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C–H Group as Proton Donor by Formation of a Weak Hydrogen Bond

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A systematic CNDO/2 study has been carried out on the weak C–H...F, C–H...O, and C–H...N hydrogen bonds. An H-bond formation has been revealed for proton donors with negative excess charge on the hydrogen. The concept of the positive character of the hydrogen as well as some essential features of the hydrogen bond have been discussed. Some useful correlations have been found and the importance of the charge shifts has been emphasized.

Key words: H-bond formation – CH-group as proton donor

Introduction

During the last 20 years the hydrogen bond has been a subject of intensive quantum chemistry research [1–4]. Generally these studies include hydrogen bonds with a moderate or considerable stability, formed by O–H, N–H or F–H groups. The weak hydrogen bonds formed by the C–H group remain however, up to now almost unstudied. Recently Goel and Rao [5] have performed CNDO/2 calculations on some H-bonded complexes of HCN, C_2H_2, and CHF_3. The possibility of CH_4 forming hydrogen bonds has been considered in the *ab initio* calculations of Pople [1a] and in more detail by J. v. Duijneveldt and F. v. Duijneveldt [6], using intermolecular perturbation theory.

The proton donor properties of the C–H group have been experimentally established for a long time [7]. It is generally accepted that C–H groups, the H-atom of which is activated by the presence of electronegative substituents on the carbon, can form hydrogen bonds. Such an effect is however rejected or disputed [8] for inactivated or weak activated C–H groups as in C_6H_6, CH_4, HCHOHCOOH, NH_2CHO molecules.

A systematic study on the proton donor property of different C–H groups is performed here by means of theoretical calculations. Three electron donors, namely NH_3, OH_2 and FH, have been used for a better scaling of the H-bond properties. Most of the considered cases are on the border of what is accepted as hydrogen bond. Is there however such a limit beyond which the possibility of H-bond formation may be definitely rejected? Is there also a reliable

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criterion (like the degree of positive character of the hydrogen in the bond [9]) to predict stability and properties of a given hydrogen bond?

Method of Calculation. Starting Geometries and Energies

The semiempirical SCF–MO method CNDO/2 has been used in its original parametrization [10]. This method has proved its applicability to hydrogen bonding studies, leading to geometries and formation energies in reasonable agreement with the experimental data [1, 2, 11, 12].

The minimum energy CNDO geometries of the isolated molecules have been defined (Table 1) as a basis for the further calculations. The energy of the hydrogen-bonded complexes has been obtained by simultaneous variation of the H...X and C–H bonds, assuming the hydrogen bond C–H...X as linear and as situated in the σ-plane of the proton donor. A third variational parameter, the length of one of the neighbouring bonds ($C \equiv N$ or X–H′), has been also used in several cases without any influence on the results.

Table 1. CNDO/2 Geometries and energies of the isolated molecules[a]

Quantities Molecules	R	θ	E_{tot}
Electron Donors			
HF	$R_{HF} = 1.000$		-28.43669
H_2O	$R_{OH} = 1.029$	$\widehat{HOH} = 104.5$	-19.89117
NH_3	$R_{NH} = 1.067$	$\widehat{HNH} = 105.1$	-13.88975
Proton Donors			
HCN	$R_{CH} = 1.091$ $R_{CN} = 1.182$		-19.15707
C_2H_2	$R_{CC} = 1.197$ $R_{CH} = 1.093$		-15.34482
C_2H_4	$R_{CC} = 1.311$ $R_{CH} = 1.113$	$\widehat{HCH} = 111.8$	-17.07318
CH_4	$R_{CH} = 1.114$	$\widehat{HCH} = 109.5$	-10.11599
C_6H_6	$R_{CC} = 1.385$ $R_{CH} = 1.118$	$\widehat{HCC} = 120.0$	-47.11247
H_2CO	$R_{CO} = 1.247$ $R_{CH} = 1.114$	$\widehat{HCH} = 116.2$	-44.17794
HCOOH	$R_{C=O} = 1.259$ $R_{CO} = 1.349$ $R_{CH} = 1.116$ $R_{OH} = 1.031$		-45.32424
NH_2CHO	$R_{CH} = 1.122$ $R_{CO} = 1.264$ $R_{CN} = 1.365$ $R_{HN} = 1.060$		-39.32494

[a] E in atomic units, R in Å, θ in degrees.

