ELECTRONIC INTERACTIONS IN AROMATIC AND HETEROAROMATIC TWO-RING SYSTEMS.

3.* IR AND PMR SPECTRA OF METHYL DERIVATIVES

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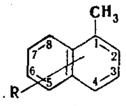
The chemical shifts of the methyl protons (δ^{CH_3}) in the PMR spectra and the integral intensities ($A^{1/2}$) of the band of the symmetrical CH stretching vibration of the methyl group in the IR spectra were measured for an extensive series of methyl derivatives of aromatic and heteroaromatic compounds including 3-, 4-, 5-, and 6-substituted 1- and 2-methylnaphthalenes, 4-, 5-, 6-, and 7-substituted 2-methylquinolines, and 5- and 6-substituted 2-methylbenzothiazoles, as well as a number of two- and three-ring systems that do not contain substituents. The changes in the chemical shifts are interpreted with allowance for two principal contributions: the contribution from the ring currents and the contribution from the changes in the electron densities (q) on the H and C atoms of the methyl group. The fact of the existence of a linear relationship between the corrected (for the ring current) δ^{CH_3} values and the calculated (by the CNDO/2 method) electron charges q_C and q_H (the latter plays the dominant role) indicates that the electronic effects of the substituent make the principal contribution to the changes in the shielding constants of the protons of the methyl group in most of the investigated compounds. Similarly, the charges on the H and C atoms of the methyl group convey the trend of the integral intensities of the IR bands, thereby confirming the primarily electronic nature of the effects of structural factors on the $A^{1/2}$ values.

Continuing our study of the peculiarities of the mechanism of the transmission of electronic effects through two-ring aromatic and heteroaromatic systems [1, 2] we investigated the effect of substituents and heteroatoms on the integral intensities of the band of the symmetrical stretching vibration of C–H bonds ($A^{1/2}$) in the IR spectra and the chemical shifts of the protons of the methyl group in the PMR spectra (δ^{CH_3}) of a number of substituted methyl derivatives of naphthalene (I, II), quinoline (III), and 2-methylbenzothiazole (IV), as well as some aromatic and heteroaromatic two- and three-ring compounds that do not contain a substituent (V-X):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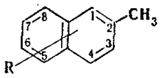
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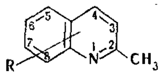
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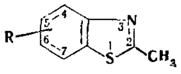
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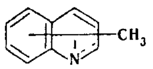
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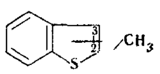
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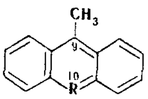
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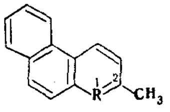
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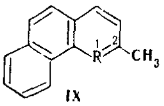
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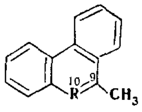
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(see Table 1 for R)

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*See [2] for communication 2.

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TABLE 1. Chemical Shifts,[a] Integral Intensities of the Band of the Symmetrical CH Vibration, and Surplus Electron Charges on the H and C Atoms of the Methyl Group in I-X

