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Abstract

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DIPOLE MOMENTS AND REACTIVITY OF VINYLACETYLENE HYDROCARBONS

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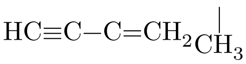
The study of addition reactions of 1,3-enyne hydrocarbons led to the conclusion that in the molecules of vinylacetylene and of n-alkenylacetylenes (II) the electron cloud is shifted toward the triple bond (^{1}). In the case of vinylalkylacetylenes (III) and certain isoalkenylacetylenes (IV), however, it was necessary to assume a dual polarization of their molecules, intensifying in one direction or another depending on the nature of the addends: in interaction with hydrogen halides the order of addition indicated a shift of electrons toward the triple bond (^{2}), whereas in reactions with bromine, water, and alcohols it indicated a shift toward the double bond (^{3}, ^{4}).

Such a duality in the reactivity of vinylalkylacetylenes could have as its cause a weakening of the polarity of the enyne system owing to a partial displacement of electrons under the influence of radicals in a direction opposite to the usual displacement in the 1,3-enyne system ((III), (IV)):

$HC\equiv C-CH=CH_2$ (I), $R-CH=CH-C\equiv CH$ (II), $R-C\equiv C-CH=CH_2$ (III),



$HC\equiv C-C=CH_2\underset{CH_3}{|}$ (

Some of their physical properties also testified to such polarization of vinylalkylacetylenes.

It was established by the electron-diffraction method that in the molecule of vinylmethylacetylene not only the distance : C—C : is strongly shortened, but also the distance CH_3—C : (^{5}).

In the infrared spectra the intensity of the bands corresponding to the double bond was significantly higher in the case of hydrocarbons of types (III) and (IV) than for hydrocarbons of type (II). This could be explained by a greater change in the polarity of the double bond during vibrations as a result of electron displacement toward it (^{6}).

A final judgment on the character of the polarization of molecules of vinylacetylene hydrocarbons could be made only by determining their dipole moments.

In the literature there are data on the dipole moments of vinylacetylene, two of its phenyl-substituted derivatives (^{7}), and also divinylacetylene and some other dienyne hydrocarbons (^{8}).

From the data on the dipole moments of phenylvinylacetylenes it follows that displacement of the phenyl group from position 1 to position 4 of the 1,3-enyne system sharply changes the magnitude of the dipole moment: 1-phenylbut-1-en-3-yne has larger, and 1-phenylbut-3-yn-1-ene smaller, dipole moments in comparison with vinylacetylene. Consequently, the phenyl group causes a shift of the electron cloud in the first case in the same direction, and in the second in the opposite direction, compared with unsubstituted vinylacetylene.

Divinylacetylene is nonpolar. Vinylisopropenylacetylene has a somewhat smaller dipole moment than vinylacetylene. Substitution at the end of the chain increases the moment.

We measured the dipole moments of seven vinylalkylacetylenes with alkyls CH_3-, C_2H_5-, C_3H_7-, C_4H_9-, $C_5H_{11}-$, $C_6H_{13}-$, and $C_8H_{17}-$, as well as of cis- and trans-propenylacetylenes, isopropenylacetylene, and β-tert-butylvinylacetylene. For comparison with the data of other authors, the moment of phenylacetylene was also measured. The following results were obtained:

1. The dipole moments of vinylmethyl- and isopropenylacetylenes proved to be considerably lower than the moment of vinylacetylene (0.77 D). Thus, the presence of electron displacement in the direction opposite to that in unsubstituted vinylacetylene was demonstrated experimentally.
2. With an increase in the hydrocarbon radical, the dipole moment increases somewhat and then remains approximately constant.
3. The dipole moments of cis- and trans-propenylacetylenes are considerably greater than the moment of vinylacetylene; moreover, in accordance with the spatial model of these hydrocarbons, the moment of the trans form is higher than the moment of the cis form.

Thus it was shown that in these compounds electron displacement occurs in the same direction as in unsubstituted vinylacetylene.

4. In comparison with isopropenylacetylene, β-tert-butylvinylacetylene has a larger moment. However, this moment is close to the moment of vinylbutylacetylene, and therefore these data cannot serve as direct proof of the presence of the Becker–Natan effect in the isopropenylacetylene molecule.

Since the changes in the magnitude of the dipole moment in all the cases considered are due to the influence of alkyl groups with a moment of the order of 0.35 D, whereas the moment of vinylacetylene is twice as large, it should be assumed that in all cases the moment is directed toward the triple bond.

