

Infrared intensity parameters of the diacetylene and acidity of acetylenic hydrogens

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Abstract—Preferred signs of the dipole moment derivatives of the diacetylene have been determined by using *G*-sum rule graph and molecular orbital calculations. Atomic polar tensors and effective charges of the diacetylene are reported. The hydrogen effective charge calculated from the atomic polar tensor ($\xi_H = 0.369e$) is in excellent agreement with that obtained from *G*-sum rule graph ($\xi_H = 0.371e$). MNDO calculations on the $H(C\equiv C)_nH$ ($n = 1, 2, 3, 4$ and 5) series indicate that the hydrogen effective charge increases with increasing number of $C\equiv C$ units. This is due to the magnitude of the $\partial p_z/\partial z_H$ polar tensor element, as a consequence of the increasing charge flux along the series. Finally, this element seems to be a good indicator of the intrinsic acidity of acetylenic protons.

INTRODUCTION

Hydrogen effective charges obtained from infrared intensities show that these values in acetylenic compounds are much larger than those found in saturated hydrocarbons, aromatic compounds and carbon-carbon double bonded molecules [1]. Basically, this can be associated to the greater acid character of these hydrogens bonded directly to carbon-carbon triple bond [2]. In this sense, one question which is particularly interesting is what happens with the hydrogen effective charge along a homologous series such as $H(C\equiv C)_nH$. Would the hydrogen be progressively more acid?

The first molecule of this series, acetylene, HC_2H , has been the subject of numerous spectroscopic investigations [3], whereas the second, diacetylene, HC_4H , only recently was the object of an ample study on its experimental force field and infrared fundamental intensities [4]. Although the fundamental intensities of the diacetylene have been reduced to dipole moment derivatives with respect to symmetry coordinates, $(\partial p/\partial S_i)$, the atomic polar tensors and effective charges have not been reported. Furthermore, the signs of the $\partial p/\partial Q_i$'s have not been tested by *G*-sum rule graph and quantum chemical calculations. All these aspects and also the effect of the substituent ($R-C\equiv C-H$; $R=H$, CCH , CH_3 and CN) on the intrinsic acidity of the acetylenic proton are the basic targets of this paper.

RESULTS AND DISCUSSION

Diacetylene

The fundamental intensities of the diacetylene were initially reported by POPOV *et al.* [5] for the C_4H_2 species, except to the band relative to $C-C\equiv C$ deformation. Recently, KOOPS *et al.* [4] remeasured all the C_4H_2 intensities and also C_4D_2 ones. The intensities reported by POPOV *et al.* are in very good agreement

with these recent measurements within the experimental error, except the one related to the CH stretching band by a factor of ~ 2 . The reason for this large discrepancy is not clear. Nevertheless, the measured intensities by KOOPS *et al.* reveal an internal consistency by applying the *F*-sum rule [4], in contrast with those from POPOV *et al.*

Here we make use of the *G*-sum rule [6] in its graphical representation, to analyse simultaneously the fundamental intensities of the diacetylene and to determine the preferred signs of their $\partial p/\partial Q_i$ from the isotopic invariability of the atomic effective charge. Since the diacetylene has zero permanent dipole moment, the rotational corrections to the Σ_u^+ and Π_u symmetry species are zero. The *G*-sum rule equation for C_4H_2 and C_4D_2 can be expressed as:

$$(2\xi_{c_2}^2 + 2\xi_{c_3}^2)/m_c = -[x/m_H + (2-x)/m_D] \xi_H^2 + (1/K) \sum_i A_i \quad (1)$$

where x is the number of hydrogen atoms.

In Fig. 1 *G*-sum rule graph is shown for the Σ_u^+ symmetry species. Firstly it is important to note that using the intensities measured by POPOV *et al.* for C_4H_2 and those by KOOPS *et al.* for C_4D_2 there is no intersection of the intensity pair of lines in the positive quadrant. Since the squares of the effective charges must be positive for all atoms, this is to be expected if the experimental intensity data are reasonably accurate. This is in fact true for the intensities measured by KOOPS *et al.* [4].

