Электростатические взаимодействия как фактор, определяющий структуру и реакционную способность органических соединений

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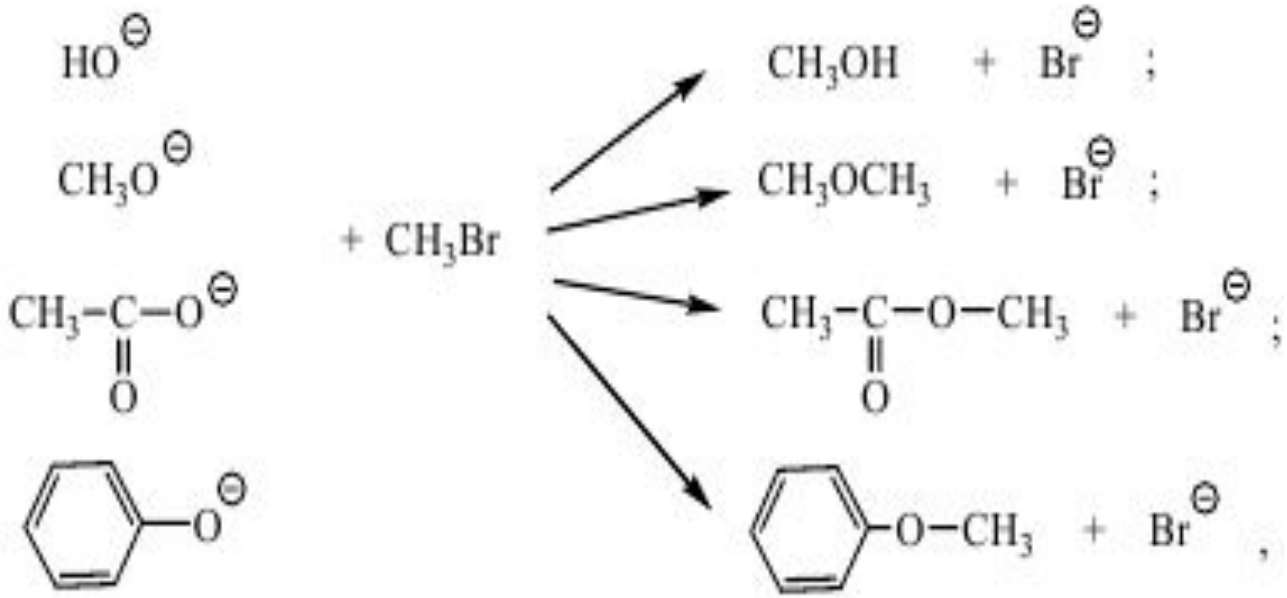
Откуда всё пошло

Effect of Multiple Substitution on pK_a.

Compound	pK_a	single ΔpK_a	total ΔpK_a
CH_3CO_2H	4.74	--	--
$ClCH_2CO_2H$	2.87	1.87	1.87
Cl_2CHCO_2H	1.29	1.58	3.45
CCl_3CO_2H	0.65	0.64	4.09

Реакционная серия



Несколько замечательных вопросов: /

1. Можно ли данные, полученные на низших членах гомологического ряда (метил-, этил-) распространить на остальные?;

2. Можно ли представления, сформированные на основе физико-химических данных в газовой фазе, переносить на жидкость (основность и кислотность через pK)?; .

3. Является ли раствор, в котором протекает реакция, истинным?;

4. Всегда ли мы помним о взаимном влиянии атомов?

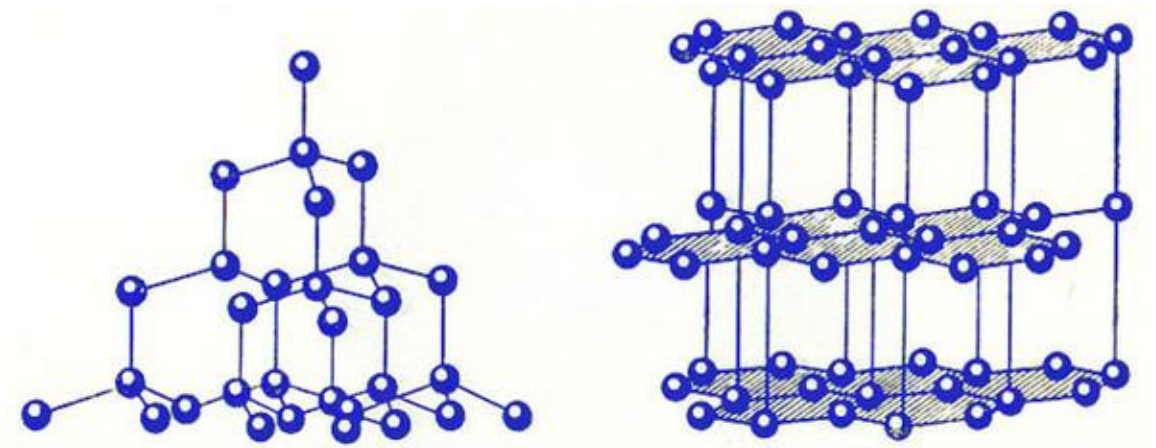
Номенклатура

S	Name	S	Name
X	halo	R(C=O)	acyl
RO	alkoxy or hydroxy	R	alkyl
R2N	amino	H	hydrogen
HSO3	sulfonic acid	R2C=CR	alkenyl
N≡C	cyano	RC≡C	alkynyl
O2N	nitro	Ar	aryl

Электронные эффекты

- The **inductive effect** has universally been represented by the symbol **I**. This is now commonly taken to include both through-bonds and through-space transmission, but **I** is also used specifically for through-bonds transmission; through-space transmission is then symbolized as (for **field effect**). The symbols for the influence of substituents exerted through electron **delocalization** have variously been (**mesomeric**), (**electromeric**), (tautomeric), (conjugative), K (konjugativ) and (resonance). Since the present fashion is to use the term resonance effect, is the most commonly used symbol, although is still seen quite often. Both the possible sign conventions are in use.
- The Ingold sign convention associates electronegativity (relative to hydrogen atom) with a negative sign, electropositivity with a positive sign. Thus the nitro group is described as electronwithdrawing by virtue of its +**I** and effects; chloro is described as a - **I**, substituent, etc. For correlation analysis and linear free-energy relationships this convention has been found inconvenient, for it is in contradiction to the sign convention for polar substituent constants (σ-constants). Authors concerned with these fields often avoid this contradiction by adopting the opposite sign convention originally associated with Robinson, for electronic effects. This practice is almost always associated with the use of R for the electron delocalization effect: thus the nitro group is a , substituent; chloro a , substituent, etc.
- **PAC, 1994, *66*, 1077** ***(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))*** **on page 1111**

