715 sh, 772 m, 782 m, 823 m, 838 m, 887 m, 913 w, 945 w, 979 w, 1005 m, 1043 m, 1060 m, 1128 m, 1160 w, 1181 w, 1203 w, 1274 s, 1293 s, 1400 m, 1505 sh, 1548 m, 1587 w, 1600 m, 1675 sh, 1692 sh, 1703 s, 1722 m, 1730 sh, 2232 m, 3123 w, 3189 w, 3227 w, 3280 m, 3395 w, 3418 w (1720 m, 1738 sh, 1786 s, 3290 m, 3415 m).

XII. 433 m, 463 w, 580 m, 600 w, 680 m, 709 m, 735 m, 781 m, 793 sh, 847 m, 867 m, 917 m, 997 w, 1045 m, 1070 w, 1090 w, 1121 m, 1169 w, 1200 w, 1271 m, 1282 m, 1312 s, 1400 m, 1419 w, 1450 m, 1500 m, 1552 sh, 1557 m, 1501 sh, 1603 m, 1670 sh, 1695 sh, 1703 s, 1723 sh, 2227 m, 3078 w, 3189 w, 3228 m, 3294 m, 3410 w (1720 m, 1739 sh, 1786 s, 3294 m, 3410 m).

XIII. 430 w, 452 w, 473 w, 530 w, 573 m, 600 m, 685 sh, 700 sh, 713 s, 751 m, 772 sh, 777 w, 788 w, 847 m, 860 m, 912 m, 933 m, 990 m, 1020 s, 1043 m, 1050 sh, 1093 sh, 1128 sh, 1145 s, 1166 m, 1189 m, 1205 s, 1261 s, 1291 s, 1322 m, 1450 m, 1505 m, 1562 s, 1605 sh, 1619 m, 1681 m, 1740 sh, 1763 s, 1785 sh, 2219, 3080 w, 3151 w, 3204 m, 3235 w, 3295 w, 3391 w, 3409 m, 3510 w (1719 m, 1738 sh, 1785 s, 3292 m, 3416 m).

XIV. 427 m, 451 w, 523 m, 553 m, 571 m, 695 m, 733 m, 782 m, 801 m, 813 m, 838 m, 896 w, 916 w, 978 w, 1025 m, 1042 s, 1115 sh, 1123 w, 1160 w, 1174 m, 1186 w, 1240 m, 1287 s, 1308 m, 1421 w, 1515 m, 1551 s, 1630 m, 1650 sh, 1695 s, 1717 s, 1725 sh, 2229 m, 3070 w, 3114 m, 3135 w, 3190 sh, 3210 m, 3231 m, 3268 m, 3383 w, 3410 w (1718 m, 1736 sh, 1783 s, 3285 m, 3412 m).

XV. 435 w, 470 w, 523 m, 547 w, 578 m, 686 m, 705 m, 733 s, 745 sh, 774 s, 807 m, 825 m, 845 m, 892 w, 918 m, 942 w, 980 w, 1048 s, 1123 m, 1173 m, 1230 sh, 1244 m, 1280 sh, 1297 s, 1325 w, 1378 s, 1422 w, 1453 s, 1514 m, 1548 s, 1555 sh, 1609 m, 1660 sh, 1688 s, 1720 s, 1730 sh, 2234 s, 3070 w, 3105 w, 3133 w, 3203 m, 3222 w, 3267 s, 3370 w, 3420 w (1721 m, 1740 sh, 1785 s, 3286 m, 3415 m).

DISCUSSION

The IR spectra of chloroform solutions of compounds *I*–*XV* show two medium bands in the 3600–3000 cm^{-1} region which we assigned to the stretching vibration

