Observation of the negative induction effect by bound hydrogen capture of π^- mesons

L. Vil'gel'mova, P. Zimrot, V. I. Petrukhin, V. E. Risin, L. M. Smirnova, V. M. Suvorov, and I. A. Yutlandov

Joint Institute for Nuclear Research

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A negative induction effect in methane and benzene derivatives is observed on the basis of suppression ϵ of the probability of π^--meson capture by hydrogen. A linear dependence of the suppression ϵ on the induction constants of the substituents σ_I is observed for the methyl derivatives. No correlation of this type is observed in the benzene derivatives, probably because of the contribution of conjugation effects to the suppression of ϵ.

It has been determined experimentally that the probability W of the capture of π^- mesons by nuclei of bound hydrogen is strongly suppressed.[1] The model of large mesic molecules has been used to elucidate the mechanism of this suppression.[2,3] This model describes the fundamental physical processes that cause suppression for all such molecules, but does not take into account individual differences in the structure of the molecules. It was later concluded[4] that the probability W is sensitive to the density distribution of the bonding electrons of the hydrogen atoms in the molecules. Indeed, in some cases considerable deviations from the predictions of the large mesic-molecule model have been observed, due to the characteristics of the hydrogen chemical bond in the molecules. We can include among these effects the sharp suppression of π^--meson capture by hydrogen nuclei in strong acids[5] and the manifestation of the effect of identical groups in bases.[6]

In the present work we undertook to observe how the induction effect of electron-accepting substituents influences the capture of π^- mesons by hydrogen in organic molecules. The induction effect is associated with the density redistribution of electrons of the C—H bonds when a substituent is introduced into a molecule. For the acceptor substituents used by us this should lead to suppression of the capture probability W. Induction effects are usually inferred from observed changes of molecular reactivity or dipole moments, from infrared spectra, or from data obtained by other more or less indirect methods.

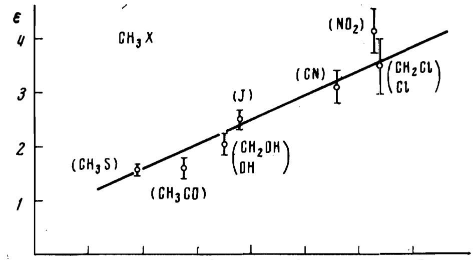

FIG. 1. Dependence of suppression ϵ on induction constants σ_I of substituents in methyl derivatives. The substituents X are shown in the parentheses. The straight line represents the equation $\epsilon = \alpha\sigma_I + \beta$, where $\alpha = 4.7 \pm 0.6$, $\beta = 0.6 \pm 0.2$, $\chi^2(7) = 2.6$, and $S(\alpha\beta) = 0.1$.

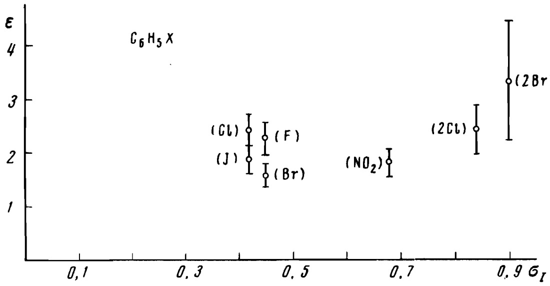

FIG. 2. Dependence of suppression ϵ on induction constants σ_I of substituents in benzene derivatives. The substituents X are shown in the parentheses).

Our method, which is sensitive to the density of electrons of the C—H bonds, is more direct; it is therefore of interest to determine its possibilities. Measurements were performed using a beam of 80-MeV π^--mesons from the JINR synchrocyclotron. The experimental setup was described in[7]; the results are here given in a table. In our case the measure of the induction effect is the suppression of capture:

$$\varepsilon = \frac{W}{W_e}, \quad W = a_Z \frac{nZ^{-2}}{mZ + qZ' + n}$$

where W and W_e were calculated from the model of large mesic molecules[3] (with a single experimentally determined parameter a_Z [1)]); the experimental values of the capture probability are given for molecules of the type $Z_m H_n Z'_q$