Два типа мостиков или о важности направления

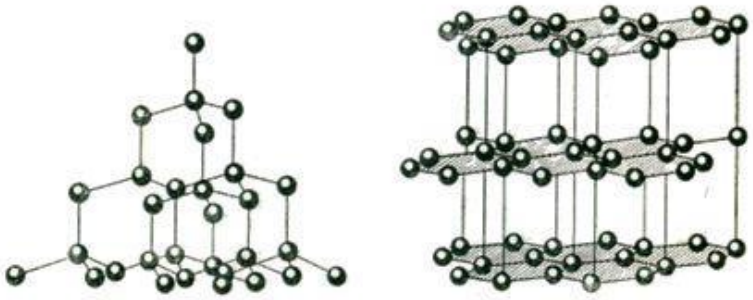


Кристаллические решетки алмаза (слева) и графита (справа)

Простые вещества

Аллотропия

- Углерод: алмаз (sp^3), графит (sp^2), карбин (sp), фуллерен.
- Олово «белое» и «серое».



Структура алмаза и графита

Олово белое

Олово серое

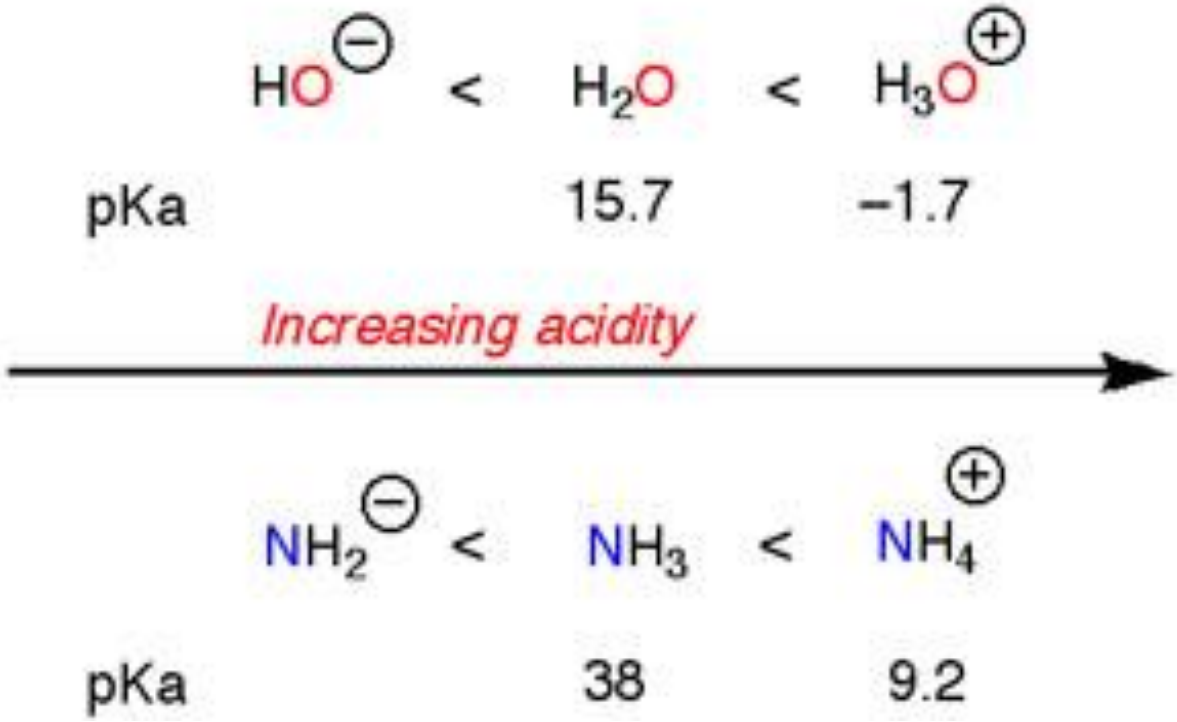
Алмаз

Графит

Пять факторов

Первый или заряд

1. Acidity Increases with Increasing positive charge on an atom



2. Across the periodic table, acidity increases with electronegativity...

	CH_4	<	NH_3	<	H_2O	<	HF
pKa	~50		38		15.7		3.2
Electronegativity	2.5		3.0		3.4		4.0

...but down the periodic table, acidity increases with size.

	HF	<	HCl	<	HBr	<	HI
pKa	3.2		–8.0		–9.0		–10
Electronegativity	4.0		3.0		2.8		2.5
Ionic radius (picometres)	133		181		196		220

Also holds for oxygen versus sulfur...

	H_2O	<	H_2S
pKa	15.7		7.0

	H_3COH	<	H_3CSH
pKa	15.5		10

И так…

- Концепция электроотрицательности работает в периоде, но не работает в группах. И не просто не работает, но дает абсолютно противоположные зависимости!
- Кто прав – Полинг или Менделеев?
- Тогда почему держимся за неё до сих пор?

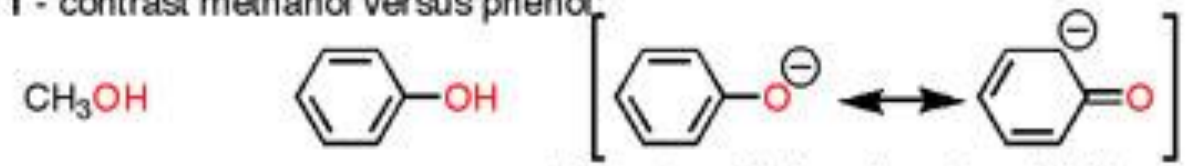
3. Resonance

Remember, **any structural feature that increases the stability of the conjugate base will increase acidity.**

Key question: can the lone pair of the conjugate base participate in resonance with an adjacent π bond?