The Σ_u^+ symmetry species have two infrared active modes and the signs of the $\partial p_z/\partial Q_i$ ($i = 4$ and 5) are easily established from the *G*-sum rule graph. Since the hydrogen effective charge is invariant to isotopic substitution, the preferred set of signs of the $\partial p_z/\partial Q_i$'s are obviously $(+ -)$ for C_4H_2 and $(+ +)$ for C_4D_2 . Note that these sets of signs fall within the region defining isotopically invariant effective charge values.

where $P_x^{(\alpha)}$ is the polar tensor of the α th atom. Table 3 shows the atomic polar tensors and effective charges for the diacetylene. The hydrogen effective charge calculated from Eqn. (4) ($\xi_H = 0.369e$) is in excellent agreement with that obtained from the G -sum rule ($\xi_H = 0.371e$). This value is similar to that found in other acetylenic compounds [10].

The $H(C\equiv C)_nH$ Series

In order to save the computational effort, MNDO semiempirical molecular orbital calculations were carried out on the $H(C\equiv C)_nH$ ($n = 1, 2, 3, 4$ and 5) series for better understanding of the effect of increasing chain length on the hydrogen atomic polar tensor. To identify more exactly the possible source that produces the APT change, we have used the charge-charge flux-overlap model (CCFO) [11]. This model applied to a hydrogen polar tensor element obtained from a molecular orbital calculation may be written as:

$$\hat{c}p_{\sigma}/\partial\sigma_H = q_H^0 + \sum_{\alpha} (\hat{c}q_{\alpha}/\partial\sigma_H)\sigma_{\alpha}^0 + \hat{c}p'_{\sigma}/\partial\sigma_H \quad (5)$$

where $\sigma = x, y$ or z . Here q_H^0 is the equilibrium net charge of the hydrogen; the summation term represents the charge flux due to the hydrogen displacement and $\hat{c}p'_{\sigma}/\partial\sigma_H$ denotes the non-classical contribution. To calculate each element of the APT the numerical difference approximation $\hat{c}p_{\sigma}/\partial\sigma_H \simeq \Delta p_{\sigma}/\Delta\sigma_H$ was employed, with $\Delta\sigma_H = 0.02\text{\AA}$. In Table 4 are shown the MNDO calculated values of

$\partial p_z/\partial z_H$ and $\partial p_x/\partial x_H$ for the $H(C\equiv C)_nH$ ($n = 1, 2, 3, 4$ and 5) series with their respective CCFO contributions.

MNDO values of $\partial p_z/\partial z_H$ for these molecules increase in absolute magnitude with the carbon chain length. The CCFO contributions show that these increases are due to increasing values in the charge flux contributions to $\partial p_z/\partial z_H$. This result suggests that the growth of the $\partial p_z/\partial z_H$ is mainly due to charge transfer effect along the carbon chain rather than to varying electronic structure of the hydrogen atom in these molecules. Indeed, since the $\partial p_z/\partial z_H$ element reflects principally the CH stretching, the above result is in agreement with the increasing intensity values for the CH stretchings in C_2H_2 [3] and C_4H_2 [4] i.e., 70.4 and $136.0 \text{ km} \cdot \text{mol}^{-1}$, respectively.

In contrast to $\partial p_z/\partial z_H$, the $\partial p_x/\partial x_H$ element remains remarkably constant along the series and its magnitude depends mostly to the equilibrium net charge value. This invariance of the $\partial p_x/\partial x_H$ reflects the similar intensity values observed for the HCC deformations in HC_2H [3] and HC_4H [4], i.e., 177.1 and $172.0 \text{ km} \cdot \text{mol}^{-1}$.

Acetylenic proton acidity

The effect of the substituent on the rates of proton transfer from monosubstituted acetylenes has been the object of several studies [12]. In general, this information in the gas phase is more difficult to be obtained directly, and the same for the measure of the acetylenic intrinsic acidity. In this sense, molecular orbital calculations have contributed enormously, see Ref. [13].

