

INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA OF NITROPHENOXAZINES

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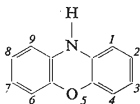
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The IR ($4000\text{--}400\text{ cm}^{-1}$, Nujol, CCl_4) and PMR spectra (80 MHz, dimethylsulfoxide) of phenoxazine and its eleven nitro derivatives have been measured. The nitro group in the position 1 forms an intramolecular hydrogen bond with the NH group. The intense absorption band at 740 cm^{-1} has been attributed to the skeletal vibration of the phenoxazine ring.

In connection with the study of phenoxazine dyes¹ we have measured the IR and PMR spectra of eleven nitrophenoxazines in order to evaluate the effect of the nitro groups on the parameters of the IR and PMR spectra.

EXPERIMENTAL

The preparation of nitrophenoxazines has been described¹. The IR spectra were measured by using the spectrophotometer UR 20 Zeiss (Jena) at $25\text{--}35^\circ\text{C}$ in Nujol mulls and in diluted solutions in tetrachloromethane in the region above 3000 cm^{-1} in 2 cm cells. The spectrophotometer was calibrated by using polystyrene. Deuteration of nitrophenoxazines was carried out by crystallizing the compounds from a mixture of acetone and heavy water. The PMR spectra were measured by means of the 80 MHz spectrophotometer Tesla BS-487 B in dimethylsulfoxide at 35°C . The compounds VIII–XII were not sufficiently soluble in dimethylsulfoxide for the PMR measurements, the compound VIII was not soluble in tetrachloromethane enough for the determination of the frequency of the stretching vibration of the N–H bond. The results of measurements are summarized in the following text, the frequencies of the $\nu(\text{N–H})$, $\nu(\text{N–D})$, and $\gamma(\text{N–H})$, vibrations are given in Table I as well as δ_{NH} .



Phenoxazine (I). IR spectrum: 464 w, 732 s, 745 s, 826 m, 881 w, 923 m, 1035 w, 1117 m, 1205 m, 1235 m, 1287 s, 1304 s, 1497 s, 1585 m, 1600 m, 1634 m. PMR spectrum: 6.32–6.93 p.p.m. ($\text{H}_{(1)}$ – $\text{H}_{(9)}$).

1-Nitrophenoxazine (II). IR spectrum: 450 w, 480 w, 555 s, 596 w, 708 m, 739 s, 752 s, 792 m, 815 m, 856 w, 926 m, 1078 m, 1272 s, 1298 m, 1328 s, 1350 m, 1400 m, 1508 s, 1530 s, 1580 s,

1608 m, 1638 m. PMR spectrum: 7.52 p.p.m. ($H_{(2)}$), 6.9—7.3 p.p.m. ($H_{(3)}$ + $H_{(4)}$), 6.60—6.93 p.p.m. ($H_{(6)}$ — $H_{(9)}$).

3-Nitrophenoxazine (III). IR spectrum: 450 w, 708 m, 736 s, 750 sh, 825 m, 880 m, 920 w, 1072 m, 1235 m, 1280 s, 1323 s, 1358 s, 1500 s, 1510 sh, 1532 s, 1581 s, 1635 m. PMR spectrum: 7.70 p.p.m. ($H_{(2)}$), 7.35 p.p.m. ($H_{(4)}$), 6.55 p.p.m. ($H_{(1)}$), 6.51—6.92 p.p.m. ($H_{(6)}$ — $H_{(9)}$).

1,3-Dinitrophenoxazine (IV). 448 w, 533 m, 580 w, 602 m, 610 s, 690 w, 713 w, 735 s, 745 s, 765 m, 810 s, 845 w, 882 m, 908 m, 928 m, 945 m, 1076 m, 1110 m, 1160 m, 1230 w, 1270 sh, 1282 s, 1297 m, 1323 s, 1359 s, 1409 m, 1437 m, 1467 w, 1485 s, 1512 sh, 1528 s, 1583 s, 1596 sh, 1608 sh, 1635 m. PMR spectrum: 8.25 p.p.m. ($H_{(a)}$), 7.50 p.p.m. ($H_{(4)}$), 6.82—7.25 p.p.m. ($H_{(6)}$ — $H_{(9)}$).

1,3,7-Trinitrophenoxazine (V). IR spectrum: 450 w, 533 w, 633 s, 712 w, 738 m, 746 m, 766 w, 778 m, 817 s, 845 m, 888 m, 908 w, 930 m, 1074 m, 1161 m, 1200 m, 1262 s, 1273 m, 1297 s, 1308 sh, 1325 s, 1340 sh, 1364 m, 1395 m, 1432 w, 1490 sh, 1500 s, 1520 m, 1545 m, 1575 m, 1605 w, 1630 m. PMR spectrum: 8.27 p.p.m. ($H_{(2)}$), 7.85 p.p.m. ($H_{(4)}$), 7.25—7.50 p.p.m. ($H_{(6)}$, $H_{(8)}$, $H_{(9)}$).