Compound	R	δ^{CH_3},[b] ppm	δ^{C} ppm	$(A^{S})^{1/2}$, liter · mole^{-1} · cm^{-1}	$\Delta\bar{q}_H$, av	Δq_C, av	$\Delta q_{C'}$, av
1	2	3	4	5	6	7	8
Ia	H	2,63	1,80	30,0 (30,6)[d]	0,0050	−0,0193	0,0289
Ib	5-OH	2,64	1,8!	30,7	0,0052	−0,0180	0,0240
Ic	4-OCH_3	2,55	1,72	—	0,0019[e]	−0,0140[e]	0,0010[e]
Id	4-OH	2,56	1,73	—	0,0019	−0,0140	0,0010
Ie	4-F	2,58	1,75	30,5	0,0047	−0,0163	0,0113
If	5-F	2,65	1,82	29,3	0,0067	−0,0210	0,0370
Ig	4-NH_2	2,51	1,68	—	−0,0001 0,0017[f]	−0,0130 −0,0150[f]	−0,0060 0,0060[f]
Ii	4-Br	2,63	1,80	—	0,0060[g]	−0,0170[g]	0,0210[g]
Ij	3-NO_2	2,67	1,84	(27,0)[h]	0,0110	−0,0210	0,0350
Ik	4-NO_2	2,72	1,89	(24,0)[h]	0,0135 0,0123[f] 0,0113[i]	−0,0252 −0,0230[f] −0,0220[i]	0,0491 0,0449[f] 0,0442[i]
Il	4-CN	2,71	1,88	—	0,0067	−0,0210	0,0370
IIa	H	2,45	1,79	31,2	0,0051	−0,0206	0,0403
IIb	6-F	2,47	1,81	32,4	0,0059	−0,0202	0,0367
IIc	6-CN	2,50	1,84	—	0,0069	−0,0210	0,0440
IId	6-NH_2	2,37	1,71	37,2	0,0024	−0,0180	0,0250
IIe	5-NO_2	2,52	1,86	(31,6)[h]	0,0080	−0,0218	0,0427
IIf	1-NO_2	—	—	(23,0)[h]	0,0223 0,0191[i]	−0,0255 −0,0280[i]	0,0725 0,0570[i]
IIIa	H	2,67	2,01	26,0	0,0151	−0,0353	0,1269
IIIb	4-OCH_3	2,61	1,95	—	0,0167	−0,0372	0,1468
IIIc	6-OCH_3	2,66	2,00	—	0,0139	−0,0337	0,1177
IIId	6-F	2,69	2,03	28,0	0,0160	−0,0348	0,1232
IIIe	4-Cl	2,68	2,02	25,0	0,0181	−0,0363	0,1390
IIIf	6-Cl	2,68	2,02	23,0	0,0162	−0,0354	0,1263
IIIg	7-Cl	2,70	2,04	20,8	0,0169	−0,0364	0,1331
IIIi	4-CN	2,74	2,08	23,0	0,0169	−0,0352	0,1250
IIIj	5-NO_2	2,75	2,09	(21,0)[h]	0,0181	−0,0365	0,1303
IIIk	6-NO_2	2,75	2,09	(20,0)[h]	0,0203	−0,0382	0,1412
IVa	H	2,81 (2,79)	(2,30)	18,2	0,0259	−0,0405	0,1610
IVb	5-NH_2	2,72	(2,21)	20,2	0,0253	−0,0414	0,1640
IVc	5-Cl	2,85 (2,80)	(2,34)	17,5	0,0279	−0,0413	0,1540
IVd	5-NO_2	2,87	(2,36)	(17,0)[h]	0,0309	−0,0416	0,1685
IVe	6-NH_2	2,63 (2,70)	(2,12) (2,22)	21,2	0,0239	−0,0390	0,1500
IVf	6-Cl	2,83	(2,32)	17,5	0,0275	−0,0410	0,1610
IVg	6-NO_2	2,89 (2,88)	(2,38)	(17,0)[h]	0,0350 0,0291[i]	−0,0430 −0,0370[i]	0,1740 0,1650[i]
IVi	5-OCH_3	2,76	(2,25)	—	0,0247	−0,0391	0,1538
Va	2-CH_3	2,671	2,01	26,0	0,0151	−0,0353	0,1269
Vb	3-CH_3	2,524	1,86	—	0,0038	−0,0190	0,0160
Vc	4-CH_3	2,704	1,87	26,0	0,0085	−0,0246	0,0616
Vd	5-CH_3	2,698	1,87	—	0,0056	−0,0210	0,0380
Ve	6-CH_3	2,481	1,82	30,0	0,0051	−0,0200	0,0180
Vf	7-CH_3	2,477	1,82	—	0,0069	−0,0220	0,0540
Vg	8-CH_3	2,752	1,92	—	0,0063	−0,0170	0,0110
VIa	2-CH_3	2,526	(2,02)	28,4	0,0126	−0,0228	0,0659
VIb	3-CH_3	2,356	—	30,4	0,0038	−0,0091	0,0060
VIIa	CH	3,06	1,87	—	0,0072	−0,0250	0,0160
VIIb	N	3,07	1,88	—	0,0124	−0,0330	0,0590
VIIIa	CH	2,56	1,84	—	0,0048	−0,0200	0,0390
VIIIb	N	2,67	1,95	25,0	0,0139	−0,0340	0,1220
IXe	CH	2,61	1,86	—	0,0050	−0,0210	0,0400
IXb	N	2,75	2,00	25,8	0,0142	−0,0340	0,1290
Xa	CH	2,73	1,83		0,0074	−0,0270	0,0290
Xb	N	2,94	2,04	21,4	0,0185	−0,0420	0,1190