Resonance will increase the stability of the conjugate base (therefore increasing acidity) because the negative charge can be delocalized.

Example 1 - contrast methanol versus phenol:

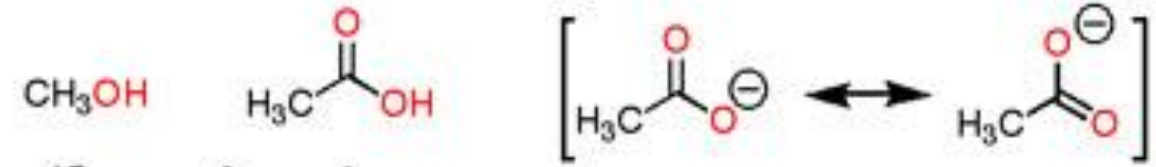


pKa 15 < **10**

more acidic

The anion of phenol can be stabilized through resonance

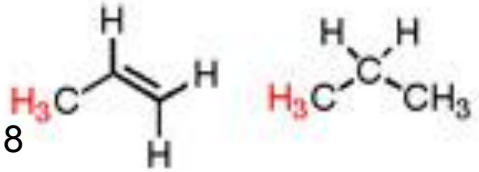
Example 2 - alcohols (e.g. methanol) versus carboxylic acids



pKa 15 < **4**

more acidic

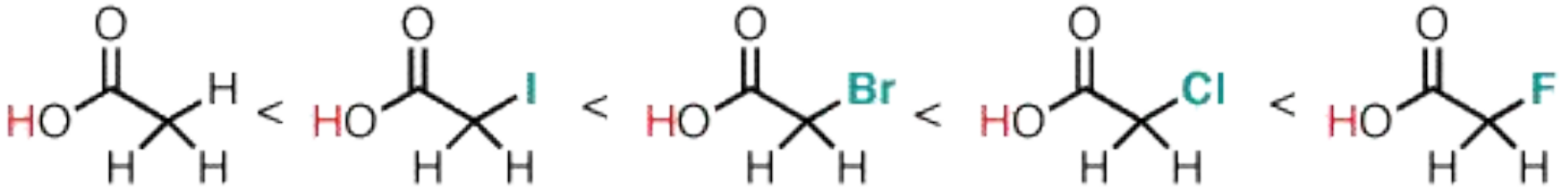
Question: Which proton (in red) would you expect to be more acidic?



4. Electronegativity and inductive effects:

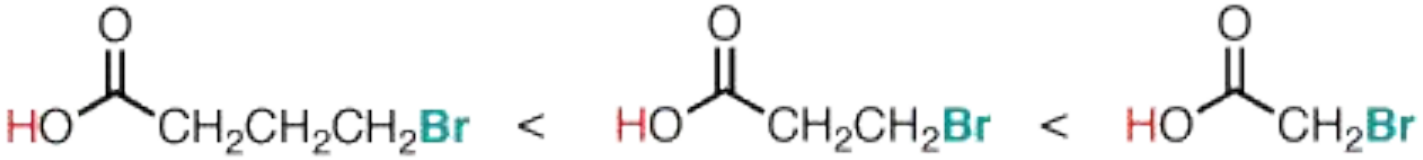
Two principles - electron-withdrawing substituents can increase acidity of a nearby atom, which increases with electronegativity and decreases with increasing distance to the atom.

Electronegativity increases in the order F > Cl > Br > I :



pKa	4.76	3.15	2.86	2.81	2.66

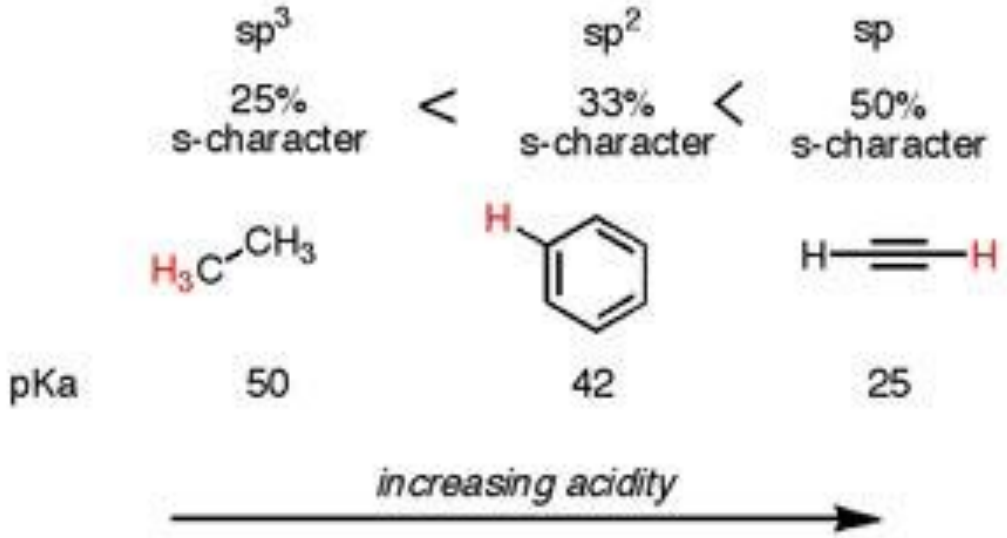
More acidic



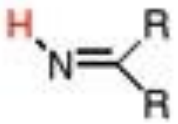
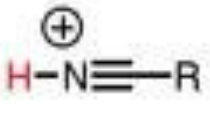
pKa	4.59	4.01	2.86

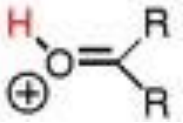
5. Orbitals

The higher the *s*-character of a bond to hydrogen, the more acidic it will be.



Questions: What do you think about the acidity of the following protons in red?