The C–H distance has been varied in some cases by the constant equilibrium bond length $R_{C..X}$ and no evidence of proton transfer has been found.

Equilibrium Geometry of the Hydrogen Bond

C–H group forms considerably more extended hydrogen bonds (Table 2) $R_{C..X} = 2.8$–3.0 Å) than the more active proton donors F–H, O–H, and N–H [2]. A still greater length is obtained in the CNDO/2 calculations of Goel and Rao [5]: $R_{C..Donor} = 2.9$–3.3 Å. Our results agree well with the experimental data of Jones, Seeland and Shepard [13] for $N{\equiv}C{-}H\ldots NH_3$: $R_{C..N} = 2.86$ Å, exp. value 2.96 Å. The underestimation of the H-bond length, typical for the CNDO/2 calculations, seems to be much smaller for weak hydrogen bonds. The CNDO/2 method seems to give, in such cases, more realistic values for the H-bond lengths than calculations by the intermolecular perturbation theory ($H_3C{-}H\ldots O = 2.59$–2.70 Å; $H_3C{-}H\ldots N = 2.22$–2.33 Å) [6].

It may be noted that for a given proton donor not the most stable bond, C–H...N, but the C–H...O bond always has a minimal length. Schuster [12] has emphasized that the distance between two heavy atoms $R_{Y..X}$ does not correlate with the strength of the hydrogen bond, but the elongation of the Y–H bond correlates satisfactorily. Our calculations confirm this conclusion, showing almost linear correlation between ΔR_{C-H} and the hydrogen bond formation energy ΔE_{HB}.

Table 2. Energies and equilibrium geometries of the Hydrogen bonded complexes formed by C–H groups[a]

Quantities Species	E_{tot}	$-\Delta E_{HB}$	$R_{C...X}$	R_{C-H}	ΔR_{C-H}
$\ldots FH$	−47.59671	1.85	2.830	1.098	0.007
$N{\equiv}C{-}H\ldots OH_2$	−39.05342	3.25	2.803	1.100	0.009
$\ldots NH_3$	−33.05263	3.64	2.864	1.104	0.013
$\ldots FH$	−43.78343	1.20	2.859	1.097	0.004
$HC{\equiv}C{-}H\ldots OH_2$	−35.23986	2.43	2.842	1.101	0.008
$\ldots NH_3$	−29.23895	2.75	2.960	1.102	0.009
$\ldots FH$	−45.51108	.75	2.970	1.114	0.001
$H_2C{=}CH_2\ldots OH_2$	−36.96709	1.72	2.894	1.117	0.004
$\ldots NH_3$	−30.96620	2.05	2.990	1.121	0.008
$\ldots FH$	−38.55372	.65	2.985	1.116	0.002
$H_3C{-}H\ldots OH_2$	−30.00957	1.51	2.940	1.118	0.004
$\ldots NH_3$	−24.00857	1.77	3.012	1.119	0.005
$\ldots FH$	−75.55017	.63	2.972	1.119	0.001
$H_5C_6{-}H\ldots OH_2$	−67.00608	1.53	2.927	1.120	0.002
$\ldots NH_3$	−61.00516	1.84	3.022	1.123	0.005
$H_2CO\ldots NH_3$	−40.73211	2.32	2.955	1.123	0.009
$HCOOH\ldots NH_3$	−59.21836	2.74	2.952	1.125	0.009
$NH_2CHO\ldots NH_3$	−53.21816	2.18	3.004	1.129	0.007

[a] E in atomic units, $-\Delta E_{HB}$ in kcal/mole, R in Å.