Thus, the results of measuring the dipole moments of vinylacetylene hydrocarbons confirmed the ideas, advanced earlier on the basis of chemical data, concerning the mechanism of addition reactions at the site of conjugated triple and double bonds.

Experimental Part

Vinylacetylene hydrocarbons were obtained and purified by the usual methods ([6]). Isoalkenylacetylenes were purified by distillation over phenylhydrazine and then, after washing with 5% sulfuric acid, were fractionated. The cis and trans forms of propenylacetylene were isolated by repeated distillation on a column ([9]).

The constants of the hydrocarbon samples used for the determinations are given in Table 1.

Dipole moments were determined by Debye' s dilute-solution method ([10]). The dielectric constant was measured on a TKE-1 instrument specially adapted for these purposes, by the beat method. The measurement error ε after calibration of the liquid capacitor did not exceed 0.02%.

Measurements were carried out in benzene solutions at 20° with concentrations of about 1.0, 1.5, 2.0, 4.0, and 5.0%. Molecular polarization and dipole moments were calculated by the usual formulas ([10]). Atomic polarization was not taken into account. The results of the measurements and calculations are given in Table 2. The value found for the dipole moment of phenylacetylene (0.72 D) corresponded exactly to that reported in the literature ([7]).

Table 1

No.	Substance	Boiling point	d_4^{20}	n_D^{20}	MR, found	MR, calc.
1	$CH_2{=}CH{-}C{\equiv}C{-}CH_3$	59–59.5°/760 mm	0.7402	1.4490	23.95	22.82
2	$CH_2{=}CH{-}C{\equiv}C{-}CH_2{-}CH_3$	83.5–84°/760 mm	0.7486	1.4519	28.87	27.44
3	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_2{-}CH_3$	108.5–109°/760 mm	0.7626	1.4550	33.50	32.06
4	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_3{-}CH_3$	62–62.5°/60 mm	0.7713	1.4560	38.13	36.68
5	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_4{-}CH_3$	59.5–60°/20 mm	0.7782	1.4580	42.85	41.29

No.	Substance	Boiling point	d_4^{20}	n_D^{20}	MR, found	MR, calc.
6	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_5{-}CH_3$	76–76.5°/20 mm	0.7873	1.4598	47.37	45.91
7	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_7{-}CH_3$	110.5–111°/20 mm	0.7964	1.4620	56.71	55.16
8	$CH_3{-}CH{=}CH{-}C{\equiv}CH$ (cis-)	44–44.5°/760 mm	0.7257	1.4340	23.72	22.82
9	$CH_3{-}CH{=}CH{-}C{\equiv}CH$ (trans-)	50–52°/760 mm	0.7270	1.4370	23.82	22.82
10	$CH_2{=}C(CH_3){-}C{\equiv}CH$	32–32.5°/760 mm	0.7044	1.4151	23.50	22.82
11	$CH_2{=}C[C(CH_3)_3]{-}C{\equiv}CH$	97.5–98°/760 mm	0.7544	1.4330	37.27	36.68

Table 2

No.	Substance	ε_0	v_0	α	β	P	μ, D
1	$CH_2{=}CH{-}C{\equiv}C{-}CH_3$	2.2832	1.1371	0.33	0.213	30.78	0.57
2	$CH_2{=}CH{-}C{\equiv}C{-}CH_2{-}CH_3$	2.2833	1.1371	0.40	0.190	36.95	0.62
3	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_2{-}CH_3$	2.2835	1.1370	0.31	0.174	42.43	0.65
4	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_3{-}CH_3$	2.2835	1.1370	0.21	0.159	46.27	0.63
5	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_4{-}CH_3$	2.2835	1.1370	0.19	0.150	51.48	0.65
6	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_5{-}CH_3$	2.2834	1.1370	0.20	0.132	56.91	0.67
7	$CH_2{=}CH{-}C{\equiv}C{-}(CH_2)_7{-}CH_3$	2.2835	1.1370	0.15	0.121	66.32	0.68
8	$CH_3{-}CH{=}CH{-}C{\equiv}CH$ (cis-)	2.2815	1.1372	0.93	0.240	38.73	0.85
9	$CH_3{-}CH{=}CH{-}C{\equiv}CH$ (trans-)	2.2815	1.1372	1.15	0.260	41.86	0.93
10	$CH_2{=}C(CH_3){-}C{\equiv}CH$	2.2833	1.1373	0.136	0.282	29.78	0.55
11	$CH_2{=}C[C(CH_3)_3]{-}C{\equiv}CH$	2.2835	1.1370	0.22	0.188	47.36	0.69

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Note: Figure translations are in progress. See original paper for figures.