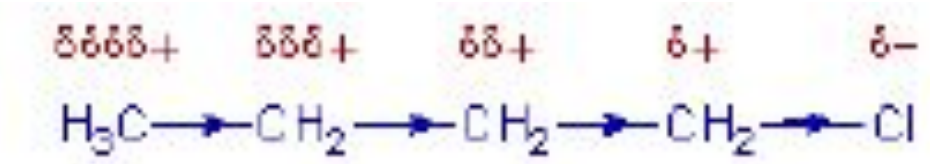
1. H_2N-CH_2R  

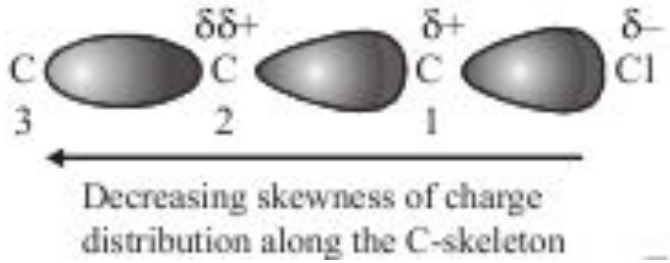
2.  $HO-CH_2R$

Парадокс ацетилена

- Связь С-Н в ацетилене по сравнению со связью в этилене **намного прочнее,** тем не менее мы говорим о том, что протон в ацетилене аномально кислый.
- Аномалия в мозгах?

Ещё один пример



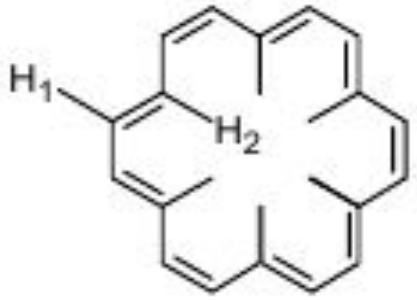


A crude orbital picture showing how the inductive effect dies down along the chain

С электроотрицательностью почти все нормально

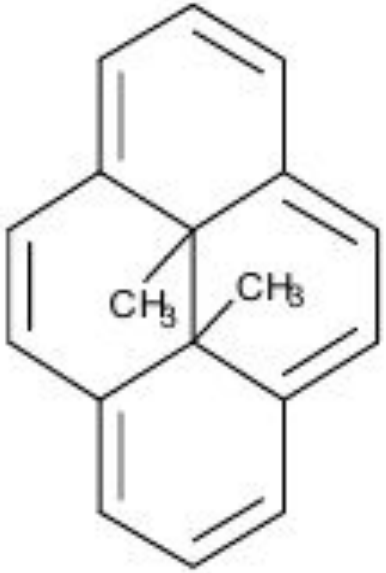
	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3H
$\delta(CH_3)$	4.13	2.84	2.45	1.98	0.13
Electonegativity (Pauling)	4.0	3.0	2.8	2.5	2.1

…но!?