Energy of the Hydrogen Bond

Presence of a hydrogen bond, with an energy from 0.6–3.6 kcal/mole, has been established for all studied systems. The weakest is the C–H...F bond and the strongest is C–H...N. The lone-pair ionization potential values of fluorine, oxygen and nitrogen (16.38 [14], 12.61 [15], and 10.65 [15]) confirm this scale of bond energies.

A relationship may be given for proton donor strength of the studied C–H groups at fixed electron donor:

$$HCN > C_2H_2 \approx HCOOH > HCHO > NH_2CHO > C_2H_4 > C_6H_6 \approx CH_4 .$$

This result agrees with the Allerhand and Schleyer's infrared studies [8] where the proton donor property of the C–H group has been found to vary with the carbon hybridization:

$$C_{sp}\text{–}H > C_{sp}^2\text{–}H > C_{sp}^3\text{–}H .$$

In the same paper, however, the property of C–H group in alkyl chains, aldehydes, formates and formamides to form H-bond has been rejected. This has been admitted for aromatic protons only when they are activated by the presence of three or more chlorines on the ring and for C–H protons only when more than one electrophilic substituent is bound to the carbon.

The present CNDO/2 calculations show for all these questionable cases a presence of an H-bond. The energies of the strongest C–H...N bonds (1.8–2.8 kcal/mole) allow us to consider as possible an experimental proof for their existence. The proton donor strength of the C–H group in acetylene and formic acid has been found to be approximately the same. This is somewhat surprising since till now only the C–H acid property of acetylene has been well known. Recently however, experimental IR-evidence has been reported [16] for the stable hydrogen bond formation between formic acid C–H groups and strong electron donors like pyridine and dioxane. Note that in these questionable cases the C–H...X hydrogen bond formation could remain undetected because of stronger hydrogen bonds deriving from other proton donors like O–H in HCOOH and N–H in formamide as from π- or n-donor action of the molecules of HCHO, C_6H_6, C_2H_4.

The experimental data for the energy of the hydrogen bonds formed by C–H group is relatively poor. They vary from 1–2.5 kcal/mole for different H-bonds with the ethynyl group [5, 17–21]. Stronger is the bond formed by the cyanic group in the dimers of cyanoacetylene [22] ($\Delta E_{HB} = -2.8$ kcal/mole) and of hydrogen cyanide [23] ($\Delta E_{HB} = -3.3$ kcal/mole). The energies of the C_2H_2- and HCN-complexes with HF, H_2O, and NH_3, calculated in this paper (Table 2), are approximately the same. For instance for the $C_2H_2 + NH_3$ system, our result, 2.75 kcal/mole, is close to the experimental one, 2.21 kcal/mole. The estimation of the average energy per one hydrogen bond in gaseous hydrates of methane [24] is intermediate between our CNDO/2 and the *ab initio* calculations of Pople [1a] and those of v. Duijneveldt [6], using intermolecular perturbation theory, for $CH_4 + H_2O$ (1.5, 1.1, and 0.8, 0.76–0.95 kcal/mole respectively). One may conclude that a satisfactory agreement is available between the calculated energies and the experimental ones, though the CNDO/2 values are overestimated to some extent. There is also a coincidence with the *ab initio* H-bond energy [6] of the system $H_3C–H...NH_3$ but for $H_3C–H...F–H$ case the CNDO/2 value is more than twice greater.

Bond Orders

There is no essential change for the bond order values in comparison with the isolated molecules. The bond order of the hydrogen bridge between the donor and acceptor fragments, presented in Table 3 ($P_{H...X} = 0.10–0.20$), corresponds to the small stability of these bonds. A linear correlation has been found between $P_{H...X}$ and the hydrogen bond formation energy ΔE_{HB} (Fig. 1).

