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ANALYTICAL CHEMISTRY

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Volume 36
Pages 843-5, April 1964

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▶ The proton chemical shifts of the methyl groups in 24 methyl-substituted naphthalenes have been determined. Those chemical shifts are correlated with empirically derived parameters related to the effects of methyl group substitution on the aromatic nucleus and to steric effects. The prediction of chemical shifts made possible by this correlation is valuable for the identification of the polymethylnaphthalenes in petroleum.

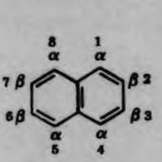
As part of a program on the identification of dinuclear aromatic hydrocarbons from petroleum, the nuclear magnetic resonance spectra of 24 polymethylnaphthalenes were obtained. A correlation of the data has provided an insight into the structural factors which affect the chemical shifts of the methyl protons.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained for 24 methyl-substituted naphthalenes with a Varian V-4203 High Resolution NMR spectrometer, operating at a frequency of 60 megacycles per second and a field strength of 14,560 gauss. The measurements were made on solutions containing 2 to 5 mole % of hydrocarbon in carbon tetrachloride, with tetramethylsilane (TMS) as an internal reference. The TMS signal was taken at 10 τ units (*5*). The chemical shifts were measured by means of the audio frequency side band technique. The effect of concentration change, in the range 1 to 10 mole %, on the chemical shifts of the methyl protons of 1- and 2-methylnaphthalenes is given in Figure 1. The chemical shifts decrease 0.02 unit as the concentration is decreased from 5 to 2 mole %. According to Pople, Schneider, and Bernstein (*10*), smaller shifts due to changes in concentration may be expected with increasing substitutions—i.e., greater molecular volume—of the aromatic ring. Therefore, the uncertainty due to concentration differences for the polymethylnaphthalenes is expected to be within ±0.01 p.p.m.

RESULTS

The 48 chemical shift values measured for methyl groups from 24 methyl naphthalenes are given in Table I. The lettering and numbering system for the naphthalene nucleus is:



The methyl groups fall into three categories: (*a*) β-methyl groups, for which chemical shifts are between 7.50 and 7.70 τ units; (*b*) α-methyl groups (except for dimethyl substitution in the 1,8- and 4,5-positions), for which chemical shifts are between 7.36 and 7.50 τ units; and (*c*) α-methyl groups, disubstituted in the 1,8- and 4,5-positions, for which chemical shifts are in the range 7.14 to 7.26 τ units.

In addition, two general trends may be observed: (*a*) The chemical shifts tend to increase as the number of substituents on the nucleus is increased; and (*b*) this increase in the chemical shifts, for a given number of substituents depends on the position of the other methyl groups. For example, the increase in the chemical shift of any methyl group with an adjacent substitution is greater than that caused by a nonadjacent substitution in the same ring, which in turn is greater than that resulting from substitution in the

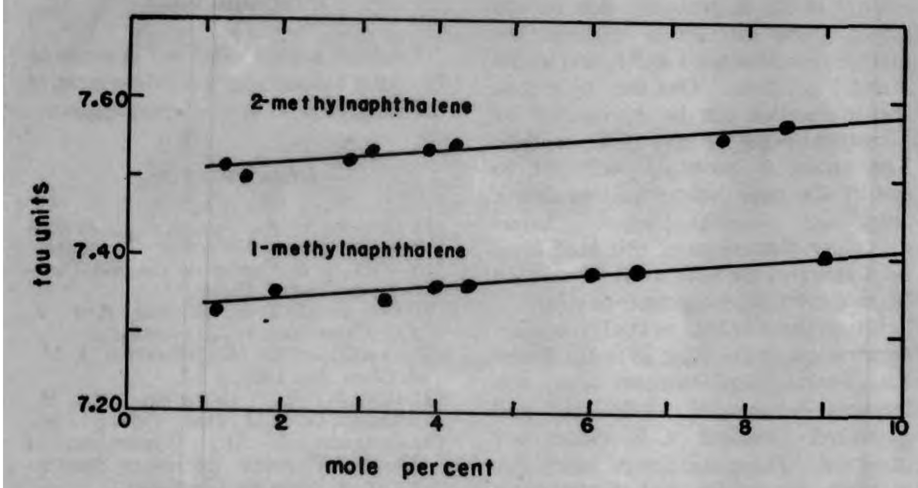


Figure 1. Chemical shifts of the methyl protons of the 1- and 2-methylnaphthalenes with respect to the concentration in carbon tetrachloride