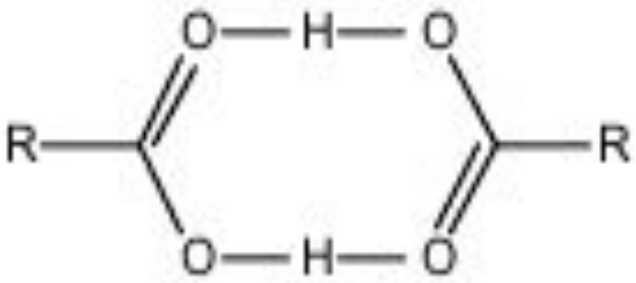
H_1 + 8.9 ppm

H_2 - 1.8 ppm

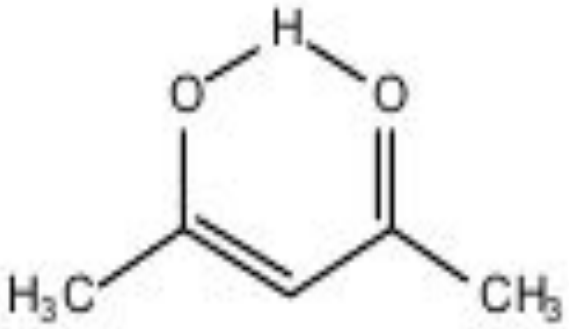


CH_3 - 4.25 ppm

Examples of strong hydrogen bonds



δ = 9-15 ppm

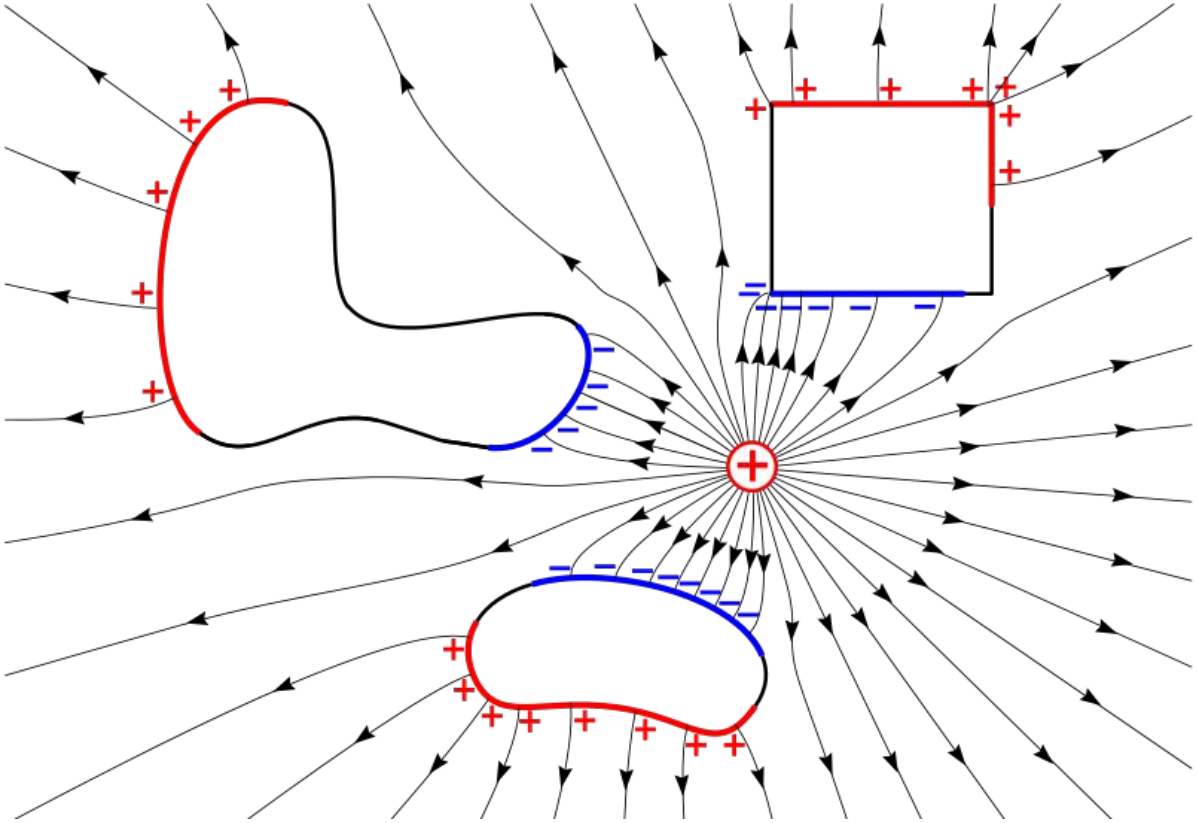


δ = 15.4 ppm

Индуктивный эффект – ещё раз

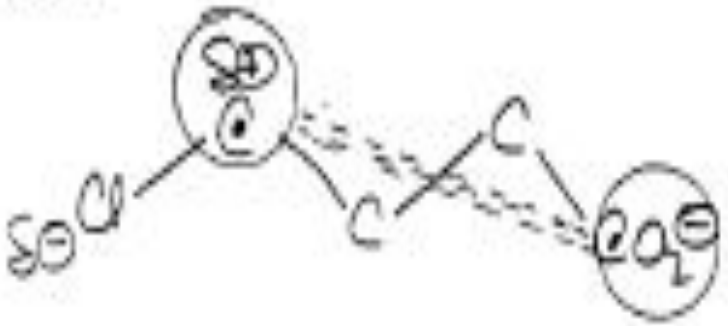
- "In strict definition, an experimentally observable effect (on rates of reaction, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. A theoretical distinction may be made between the field effect, and the inductive effect as models for the Coulomb interaction between a given site within a molecular entity and a remote unipole or dipole within the same entity. The experimental distinction between the two effects has proved difficult, except for molecules of peculiar geometry, which may exhibit 'reversed field effects'. Ordinarily the inductive effect and the field effect are influenced in the same direction by structural changes in the molecule and the distinction between them is not clear. This situation has led many authors to include the field effect in the term 'inductive effect'. Thus the separation of values into inductive and resonance components does not imply the exclusive operation of a through-bonds route for the transmission of the non-conjugative part of the substituent effect. To indicate the all-inclusive use of the term inductive, the phrase 'so-called inductive effect' is sometimes used. Certain modern theoretical approaches suggest that the 'so-called inductive effect' reflects a field effect rather than through-bonds transmission."

PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1124



Surface charges induced in metal objects by a nearby charge. The electrostatic field *(lines with arrows)* of a nearby positive charge *(+)* causes the mobile charges in metal objects to separate. Negative charges *(blue)* are attracted and move to the surface of the object facing the external charge. Positive charges *(red)* are repelled and move to the surface facing away. These induced surface charges create an opposing electric field that exactly cancels the field of the external charge throughout the interior of the metal. Therefore electrostatic induction ensures that the electric field everywhere inside a conductive object is zero.

14.16



Electrostatic Attraction through space between Cl-C and CO_2^-

Об адитивности влияния заместителей или кто на кого влияет

Table 14.05. Effect of Cl Substitution on Acidity of Acetic Acid.

Acid	pK_a	K_a	$K_{a(Cl)}/K_{a(H)}$
CH_3CO_2H	4.8	1.7×10^{-5}	1
$ClCH_2CO_2H$	2.9	1.4×10^{-3}	80
Cl_2CHCO_2H	1.3	5.1×10^{-2}	3,000
CCl_3CO_2H	0.7	2.2×10^{-1}	12,940

Ещё раз об уксусных кислотах

Effect of Multiple Substitution on pK_a.

Compound	pK_a	single ΔpK_a	total ΔpK_a
CH_3CO_2H	4.74	--	--
$ClCH_2CO_2H$	2.87	1.87	1.87
Cl_2CHCO_2H	1.29	1.58	3.45
CCl_3CO_2H	0.65	0.64	4.09

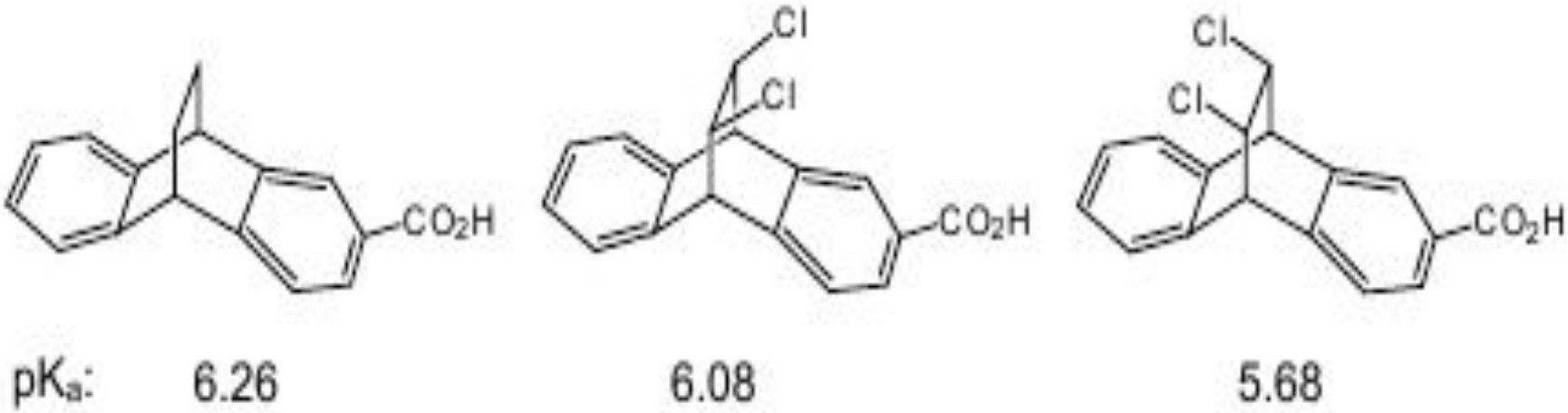
pK_a's of Monosubstituted Carboxylic Acids, $X\text{-}CH_2\text{-}C(O)OH$