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[a] The δ^{CH_3} values of IVa–i were taken from [11], and the values in parentheses were taken from [12]; the values for Va–g were taken from [9], and the values for VIIa, VIIIa, IXa, and Xa were taken from [13]. [b] The following solvents were used: CD_3CN for I–III, d_6-DMSO for IV (CCl_4 in parentheses), CCl_4 for V and VI, and d_6-DMSO for VII–X. The δ^{CH_3} values measured in other solvents were as

follows: Ia 2.64 (CCl_4), 2.63 (dioxane), and 2.63 (d_6-DMSO); IIa 2.45 (CCl_4), 2.44 (dioxane), and 2.43 (d_6-DMSO); IIIa 2.68 (dioxane), and 2.72 (CD_3OD). c) The $\delta' = \delta^{CH_3} - \delta_r$ values, where δ_r is the correction for the ring current estimated from the data in [12], for I-X and substituted toluenes (XI in Table 2) were as follows: 0.83 for Ia-l and Vc,d,g, 0.66 for IIa-f, IIIa-k, and Va,b,e,f, 0.19 for VIIa,b, 0.72 for VIIIa,b, 0.75 for IXa,b, 0.90 for Xa,b, and 0.51 for XI. The δ_r values for IVa-i and VIa are unknown; with allowance for the results of statistical treatment (Table 2), the δ_r value was assumed to be 0.51. d) For 1-methyl-d_7-2,3,4,5,6,7,8-naphthalene. e) For R = 4-OH. f) Substituent R is at an angle of 50° relative to the C−R axis. g) For R = 4-Cl. h) The value presented is evidently too low because of partial overlapping of the bands belonging to the vibrations of the methyl and nitro groups. i) Substituent R is at an angle of 90° relative to the C−R axis.

The aim of the present research included the experimental determination of the trend of the change in the indicated IR and PMR spectroscopic parameters and the establishment of the degree of its conformity with the results of a quantum-chemical calculation of the electron density distribution in the molecules.

The δ^{CH_3} and $(A^S)^{1/2}$ values for the investigated compounds are presented in Table 1 along with the results of calculation of the surplus electron charges on the C and H atoms (Δq).

The calculation was made by the CNDO/2 (complete neglect of differential overlap) method with the standard parametrization with a BÉSM-6 computer. All of the calculations were made within the assumption of a regular hexagonal form of the aromatic rings with interatomic distances r_{CC} = 1.39 Å and r_{CH} = 1.09 Å. The C−N bond length in the nitrogen-containing heterocycles was assumed to be 1.36 Å. As in previous studies, the geometrical parameters of the corresponding five-membered heteroaromatic one-ring compounds were used for the five-membered ring of two-ring systems IV and VI. The parameters of idealized geometries were used in all cases for the substituents [3, 4]. A fixed geometrical structure in which one of the hydrogen atoms is in the plane of the aromatic ring and the other two are situated symmetrically above and below this plane was assumed for the methyl group [3]. Although, as has been shown for a number of substituted toluenes, the results of the calculation of the charges on the hydrogen atoms (q_H) depend on the angle of rotation (φ) on the methyl group relative to the $C_{sp^2}-CH_3$ axis, the tendency of the change in q_H at any φ value coincides with the change in the average $\bar{q}_H$ value [5].