1,3,9-Trinitrophenoxazine (VI). IR spectrum: 432 w, 480 w, 520 w, 573 w, 615 w, 643 w, 686 s, 712 w, 730 sh, 739 s, 767 w, 792 m, 804 m, 813 m, 874 w, 898 m, 934 w, 980 w, 996 w, 1073 m, 1145 w, 1198 m, 1227 w, 1278 s, 1290 s, 1312 s, 1328 s, 1367 s, 1397 w, 1502 sh, 1511 s, 1523 s, 1550 sh, 1580 s, 1596 m, 1630 w.

1,3,7,9-Tetranitrophenoxazine (VII). IR spectrum: 440 w, 475 w, 513 w, 550 w, 647 s, 670 m, 711 w, 728 m, 737 s, 757 w, 766 w, 793 m, 814 s, 895 s, 905 m, 937 m, 987 w, 1077 m, 1160 m, 1193 m, 1215 w, 1268 s, 1293 s, 1310 sh, 1330 s, 1379 m, 1392 m, 1440 m, 1470 sh, 1505 s,

TABLE I

Frequencies of the Stretching Vibrations of N—H and N—D Bonds, Frequencies of the Out-of-plane Bending Vibrations of the Hydrogen Bonding $NH \cdots O_2N$, and PMR Chemical Shifts of Protons of the NH Group of the Nitrophenoxazines Studied

Compound	ν_{N-H}^a , cm^{-1}	ν_{N-D}^b , cm^{-1}	γ_{N-H}^b , cm^{-1}	δ_{NH}^c , p.p.m.
I	3 433 (3 396)	2 534	—	8.10
II	3 362 (3 356)	2 504	555	9.25
III	3 435 (3 358)	—	—	9.28
IV	3 353 (3 345)	2 497	610	9.96
V	3 347 (3 320)	2 477	633	10.22
VI	3 293 (3 284)	2 451	686	—
VII	3 275 (3 302)	2 464	647	11.64
VIII	— (3 330)	—	—	—
IX	3 446 (3 363)	—	—	—
X	3 444 (3 382)	—	—	—
XI	3 453 (3 456)	—	—	—
XII	3 445 —	—	—	—

^a In CCl_4 (Nujol), ^b in Nujol, ^c in dimethyl sulfoxide.

1 515 sh, 1 525 m, 1 549 s, 1 586 s, 1 620 m, 1 643 m. PMR spectrum: 8.44 p.p.m. ($H_{(2)} + H_{(8)}$), 7.83 p.p.m., ($H_{(4)} + H_{(6)}$).

3,7-Dinitrophenoxazine (VIII). IR spectrum: 445 w, 690 m, 712 w, 740 s, 765 m, 790 m, 805 m, 813 s, 821 m, 874 m, 897 m, 933 m, 980 m, 995 m, 1 072 m, 1 140 w, 1 195 m, 1 225 w, 1 277 s, 1 288 m, 1 312 s, 1 328 sh, 1 366 m, 1 400 m, 1 460 m, 1 468 s, 1 500 s, 1 505 sh, 1 523 s, 1 579 s, 1 680 m, 1 633 m.

3-Nitro-9-methylphenoxazine (IX). IR spectrum: 445 w, 685 m, 718 m, 745 s, 762 s, 805 w, 820 m, 878 m, 885 w, 940 w, 1 075 m, 1 088 w, 1 138 w, 1 200 m, 1 220 w, 1 248 w, 1 275 m, 1 290 s, 1 310 sh, 1 330 m, 1 350 w, 1 385 m, 1 418 m, 1 483 s, 1 525 s, 1 578 s, 1 612 m, 1 631 w.

3-Nitro-1,7-dimethylphenoxazine (X). IR spectrum: 450 w, 478 m, 520 w, 550 w, 576 m, 728 m, 745 m, 779 m, 805 s, 825 s, 896 m, 930 w, 965 w, 981 w, 1 058 w, 1 085 m, 1 207 w, 1 230 w, 1 248 m, 1 278 s, 1 285 m, 1 303 s, 1 318 sh, 1 380 m, 1 409 m, 1 488 sh, 1 496 s, 1 508 s, 1 528 sh, 1 581 s, 1 603 w, 1 640 w.

3-Nitro-1,9-dimethylphenoxazine (XI). IR spectrum: 450 w, 585 w, 722 m, 743 m, 775 m, 783 s, 860 m, 882 m, 940 m, 981 w, 1 035 w, 1 078 m, 1 160 w, 1 200 w, 1 283 s, 1 303 s, 1 316 sh, 1 350 m, 1 382 m, 1 415 w, 1 435 w, 1 480 s, 1 505 s, 1 522 sh, 1 577 s, 1 608 m, 1 635.