X	pK_a	X	pK_a
$-NO_2$	1.68	-I	3.16
$-\overset{+}{N}(CH_3)_3$	1.83	$-C\equiv CH$	1.84
$-OCH_3$	3.53	$-C(O)CH_3$	3.58
$-SO_2CH_3$	2.36	$-SCH_3$	3.72
-CN	2.47	$-C_6H_5$	4.31
-F	2.66	$-CH=CH_2$	4.26
-C(O)OH	2.83	-H	4.74
-Cl	2.87	$-CO_2^-$	5.69
-Br	2.90		

Effect of Distance of Substituent on pK_a

Compound	pK_a	ΔpK_a
$CH_3CH_2CH_2CO_2H$	4.82	--
$CH_3CH_2\underset{\displaystyle Cl}{\underset{\vert}{C}}HCO_2H$	2.84	1.98
$CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}HCH_2CO_2H$	4.06	0.76
$\underset{\displaystyle Cl}{\underset{\vert}{C}}H_2CH_2CH_2CO_2H$	4.52	0.30

Ангулярная зависимость эффекта

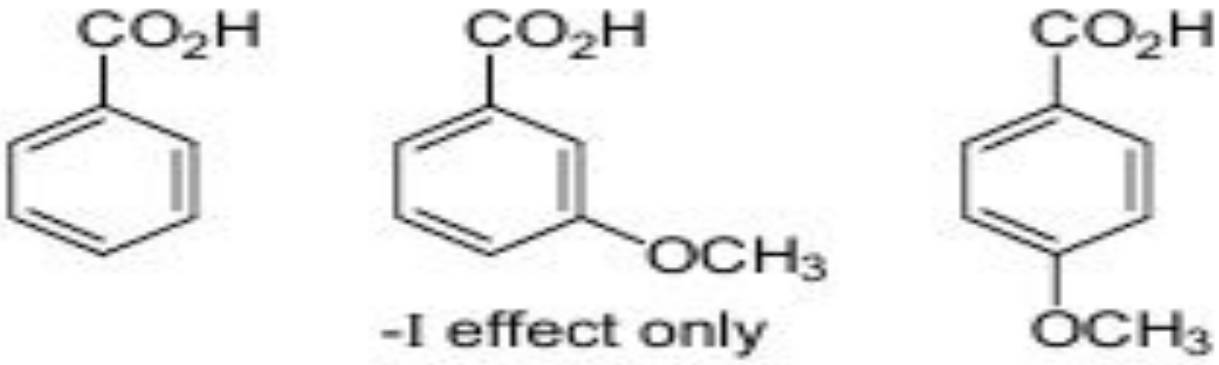


pK_a: 6.26 6.08 5.68

Grubbs and Firzgerald,
Tetrahedron Letters, 4901(1968)