Chemical Shift of the Protons (δ^{CH_3})

It follows from the approximate theory of magnetic shielding that the shielding constants of the protons are proportional to the electron density both around the resonating protons and on the adjacent atoms [6-8]. The difficulties associated with the allowance for the effect on the chemical shift of the protons in complex aromatic and heteroaromatic systems of the effects of the ring current, the magnetic anisotropy, the electric field of the charges, the dipoles of the substituents, etc., as well as steric effects, limit the possibility of obtaining sufficiently rigorous correlations between the δ^{CH_3} values and the electron densities over a wide range of changes in the structural factors. However, if one compares series of compounds of the same type in which the influence of the effects of nonlocal shielding to a first approximation can be excluded, the interrelationship between the δ and q values frequently can be observed sufficiently distinctly (for example, see [3, 7-10]). In particular, parallelism in the changes in the δ^{CH_3} values and the charges on the hydrogen atoms of the methyl groups has been shown for one-ring analogs of the investigated compounds − 3- and 4-substituted toluenes and methyl derivatives of five- and six-membered aromatic heterocycles [3, 5].

In order to form a judgment regarding the character of the dependence of the shielding constants on the electron densities on the protons and on the nuclei that make up the immediate environment of the protons of the methyl group we made a thorough analysis of the possibility of the description of the trend of the change in the δ^{CH_3} value in two-ring systems by means of expressions of the type

$$\delta = A + B\Delta\bar{q}_H;$$
$$\delta = A + B\Delta\bar{q}_H + C\Delta q_C + D\Delta q_{C'}.$$

Here, $\Delta\bar{q}_H = (\Delta q_H + \Delta q_{H_2} + \Delta q_{H_3})/3$ is the surplus charge on the investigated hydrogen atoms, and Δq_C and $\Delta q_{C'}$ are the surplus electron charges, respectively, on the carbon atom of the methyl group and the carbon atom of the aromatic ring to which the methyl group is bonded.

TABLE 2. Parameters of the Relationships between the δ^{CH_3} and ΔqH Values ($\delta^{CH_3} = A + B\Delta q_H$)

Dependence No.	Type of compound	A	B	r'[a]	n[b]
1	I, V	2,51	21,5	0,967	10[c]
2	II, III, V	2,34	23,0	0,988	15[d]
3	IV, VIa	2,24	20,4	0,959	8[e]
4	XI[f]	2,21	21,3	0,864	13

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a) This is the correlation coefficient. b) This is the number of compounds. c) Compounds Ij-*l* and Vd,g were excluded from the correlation. d) Compounds IIIb,e and Vb were excluded from the correlation. e) Compound IVg was excluded from the correlation. f) These are 3- and 4-substituted toluenes and six-membered nitrogen-containing heterocycles. The parameters of correlation (4) were taken from [3].

The parameters of dependences (1)-(3) of the δ^{CH_3} values on $\Delta\bar{q}_H$ are presented in Table 2; for comparison, the parameters of the analogous correlation (4) established for series of substituted toluenes and their nitrogen-containing heteroanalogs are also presented in Table 2. It is apparent from the data in Table 2 that the charges on the hydrogen atom sufficiently correctly reproduce the changes in the shielding constants within the limits of the following groups of two-ring compounds: 1) substituted 1-methylnaphthalenes (I) and their nitrogen-containing heteroanalogs (V); 2) substituted 2-methylnaphthalenes (II) and their nitrogen-containing heteroanalogs (III, V); 3) substituted 2-methylbenzothiazoles (IV) and 2-methyl benzothiophene (VIa).