Table 3. Dipol moments and bond orders of C–H...X bonds

Quantities Species	$\mu(D)$	$P_{H...X}$
$...FH$	4.56	0.141
$N{\equiv}C–H...OH_2$	4.91	0.184
$...NH_3$	5.03	0.208
$...FH$	2.04	0.130
$HC{\equiv}C–H...OH_2$	2.37	0.165
$...NH_3$	2.44	0.168
$...FH$	1.99	0.105
$H_2C{=}CH_2...OH_2$	2.33	0.148
$...NH_3$	2.42	0.155
$...FH$	1.95	0.101
$H_3C–H...OH_2$	2.26	0.134
$...NH_3$	2.35	0.144
$...FH$	2.05	0.105
$H_5C_6–H...OH_2$	2.38	0.138
$...NH_3$	2.46	0.146
$H_2CO...NH_3$	3.94	0.167
$HCOOH...NH_3$	2.87	0.175
$NH_2CHO...NH_3$	2.72	0.153

Charge Distribution Analysis

The data for the charge changes upon H-bond formation are summarized in Table 4 where the symbols H^a and C^a are used for the atoms of the C–H proton donor group. Electron density charge on the molecular fragments of the electron acceptor is moved from the bridged hydrogen mainly to the neighbouring carbon and to a lesser extent to all the other atoms (H, C, O, N). The main acceptor atom C^a acts simultaneously as a good σ-acceptor and weak π-donor,

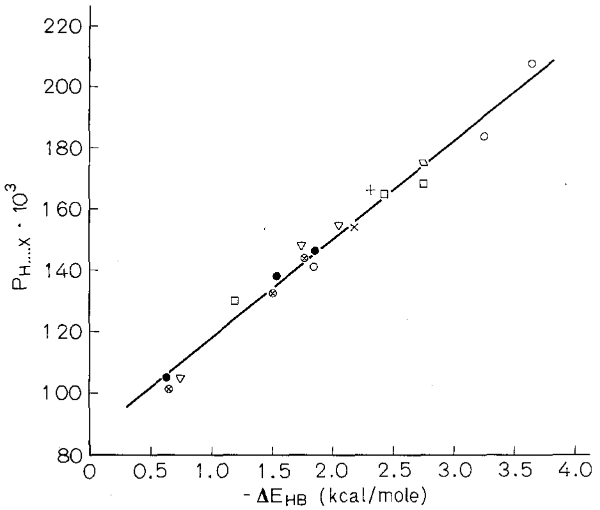


Fig. 1. H-bond energy as a function of the H...X bond order, ○ – HCN, □ – C_2H_2, ▽ – C_2H_4, ⊗ – CH_4, ● – C_6H_6, ⧅ – HCOOH, + – HCHO, × – NH_2CHO

the second carbon and the nitrogen in formamide as weak σ-donors and π-acceptors, the nitrogen in $C\equiv N$ and the oxygen in $C=O$ and O–H groups as weak σ- and π-acceptors. Both carbons neighbouring to C^a on the benzene fragment are very weak electron density donors but all the carbons not included in the hydrogen bond donate a minimal amount of π-charge to C^a.

The charge distribution on the electron donor fragment depends on the H-bond energy. All the hydrogens are electron donors and the heavy atom is an electron acceptor by more stable bonds. When the stability of the bond decreases the heavy atom turns into a donor and the electron donor property of hydrogens decreases and in some cases these even become weak acceptors.

Charge Transfer and Charge Shifts

A weak transfer of σ-charge (0.002–0.020) to the proton donor fragment has been found in all systems considered by us. The charge transfer increases, at fixed proton donor, from HF to H_2O to NH_3 in connection with the decreasing in the same order of the lone-pair ionization potentials of F, O and N. When the electron donor is fixed the charge transfer follows the relation

$$HCN > HCOOH > HCHO \approx C_2H_2 > NH_2CHO > C_6H_6 \approx C_2H_4 > CH_4$$

which is near to the one obtained earlier for the stability of the hydrogen bond.