3-Nitro-1-methylphenoxazine (XII). The IR spectrum was measured only in tetrachloromethane.

DISCUSSION

The absorption bands were assigned empirically, by comparing the IR spectra measured with those of *o*-nitroaniline, diphenylamine², and the deuterio analogs of nitrophenoxazines.

As expected, the IR spectra of nitrophenoxazines exhibit intense bands in the regions of absorption by the out-of-plane bending vibrations of the C—H bonds ($890-700\text{ cm}^{-1}$), anti-symmetric stretching vibration of the C—O—C grouping³ (1200 cm^{-1}), C—N bonds (1300 cm^{-1}), nitro group (1320 and 1520 cm^{-1}), and aromatic C=C bonds (1635 , 1605 , and 1580 cm^{-1}). In the range of the out-of-plane bending vibrations of the C—H bonds, the expected increase of the number of absorption bands appears with increasing number of nitro groups. This increasing number of nitro groups, however, had no effect on the position of the band near 740 cm^{-1} and on the medium intensity band near 815 cm^{-1} . On deuteration, the position of the former did not change, whereas that of the latter displayed a 20 cm^{-1} decrease. We attributed the intense band at 740 cm^{-1} to the skeletal vibration of the phenoxazine ring. Bands of medium intensity in the ranges near 920 and 1075 cm^{-1} were in addition observed in the IR spectra of all the phenoxazines. In the spectra of N-deuteriophenoxazines, an additional intense band appeared near 1375 cm^{-1} , probably due to the in-plane bending vibration of the C—N—C grouping; the high frequency value indicates coupling with other vibrations.

D

The presence of nitro groups in the molecule affected markedly the frequencies of the stretching vibration of the N—H bonds, $\nu(\text{N—H})$, and those of the out-of-plane bending vibrations of the NH group bonded by an intramolecular hydrogen bond to the nitro group in the position 1. For the evaluation of the effect of the nitro groups on the $\nu(\text{N—H})$ value, the results obtained in diluted solutions in tetrachloromethane are the most important, when the phenoxazine molecules can be assumed to be influenced by the molecules of the solvent only. The presence of the nitro group in the

position 3 affects $\nu(\text{N—H})$ only slightly, the nitro group introduced in the position 1 lowers $\nu(\text{N—H})$ considerably as a consequence of the intramolecular hydrogen bond formation between the NH group and the 1-nitro group. The introduction of additional nitro groups in the 1-nitrophenoxazine molecule causes an additional considerable decrease of $\nu(\text{N—H})$, probably due to the effect of those additional nitro groups on the strength of the intramolecular hydrogen bond formed⁴. The effect of additional substitution in the position 9 is approximately ten times higher than in the position 3 or 7. The effect of the nitro groups described appears roughly to the same extent also for Nujol mulls. The effect of methyl groups in 1,9-dimethyl-3-nitrophenoxazine is interesting: the methyl groups obviously hinder the formation of the intermolecular hydrogen bond, so that $\nu(\text{N—H})$ of this compound is identical in Nujol mull and in tetrachloromethane solution.

In the spectra of N-deuterated nitrophenoxazines, the $\nu(\text{N—D})$ absorption band appeared in the region of $2550\text{--}2450\text{ cm}^{-1}$, the ratio $\nu(\text{N—H})/\nu(\text{N—D})$ was 1.34 in all cases. The substitution of hydrogen by deuterium lead also to remarkable changes in the positions of bands near 1500 cm^{-1} and of intense bands in the region of $700\text{--}400\text{ cm}^{-1}$. In the case of nitrophenoxazines with the nitro group in the position 1 an intense band appeared in that region; its wavenumber increased considerably with the increasing number of nitro groups in the molecule. We attributed this band to the out-of-plane bending vibration of the intramolecular hydrogen bond $\text{NH}\cdots\text{NO}_2$. Additional nitro groups in the molecule strengthen this hydrogen bond and thus increase also the wavenumber of its out-of-plane bending vibration⁵.

As to the PMR spectra, a change of the chemical shift of the signal of the NH group proton to lower fields obviously occurs on increasing the number of nitro groups. The change caused by the nitro group is lower than in the case of substituted anilines measured under equal conditions⁶, probably due to the nonplanarity of the complete system and a partial levelling-up the electron deficit at nitrogen by electrons of the other ring. The chemical shift of the aromatic ring protons is affected by the nitro groups as expected. The effect of the nitro group in the position 7 is transferred quite markedly also through the phenoxazine skeleton, as obvious from the chemical shifts of the protons 2 and 4 in IV and V.

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