In the case of expression (5), which was obtained for substituted 2-methylnaphthalenes, it is apparent that the sensitivity of the chemical shift to changes in the electron density on the H atoms exceeds by almost an order of magnitude its sensitivity to changes in the electron density on the C and C' atoms:

$$\delta^{2\text{-}CH_3} = 2.34 + 25.9\Delta\bar{q}_H + 3.5\Delta q_C + 1.1\Delta q_{C'} \quad (R = 0.998,\ n = 5). \tag{5}$$

This makes it possible to disregard the last two terms in dependence (5) without substantial deterioration in the agreement between the calculated and experimental values. It is most valid to link the result with the fact that, at least within the limits of the indicated series of compounds, the changes in the chemical shift are determined primarily by the local diamagnetic shielding factor.

The shift in correlation lines (1) and (2) for 1- and 2-methyl-naphthalene-like compounds relative to one another ($\Delta\delta^0 \sim 0.17$ ppm) and relative to a series of substituted toluenes ($\Delta\delta_{1\text{-}CH_3} \sim 0.3$ ppm, $\Delta\delta_{2\text{-}CH_3} \sim 0.13$ ppm) corresponds to the shift expected from the results of an approximate estimate of the differences in the ring currents of the systems under comparison. According to the available data for methylarenes [13], the contributions of the ring current to the shielding constant of the protons of the methyl group in toluene and in the 1 and 2 positions of the naphthalene ring are, respectively, 0.51, 0.83, and 0.66 ppm, whence $\Delta\delta^0 \sim 0.17$ ppm, $\Delta\delta_{1\text{-}CH_3} \sim 0.32$ ppm, and $\Delta\delta_{2\text{-}CH_3} \sim 0.15$ ppm.

The fact that the established correlations in many cases satisfactorily convey the trend of the δ^{CH_3} values not only in aromatic but also in nitrogen-containing heteroaromatic two-ring systems is in agreement with the well-known assumption that the nitrogen heteroatom does not have a substantial effect on the intensity of the ring current in aromatic systems [9, 14, 15]. Although, generally speaking, the anisotropy of the aromatic ring may change under the influence of a polar substituent [7], the close angular coefficients of dependences (1)-(4) provide a basis for the conclusion that the current contributions remain approximately constant when a substituent is introduced in most of the investigated compounds.

We did not make a numerical estimate of the contribution of the ring current to the shift of the protons of the methyl group in substituted 2-methylbenzothiazoles (IV). However, judging from the fact that the parameters of correlations (3) are close to the parameters for substituted toluenes [compare Eqs. (3) and (4) in Table 2], the two factors by which the differences in the ring currents of the system under comparison – the effect of an annelated benzene ring (which leads to an increase in the contribution of the ring current) and replacement of a six-membered aromatic (or heteroaromatic) ring by a five-membered sulfur-containing ring (the latter is accompanied by a decrease in the magnetic anisotropy of the ring [16]) – are determined in this special case compensate one another to a considerable extent.

It follows from the above account that, if the ring contribution to the δ^{CH_3} value is eliminated by introduction of the above-indicated corrections (see the δ' values in Table 1), the trend of the change in the shielding constants of the protons of the methyl group in most of the investigated two-ring systems (I-VI) can be conveyed by general correlation dependence (6). This dependence is also applicable to the methyl derivatives of one-ring [3] and three-ring compounds (VII-X) after allowance for the effect of the anisotropy of the ring currents by the method described above:

$$\delta' = 1.70 + 21.7\Delta\bar{q}_H \quad (r = 0.978,\ n = 49). \tag{6}$$

Although the agreement between the experimental results and the values obtained by calculation is, upon the whole, quite good, individual compounds deviate appreciably from the correlation lines (see the notes to Table 2). Because of the rather complex nature of the chemical shift, it is difficult to unambiguously evaluate the factors responsible for the observed scatter. In addition to the above-noted sources of errors in the estimate of the diamagnetic component of the chemical shift, one should point out the existence of limitations associated with the imperfection of the computational method used and with the lack of data on the real geometry of the investigated compounds. In the fact of such great diversity in the structural factors, one also cannot reckon with the possibility of different effects of the solvent on the trend of the change in the δ^{CH_3} values.