On the other hand, GUSSONI *et al.* [2] have classified acid and neutral hydrogens from infrared intensity parameters. Here we have observed (see Table 5) a good correlation comparing the $\partial p_z/\partial z_H$ or $P_{ZZ}^{(H)}$ experimental element with the acetylenic intrinsic acidity calculated from *ab initio* 4-31G calculations (ΔE). According to POWELL *et al.* the theoretical intrinsic acidity is the difference between the calculated molecular energy for the parent acetylene ($R-C\equiv C-H$) and the corresponding acetylenic anion ($R-C\equiv C^-$). The results show that the greater is $P_{ZZ}^{(H)}$

Table 3. Experimental atomic polar tensors and effective charges of the diacetylene. Units of electrons, e^*

α	$P_{xx}^{(\alpha)} = P_{yy}^{(\alpha)}$	$P_{zz}^{(\alpha)}$	ξ_{α}
H ₁	0.200	0.238	0.369
C ₂	-0.221	-0.394	0.503
C ₃	0.021	0.156	0.159

*Atomic numbering: $H_6C_5C_4C_3C_2H_1 \rightarrow Z$.

Table 4. MNDO calculated CCFO contributions to $\partial p_z/\partial z_H$ and $\partial p_x/\partial x_H$ for the HC_nH molecule. Units of electrons, e

	$\partial p_z/\partial z_H$	$(\partial p_z/\partial z_H)_{Ch}$	$(\partial p_z/\partial z_H)_{Ch-flux}$	$(\partial p_z/\partial z_H)_{overl}$
HC ₂ H	0.288	0.157	0.198	-0.067
HC ₄ H	0.404	0.171	0.303	-0.070
HC ₆ H	0.462	0.172	0.363	-0.073
HC ₈ H	0.502	0.173	0.404	-0.075
HC ₁₀ H	0.531	0.173	0.436	-0.078
	$\hat{c}p_x/\partial x_H$	$(\hat{c}p_x/\partial x_H)_{Ch}$	$(\hat{c}p_x/\partial x_H)_{Ch-flux}$	$(\hat{c}p_x/\partial x_H)_{overl}$
HC ₂ H	0.174	0.157	0	0.017
HC ₄ H	0.178	0.171	0	0.007
HC ₆ H	0.178	0.172	0	0.006
HC ₈ H	0.178	0.173	0	0.005
HC ₁₀ H	0.178	0.173	0	0.005

Table 5. APT's element ($P_{ZZ}^{(H)}$), 4-31G intrinsic acidity (ΔE) and rates of detritiation by hydroxide ion (K_{OH^-}) of acetylenic hydrogens

Substituent R-C≡C-H	$P_{ZZ}^{(H)}$ (e)	$\Delta E(H)^*$	K_{OH^-} ($M^{-1}s^{-1}$)*
C≡N	0.267	0.5889	3.93×10^6
C≡C-H	0.238	0.6215	—
H	0.183	0.6523	5.41×10^1
CH ₃	0.180	0.6595	1.50×10^1

*From Ref. [13].

more acid is acetylenic proton, i.e., the greater the rate of detritiation by hydroxide ion (K_{OH^-}), see Table 5. Thus, the cyanoacetylene (HC_3N) is the most acid, whereas the propyne is the least acid of them.

If this can be extended to the $H(C\equiv C)_nH$ series, we can expect an increasing acidity along the series, since the $P_{ZZ}^{(H)}$ value increases with the carbon chain length. Thus, the greater the charge flux due to the displacement of the proton, the more acid should be the acetylenic compound.

CONCLUSIONS

G-sum rule graph and quantum chemical calculations strongly establish the $\partial p/\partial Q_i$ signs, atomic polar tensors and effective charges of the diacetylene. The senses of the dipole moment changes for diacetylene are exactly those observed for other similar acetylenic compounds. The hydrogen effective charge in the diacetylene is greater than that in acetylene, as a consequence of the charge flux increasing reflected in the $P_{ZZ}^{(H)}$ element. MNDO calculations show that the increasing carbon chain length tends to increase the charge flux due to the CH stretching. However, it will be interesting to investigate the problem from more sophisticated theoretical calculations, i.e., *ab initio* 6-

31G* calculations. Unfortunately, this goes beyond our computational facilities.

Finally, we have observed that the $P_{ZZ}^{(H)}$ element of acetylenic hydrogens can be a good indicator of its acid character, through a direct comparison with both the theoretical intrinsic acidity and the rate of detritiation by hydroxide ion.

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