A considerable redistribution of electron density takes place when two molecules approach each other and form a hydrogen bond. The total charge shift of the complex, TCS, as well as the shifts (not including charge transfer)

Table 4. Changes in Atomic Populations upon Hydrogen Bond Formation

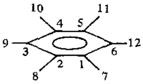
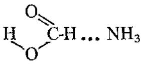
Acceptor Donor	N≡C–H...	HC≡C–H...	$H_2C≡CH_2$...	H_3C–H...		OHC–H...NH_3
HF...	H^a +.0234 C^a –.0186 σ –.0250 π +.0064 N –.0099 σ –.0035 π –.0064 F –.0017 H +.0067	H^a +.0223 C^a –.0155 σ –.0229 π +.0074 C –.0052 σ +.0022 π –.0074 H –.0054 F +.0009 H +.0029	H^a +.0210 C^a –.0108 σ –.0162 π +.0054 C –.0006 σ +.0048 π –.0054 H –.0036 H –.0050 H –.0029 F +.0024 H –.0002	H^a +.0186 C^a –.0097 H –.0036 H –.0036 H –.0036 F +.0023 H –.0004	H^a +.0226 C^a –.0109 σ –.0166 π +.0057 $C_{1,5}$ +.0007 σ +.0012 π –.0005 $C_{2,4}$ –.0009 σ +.0001 π –.0010 C_3 –.0012 σ +.0015 π –.0027 $H_{7,8,10,11}$ –.0023 H_9 –.0021 F +.0027 H –.0008	H^a +.0283 C^a –.0260 O –.0073 H –.0080 N –.0014 H +.0055 H +.0055 H +.0034 
H_2O...	H^a +.0301 C^a –.0301 σ –.0367 π +.0066 N –.0113 σ –.0047 π –.0066 O –.0050 H +.0081 H +.0081	H^a +.0277 C^a –.0241 σ –.0319 π +.0078 C –.0054 σ +.0024 π –.0078 H –.0067 O –.0007 H +.0046 H +.0046	H^a +.0278 C^a –.0184 σ –.0247 π +.0063 C –.0001 σ +.0062 π –.0063 H –.0053 H –.0062 H –.0036 O +.0025 H +.0017 H +.0017	H^a +.0238 C^a –.0158 H –.0044 H –.0044 H –.0044 O +.0026 H +.0011 H +.0011	H^a +.0294 C^a –.0181 σ –.0248 π +.0067 $C_{1,5}$ +.0013 σ +.0021 π –.0008 $C_{2,4}$ –.0011 σ –.0001 π –.0010 C_3 –.0013 σ +.0018 π –.0031 $H_{7,11}$ –.0038 $H_{8,10}$ –.0026 H_9 –.0023 O +.0032 $H_{1,2}$ +.0011	H^a +.0289 C^a –.0287 O –.0062 O –.0021 H –.0064 N –.0037 H +.0066 H +.0066 H +.0051 NH_2CHO... NH_3
H_3N...	H^a +.0293 C^a –.0380 σ –.0428 π +.0048 N –.0106 σ –.0058 π –.0048 N –.0072 H +.0088 H +.0088 H +.0088	H^a +.0230 C^a –.0255 σ –.0313 π +.0058 C –.0039 σ +.0019 π –.0058 H –.0062 N –.0022 H +.0049 H +.0049 H +.0049	H^a +.0239 C^a –.0206 σ –.0256 π +.0050 C +.0007 σ +.0057 π –.0050 H –.0050 H –.0056 H –.0031 N +.0023 H +.0025 H +.0025 H +.0025	H^a +.0215 C^a –.0189 H –.0039 H –.0039 H –.0039 N +.0026 H +.0022 H +.0022 H +.0022	H^a +.0262 C^a –.0210 σ –.0266 π +.0056 $C_{1,5}$ +.0015 σ +.0022 π –.0007 $C_{2,4}$ –.0010 σ –.0002 π –.0008 C_3 –.0011 σ +.0015 π –.0026 $H_{7,11}$ –.0039 $H_{8,10}$ –.0023 H_9 –.0019 N +.0033 $H_{1,2,3}$ +.0023	H^a +.0265 C^a –.0247 O –.0049 N +.0018 H –.0050 H –.0049 N –.0005 H +.0023 H +.0023 H +.0070