Intensities of the IR Bands

The IR spectra of substituted 2-methylnaphthalenes (II), 2-methylquinolines (III), 2-methylbenzothiazoles (IV), and three isomeric methylbenzoquinolines (VII-X) in the region of the CH stretching vibrations of the methyl group contain bands whose identification is quite obvious ($\nu^s \sim 2925$ cm^{-1}, $\nu^{as} \sim 2945$ and 2970 cm^{-1}) in view of their similarity to the corresponding bands of substituted toluenes.

1-Methylnaphthalene and a large number of its derivatives give five stable (with respect to their position) markedly overlapped bands in the same region of the IR spectrum. This complication of the spectral picture is apparently associated with splitting of the fundamental ν^s and ν^{as} bands that arise as a consequence of peri interactions of the hydrogen atoms of the methyl group with the ring hydrogen atoms in the 8 and (or) 2 positions [17].

For comparison with the calculated characteristics of the electron density on the C and H atoms of the methyl group in 2-methylnaphthalene-like compounds we selected the integral intensities of the band of the symmetrical CH vibration ($\nu^s \sim 2925$ cm^{-1}) as the most isolated band in this region of the spectrum. Since two bands (~2925 and ~2905 cm^{-1}) correspond to this vibration in the IR spectra of 1-methylnaphthalene and its derivatives, we used the sum of the integral intensities of the indicated bands for a similar study in the case of 1-methylnaphthalene-like compounds.*

It follows from the results of statistical treatment that the following expressions are satisfied for most of the investigated compounds:

$$(A^s)^{1/2} = 34.7 - 462.7\Delta\bar{q}_H + 96.4\Delta q_C \quad (R = 0.970,\ n = 26); \tag{7}$$

$$(A^s)^{1/2} = 33.2 - 548.8\Delta\bar{q}_H \quad (r = 0.962,\ n = 26). \tag{8}$$

The existence of dependences (7) and (8) confirms that, as in the case of methyl derivatives of one-ring systems [3], there is an approximate correlation between the changes in the derivatives of the dipole moments with respect to the normal coordinates ($\partial\mu/\partial Q$) and the electron charges on the atoms that participate in vibration in the series of compounds under examination. Judging from the data obtained, the changes in the charges on the hydrogen atoms play the dominant role.

With respect to their character, the expressions obtained in this research are of the same type as those established above for the chemical shift of the protons of the methyl groups. However, taking into account the fact that, in contrast to the latter, the experimentally measured $A^{1/2}$ values do not need additional correction and that the trend of the change in the integral intensity of the IR bands, at least in the case of condensed aromatic and heteroaromatic compounds, evidently more adequately reflects the effect of the structural factors on the electronic state of the C–H bonds of the methyl group.

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*It should be noted that only one band at 2922 cm^{-1} is observed in the IR spectrum of 1-methyl-d_7-2,3,4,5,6,7-naphthalene in the region of the symmetrical CH stretching vibration of the methyl group and that its intensity is equal to the sum of the intensities of the two bands (2925 and 2905 cm^{-1}) in the spectrum of nondeuterated 1-methylnaphthalene (see Ia in Table 1).

EXPERIMENTAL

The investigated compounds (Table 1) were commercial preparations or were compounds synthesized by known methods.

The PMR spectra of 5-10% (by weight) solutions of the compounds (the solvents are indicated in the footnote to Table 1) were recorded with a JNM-100 spectrometer with hexamethyldisiloxane as the internal standard. The chemical shifts in parts per million relative to tetramethylsilane are presented in Table 1. The IR spectra of solutions of the compounds in carbon tetrachloride were recorded with an IKS-14 spectrometer with an LiF prism. The concentrations of the solutions ranged from $2 \cdot 10^{-2}$ to $5 \cdot 10^{-2}$ M, and the layer thickness was 5 mm. Graphical separation of the bands was carried out for all of the compounds. The integral intensities are expressed in IUPAC practical units.

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