Table I. Measured and Calculated Values for Chemical Shifts of Methyl Protons in Polymethylnaphthalenes

		$\delta\alpha(\tau)$			$\delta\beta(\tau)$		
Type	Compound[a]	Position	Measured	Calculated[b]	Position	Measured	Calculated[b]
α	1-Methyl-[c]	1	7.36[d]				
β	2-Methyl-[c]				2	7.52[d]	
2α	1,4-Dimethyl-[e]	1,4	7.41	7.41			
	1,5-Dimethyl-[f]	1,5	7.38	7.37			
	1,8-Dimethyl-[g]	1,8	7.18	7.16			
2β	2,3-Dimethyl-[e]				2,3	7.65	7.62
	2,6-Dimethyl-[e]				2,6	7.54	7.53
	2,7-Dimethyl-[f]				2,7	7.54	7.53
α, β	1,2-Dimethyl-[f]	1	7.48	7.46	2	7.60	7.62
	1,3-Dimethyl-[e]	1	7.41	7.41	3	7.55	7.57
	1,7-Dimethyl-[e]	1	7.38	7.37	7	7.52	7.53
3α	1,4,5-Trimethyl-[e]	1	7.43	7.42			
		4	7.18	7.21			
		5	7.14	7.17			
3β	2,3,6-Trimethyl-[h]				2,3	7.65	7.63
					6	7.55	7.54
$2\ \alpha,\beta$	1,2,4-Trimethyl-[e]	1	7.49	7.51	2	7.62	7.67
		4	7.43	7.46			
	1,3,5-Trimethyl-[e]	1	7.42	7.42	3	7.58	7.58
		5	7.42	7.38			
$2\ \alpha,\beta$	1,4,6-Trimethyl-[e]	1	7.42	7.42	6	7.53	7.54
		4	7.42	7.42			
$\alpha,2\beta$	1,6,7-Trimethyl-[h]	1	7.41	7.38	6	7.65	7.62
					7	7.63	7.62
4α	1,4,5,8-Tetramethyl-[e]	1,4	7.26	7.22			
		5,8	7.26	7.22			
4β	2,3,6,7-Tetramethyl-[h]				2,3	7.64	7.64
					6,7	7.64	7.64
$2\alpha, 2\beta$	1,2,3,5-Tetramethyl-[e]	1	7.46	7.52 (7.46)	2	7.69	7.73 (7.67)
		5	7.40	7.39	3	7.60	7.68 (7.62)
	1,2,3,4-Tetramethyl-[e]	1	7.44	7.56 (7.43)	2	7.63	7.77 (7.64)
		4	7.44	7.56 (7.43)	3	7.63	7.77 (7.64)
$3\alpha,\beta$	1,3,5,8-Tetramethyl-[e]	1,8	7.20	7.18	3	7.60	7.63
		5	7.47	7.43			
$3\alpha, 2\beta$	1,2,3,5,8-Pentamethyl-[e]	1	7.25	7.32 (7.26)	2	7.72	7.74 (7.68)
		5	7.44	7.44	3	7.62	7.69 (7.63)
		8	7.23	7.23			
$2\alpha, 4\beta$	1,2,3,4,6,7-Hexamethyl-[e]	1,4	7.47	7.58 (7.45)	2,3	7.62	7.79 (7.66)
					6,7	7.67	7.68

[a] Letters indicate source of compound.
[b] Values given in parentheses contain an additional correction for steric effect (see text).
[c] API Research Project 58.
[d] At a concentration of 3 mole % in CCl_4.
[e] G. Dana Johnson, Kansas State University.
[f] Richard W. King, The Sun Oil Co.
[g] Commercial sources.
[h] From Petroleum by API Research Project 6.

opposite ring. These two trends are also observable in the case of 1,8- and 4,5-dimethyl substitution.