of the N—H bonds. The 3414 cm^{-1} band was ascribed to the free N—H group and the 3290 cm^{-1} band to the N—H group bonded by intramolecular hydrogen bond to the carbonyl group. Existence of this bond has been proved by $^1\text{H-NMR}$ spectra¹. In the case of the ^{15}N -isotopomer, the 3290 cm^{-1} band was down-shifted by 9 cm^{-1} . The effect of ring substitution on both $\nu(\text{N—H})$ was negligible, the shifts were within the interval of $6\text{--}9\text{ cm}^{-1}$. In the first approximation, the wavenumber of both bands increases with increasing substituent polarity. The small polar effect of substituents correlates with the distance between the free N—H group and the aromatic ring. In the case of the associated N—H group there is an agreement with the already reported relationship between $\nu(\text{N—H})_{\text{assoc}}$ and substituent effects^{5,6}. The IR spectra of compounds I—XV in Nujol suspension contained 6—8 bands in the $3600\text{--}3000\text{ cm}^{-1}$ region. The bands in the $3100\text{--}3000\text{ cm}^{-1}$ region are associated with the stretching vibrations of the =CH bonds, the other of the N—H bonds. The number of $\nu(\text{N—H})$ bands presumably corresponds to the different intramolecular hydrogen bonds between N—H and C=O groups in the solid state and, moreover, it agrees with the number of shoulders on the $\nu(\text{C=O})$ band. Compared to the ^{14}N -isotopomers, with the ^{15}N -derivatives the bands at 3144 , 3200 , and 3234 cm^{-1} were down-shifted by 7 cm^{-1} , the maxima of 3285 and 3416 cm^{-1} bands remained constant. The $\nu(\text{C}\equiv\text{N})$ band appeared near 2225 cm^{-1} , without being influenced by substituents. The absorptions by $\nu(\text{C=O})$ were located at 1720 cm^{-1} (medium, shoulder at 1740 cm^{-1}) and at 1785 cm^{-1} in chloroform. The position of these bands was independent of ring substitution. The IR spectra of solids (in Nujol mull) showed in this region 1—2 strong bands with several shoulders. The medium band at 1556 cm^{-1} , the wavenumber of which decreased in the case of phenyl- $^{15}\text{NH—}^{14}\text{N}$ and phenyl- $^{14}\text{NH—}^{15}\text{N}$ -derivatives by 8 and 6 cm^{-1} , respectively, was slightly dependent on the nature of substituents. We ascribed it to the deformation vibration of the N—H bond. Of five strong bands in the $1300\text{--}1000\text{ cm}^{-1}$, only the band at 1297 cm^{-1} changed its position by ^{15}N -isotopic substitution: it decreased by 11 cm^{-1} for phenyl- $^{15}\text{NH—}^{14}\text{N}$ -derivative and by 13 cm^{-1} for phenyl- $^{14}\text{NH—N-}^{15}$ derivative. In the latter case a prominent shoulder rested at 1297 cm^{-1} . It seems probable that the original band 1297 cm^{-1} is a superposition of two bands due to the stretching vibrations of N—N and phenyl-N grouping. The presence of ^{15}N -isotope in the phenyl- $^{15}\text{NH—}^{14}\text{N}$ group decreased the band at 587 cm^{-1} by 3 cm^{-1} , in the other case it was unchanged. We ascribe this absorption to the out-of-plane deformation vibration of $\text{NH}\cdots\text{O}=\text{C}$ grouping, as it had been observed^{1,7} for hydrogen bonded O—H and N—H bonds. Although the out-of-plane deformation vibrations of groups bonded by intramolecular hydrogen bond are sensitive to their neighbours and correlate in the case of aromatic systems with Hammett substituent constants¹, we did not observe any significant effect of substituents on the wavenumber of $\nu(\text{N—H})$. In the earlier work¹, it was established that substituent effects are well transferred *via* the —NH—N=C—C grouping, here

however, the polar effects on proton donor NH group presumably compensate the effect on proton acceptor C=O group, similarly as in the case of $\nu(\text{N—H})$.

With phenylhydrazono-2-cyanomethylbenzimidazole in dimethylformamide, the $^1\text{H—NMR}$ spectra proved existence of the two tautomers. The IR spectrum confirmed both forms even in the solid state. With ^{14}N -compound, in the spectral region characteristic for the stretching vibration of phenyl-N bond, there were two bands at 1282 and 1267 cm^{-1} , lowered in the case of ^{15}N -compound by 4 cm^{-1} . The deformation vibration manifested itself by the 1552 cm^{-1} band with a shoulder at 1535 cm^{-1} , the maximum for ^{15}N -derivative being shifted to 1546 cm^{-1} . ^{15}N -isotopic substitution lowered also the maxima of 601 and 708 cm^{-1} bands by 2.5 cm^{-1} . We assigned these absorptions to the out-of-plane deformation vibrations of associated N—H bonds in both tautomers.

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