The strongest effect ($\epsilon \sim 2$—5) is observed for methyl derivatives. This result is associated with the fact that in saturated compounds the induction effect is manifested most strongly at the carbon atom in the α position for attachment of the substituent. The considerably smaller effect ($\epsilon \sim 1.6$) in chloro- and nitropentane and in cyclohexanone is associated with the fact that electronic effects are transmitted weakly along a saturated chain. The linear dependence of the suppression (ϵ) of π^- capture by hydrogen in methyl groups, upon the induction constants of the substituents[8] (see Fig. 1) shows that the shifting of the electron cloud of the hydrogen atoms, which is induced by the acceptor substituents, plays the fundamental role in the suppression of nuclear capture. For dichloroethane and ethylene glycol the induction constants were taken to equal, in first approximation, the sum of the constants of the individual substituents.[9] In calculating the suppression ϵ for ethylene glycol it was assumed that the probability of π^- capture by the hydrogen of the OH groups is the same as in water and alkalis ($a_0 = 1.28 \pm 0.15$). With $\epsilon \sim 2$—2.5 the aromatic derivatives are situated between the methyl derivatives and the derivatives of pentane. However, in this case the induction effect is not dominant; its contribution to sup-

Compound	W_e, 10^{-3}	W, 10^{-3}	$\epsilon = W/W_e$	σ_I
CH_3J	1,11±0,07	2,76±0,05	2,48±0,16	0,38
CH_3NO_2	1,29±0,13	5,33±0,10	4,14±0,42	0,63
CH_3CN	2,50±0,21	7,76±0,15	3,10±0,27	0,56
CH_3COCl	0,87±0,08	4,27±0,08	4,91±0,46	—
$(CH_3)_2S$	6,46±0,40	10,05±0,20	1,56±0,10	0,19
$(C_2H_5)_3N$	12,30±1,30	14,73±0,29	1,20±0,13	0,10
$(C_2H_5)_4NJ$	4,20±0,45	8,90±0,17	2,12±0,23	0,92
$(CH_2OH)_2$	3,26±0,30	6,70±0,13	2,05±0,20	0,35
C_3H_6 [4] (acetone)	6,6±0,8	10,7±0,2	1,6±0,2	0,28
$C_2H_4Cl_2$ [1] (dichloroethane)	1,3±0,2	4,6±0,1	3,5±0,5	0,64
$C_5H_{11}Cl$	7,30±0,47	10,80±0,21	1,48±0,10	—
$C_5H_{11}NO_2$	6,00±0,39	9,79±0,19	1,63±0,11	—
$(C_3H_7)_2O$	10,50±0,50	13,74±0,27	1,31±0,07	—
$C_6H_{10}O$ (cyclohexanone)	6,12±0,32	10,54±0,21	1,72±0,10	—
C_6H_5F	1,23±0,12	2,76±0,24	2,24±0,29	0,45
C_6H_5Cl	1,00±0,10	2,38±0,21	2,38±0,32	0,42
C_6H_5Br	1,17±0,11	1,82±0,16	1,56±0,20	0,45
C_6H_5J	0,85±0,09	1,58±0,14	1,86±0,26	0,42
$C_6H_5NO_2$	1,22±0,13	2,17±0,18	1,78±0,24	0,68
C_6H_5COCl	0,45±0,08	2,24±0,20	4,98±0,99	—
C_5H_5N	2,37±0,16	3,29±0,30	1,39±0,16	—
o-$C_6H_4Cl_2$	0,63±0,10	1,50±0,14	2,38±0,44	0,84
n-$C_6H_4Br_2$	0,30±0,10	0,99±0,09	3,30±1,10	0,90
$C_{12}H_{10}N_2$ (azobenzene)	1,60±0,20	2,89±0,18	1,81±0,25	—

pression may be distorted by conjugation effects, which can act in the opposite direction. Indeed, Fig. 2 shows that the observed effect (ϵ) is weakly correlated with the induction constants σ_I.[8] For disubstituted benzenes doubled constants σ_I^M were assumed in first approximation. We note that the $\epsilon(\sigma_I)$ curve for methyl derivatives (Fig. 1) can be used to evaluate the induction constant σ_I for the COCl group; the value 0.92 ± 0.10 is obtained.

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1) $a_Z = 2.05 \pm 0.04$ for aliphatic and $a_Z = 0.98 \pm 0.08$ for aromatic hydrocarbons.

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