By assigning suitable values to the substitutional and steric factors suggested by the foregoing trends, an empirical equation was developed to permit the calculation of the chemical shifts for all the methylnaphthalenes. The values of the constants were adjusted by the method of least squares;

$$\delta_{\alpha,\beta} = \delta^0_{\alpha,\beta} + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4 \qquad (1)$$

where

δ^0_α = 7.36 τ for 1-methylnaphthalene
δ^0_β = 7.52 τ for 2-methylnaphthalene
$\Delta\delta_1$ = 0.10 p.p.m., contribution to the chemical shift of any methyl group by an adjacent methyl substitution
$\Delta\delta_2$ = 0.05 p.p.m., contribution to the chemical shift of any methyl group for each nonadjacent methyl group substituted on the same ring
$\Delta\delta_3$ = 0.01 p.p.m., contribution to the chemical shift of any methyl group for each additional methyl group substituted on the opposite ring (excepting 1,8- and 4,5-substitution)
$\Delta\delta_4$ = −0.20 p.p.m., contribution to the chemical shift of a methyl group at C-1 by the substitution of a methyl group at C-8 and vise versa

The chemical shifts calculated for each compound are listed in Table I. The differences between experimental and calculated values are less than 0.04 p.p.m., except for 1,2,3- and 1,2,3,4-multisubstituted compounds. Those cases are discussed later.

DISCUSSION

The constants in the empirical equation provide some insight into the factors responsible for the differences in the chemical shifts of the methyl groups.

The positive contribution to the chemical shift of any methyl group has been noted for the methyl substituted benzenes (*11*) and for some dimethylnaphthalenes (*6*). It has also been noted that the NMR signals of aromatic ring protons shift upfield as the number of methyl substitutions increases (*6, 7*). There are several factors which may give rise to this upfield shift: (*a*) the perturbation of ring current by the substitutions; (*b*) the redistribution of charges caused by the resonance and inductive or field effect of methyl substitutions; (*c*) a possible magnetic anisotropy of the methyl group. Each of these effects may be both distance and direction dependent. Our attempt to interpret quantitatively the chemical shifts of the methyl protons in terms of one or the other of the effects individually was not successful; for example, Hammet constants, derived from the expression given by Dewar (*2*) for substituted naphthalenes and from the electronic atom-atom polarizabilities calculated by Coulson and Daudel (*1*), did not correlate with the shifts nor did plots of the form $(1 - 3 \cos^2\theta)/R^3$, a formula representing anisotropy effects, correlate with the chemical shifts. We feel that any attempt to combine quantitatively the effects giving rise to the shifts would not be meaningful in view of the large number of parameters involved; we therefore prefer to interpret these shifts on a qualitative basis.

The abnormally low chemical shifts for 1,8- and 4,5-methyl groups may be interpreted in terms of a steric effect. Reid (*12*) and MacLean and Mackor (*6*) have observed that protons which are sterically hindered give NMR signals at lower fields than those which are unhindered. They also found that 4,8-aromatic protons in 1,4-dimethylnaphthalene give lower chemical shifts than the corresponding protons in naphthalene. The downfield shift resulting from steric hindrance may be satisfactorily explained in terms of Pople's treatment of nuclear magnetic deshielding in an electrostatic field (*9*), since distortion of the electron clouds in hindered groups is always expected. The relatively large negative contribution ($\Delta\delta_4 = -0.20$) to the 1,8- or 4,5-methyl shifts is probably due to the strong steric interaction between the methyl groups at the 1 and 8, and at the 4 and 5 positions. One may note that this interaction can be represented by Hirschfelder-Taylor molecular models. The strain is probably sufficient to distort the naphthalene nucleus into a nonplanar configuration. Intramolecular distortions of this kind have been revealed by both x-ray diffraction (*3*) and ultraviolet spectrometry (*8*).

Where three or four methyl groups are substituted on one ring, as in 1,2,3- and 1,2,3,4-methylnaphthalenes, large differences between the calculated and measured chemical shift values are observed. These also are probably due to steric interaction and distortion of the ring (*10*). [X-ray measurements show, though not conclusively, that adjacent methyl groups in 1,2,4,5-tetramethylbenzene cause a slight distortion of the ring (*4*).] If negative contributions to chemical shift (−0.06 p.p.m. for 1,2,3-substitution and −0.13 p.p.m. for 1,2,3,4-substitution) are attributed to this increasing steric effect; the calculated chemical shift values are in satisfactory agreement with the experimental values (values in the parentheses in Table I). Methyl group shifts for additional compounds are needed to determine this effect with greater accuracy.

ACKNOWLEDGMENT

Grateful acknowledgment is made to G. Dana Johnson for providing most of the samples used in this investigation.

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RECEIVED for review November 13, 1963. Accepted January 2, 1964. This research was supported by a grant from the American Chemical Society Petroleum Research Fund.