Резонансные или мезомерные эффекты

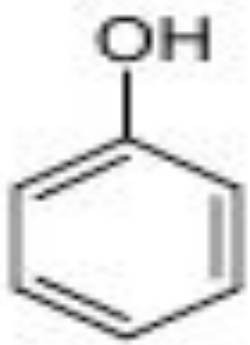
I,- +R-эффекты

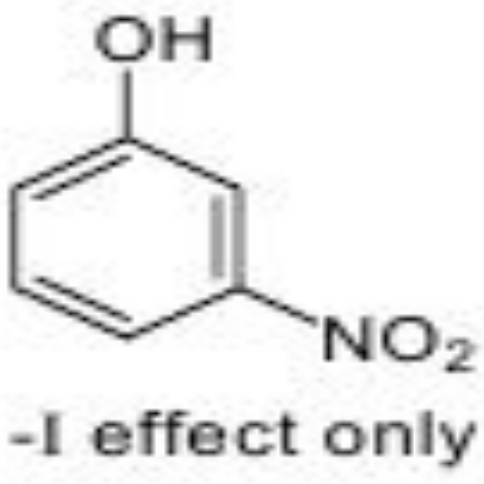


pKa	**4.18**	**4.09**	**4.47**

Стабилизация отрицательного заряда

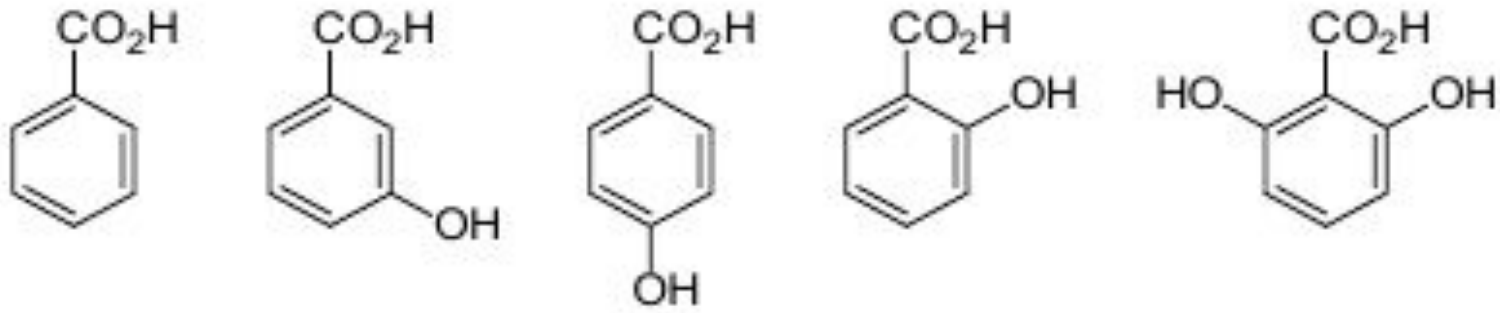
-I, -R заместители



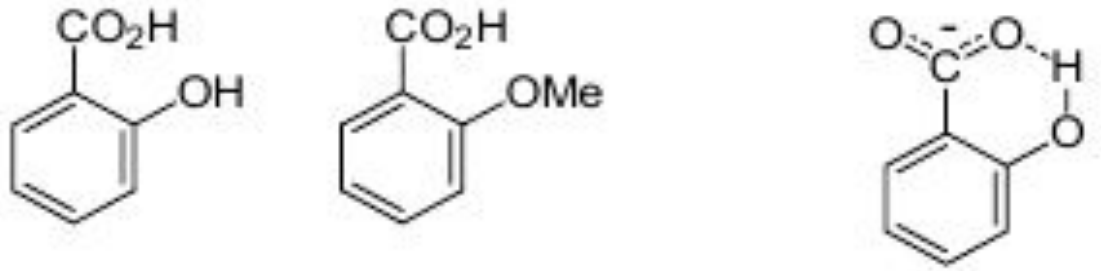


pK_a	**9.92**	**8.40**	**5.17**

Влияние ВС

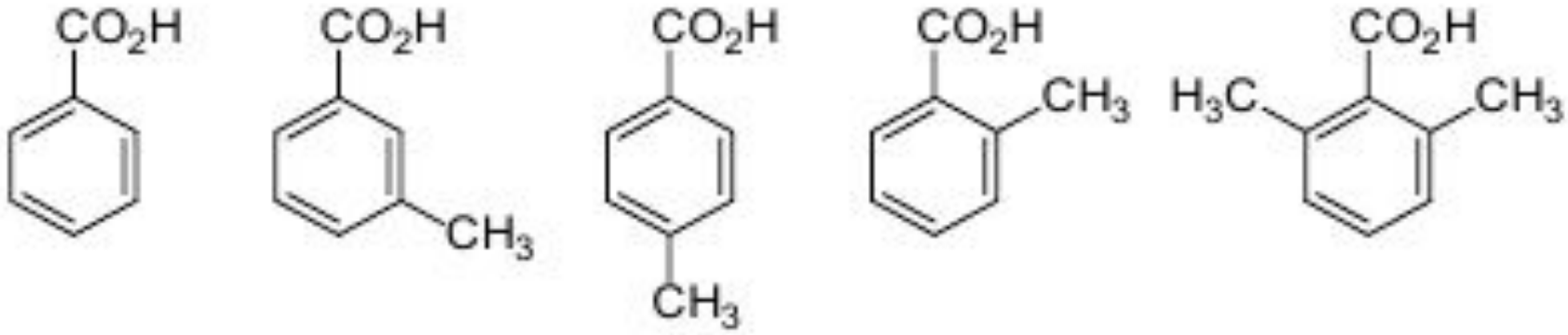


pK_a: 4.18 4.08 4.58 2.98 2.30

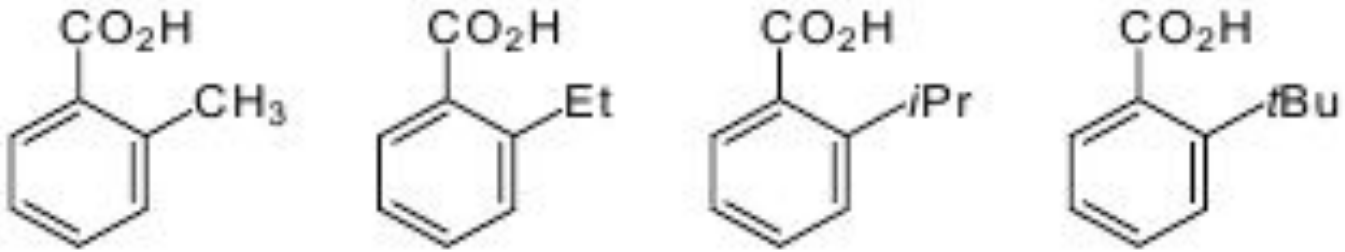


pk_a: 2.98 4.09

Стерическое ингибирование

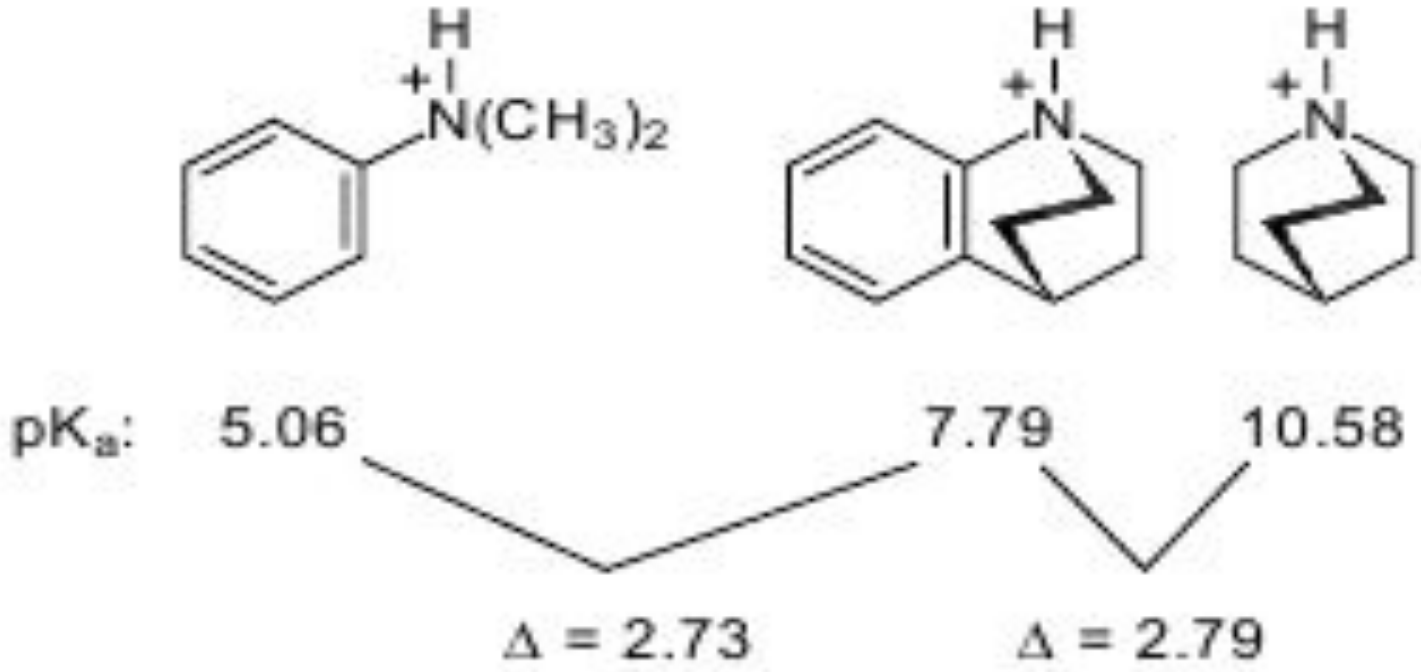


pK_a: 4.18 4.24 4.34 3.91 3.25

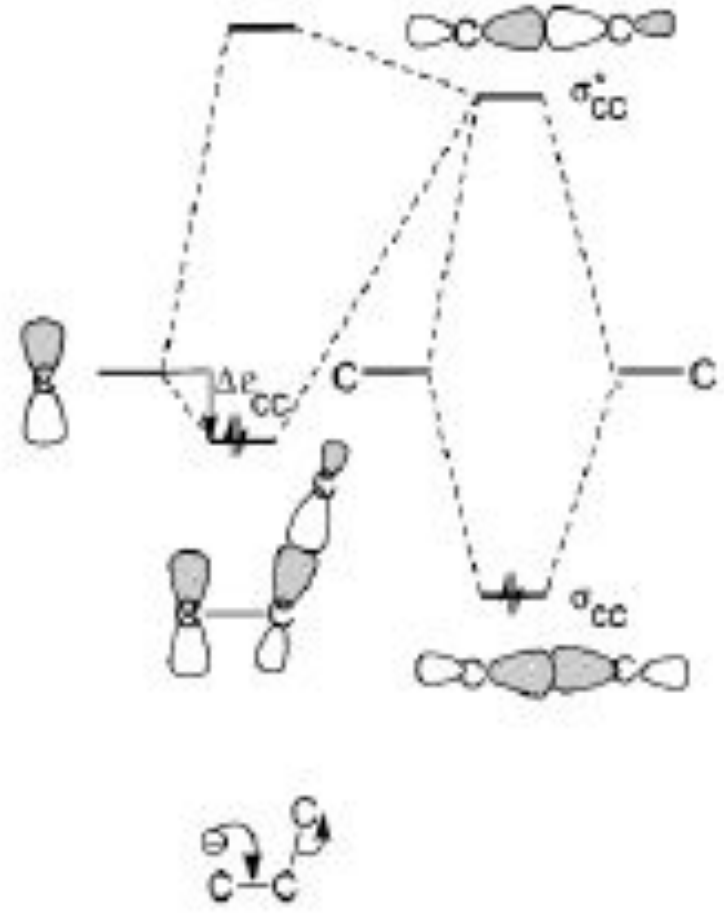


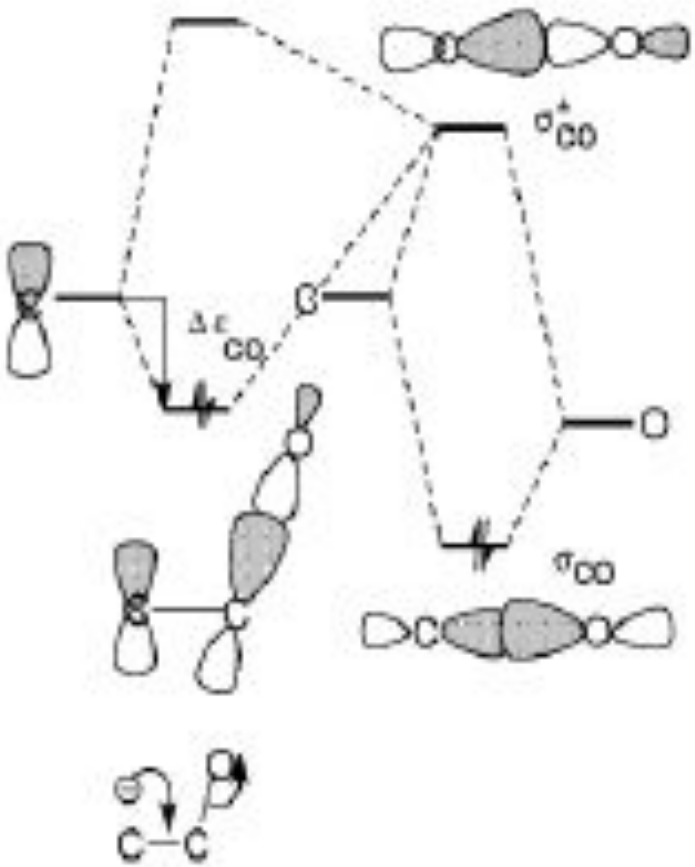
pK_a: 3.91 3.79 3.64 3.46

Сопряжение в ряду солей



Гиперконьюгция





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A PART OF

A DISSERTATION

PRESENTED TO
THE FACULTY OF THE UNIVERSITY OF UTAH
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

[Contribution from the Department of Chemistry, University of Utah]

The Inductive Effect and Chemical Reactivity. I. General Theory of the Inductive Effect and Application to Electric Dipole Moments of Haloalkanes

By Richard P. Smith, Taikyue Ree, John L. Magee[1] and Henry Eyring

The inductive effect is discussed qualitatively in terms of bond orbital theory, and the main features of the effect are pointed out. A simple semi-classical model for the inductive effect is then introduced, and the analysis of this model leads to a method for calculating approximately net charges on atoms in molecules having no conjugation. All of the parameters are obtained from accepted longitudinal polarizabilities, screening constants, covalent bond radii and electric dipole moments. The method is checked by comparing calculated and observed electric dipole moments of some halogen substituted alkanes, and excellent agreement is found. The method will be shown, in succeeding papers, to be of great utility in understanding relative organic reaction rates and equilibria.

(19) Y. K. Syrkin and M. E. Dyatkina, "The Structure of Molecules and the Chemical Bond," Translated and Revised by M. A. Partridge and D. O. Jordan, Interscience Publishers, Inc., New York, N. Y., 1950.