Table 5. Charge transfer and charge shifts

Quantities Species	CT	CS_{acc}	CS_{don}	TCS	$TCS^{\sigma,\pi}$
$\ldots FH$	0.0051	0.0234	0.0017	0.0251	0.0315
$N{\equiv}C{-}H\ldots OH_2$	0.0113	0.0301	0.0050	0.0351	0.0417
$\ldots NH_3$	0.0193	0.0293	0.0072	0.0365	0.0413
$\ldots FH$	0.0038	0.0223	0	0.0223	0.0319
$HC{\equiv}C{-}H\ldots OH_2$	0.0085	0.0277	0.0007	0.0284	0.0386
$\ldots NH_3$	0.0126	0.0230	0.0022	0.0252	0.0329
$\ldots FH$	0.0022	0.0210	0.0002	0.0212	0.0314
$H_2C{=}CH_2\ldots OH_2$	0.0057	0.0278	0	0.0278	0.0403
$\ldots NH_3$	0.0099	0.0246	0	0.0246	0.0346
$\ldots FH$	0.0019	0.0186	0.0004	0.0190	0.0190
$H_3C{-}H\ldots OH_2$	0.0048	0.0239	0	0.0239	0.0239
$\ldots NH_3$	0.0092	0.0215	0	0.0215	0.0215
$\ldots FH$	0.0016	0.0240	0.0008	0.0248	0.0332
$H_5C_6{-}H\ldots OH_2$	0.0054	0.0320	0	0.0320	0.0421
$\ldots NH_3$	0.0101	0.0292	0	0.0292	0.0377
$H_2CO\ldots NH_3$	0.0130	0.0283	0.0014	0.0297	0.0386
$HCOOH\ldots NH_3$	0.0146	0.0289	0.0037	0.0326	0.0427
$NH_2CHO\ldots NH_3$	0.0111	0.0283	0.0005	0.0288	0.0346

within the electron donor and acceptor, CS_{don} and CS_{acc}, can be obtained by summarizing all the atomic charge changes Δq^x in the systems:

$$\mathrm{TCS} = \mathrm{CS}_{acc} + \mathrm{CS}_{don} = 1/2\left(\sum_x \Delta q^x_{acc} - \mathrm{CT}\right) + 1/2\left(\sum_x \Delta q^x_{don} - \mathrm{CT}\right).$$

We have calculated these quantities for the atomic charge shifts, as well as for the σ- and π-charge shifts (Table 5).

Some π-charge shifts have a place within the electron acceptor but they are usually small and only in few cases come near to 1/3 of the corresponding σ-shifts.

The comparison of the total charge shifts on both the molecular fragments confirms the greater perturbation of the electron acceptor upon the H-bond formation [9]. This tendency gains in force when there is a lack of dipol moment in the isolated electron acceptor molecules (C_2H_2, C_2H_4, C_6H_6, CH_4).

As a result of the works of Bratož [25] and Puranik and Kumar [26] lots of properties of the hydrogen bond have been associated with the charge transferred through the bond. Kollman and Allen [9] first remarked that the charge shift, but not the charge transfer, is the major physical effect for moderate to weak H-bonds. Our study on the weak hydrogen bonds C–H...F, C–H...O, and C–H...N confirms this conclusion and indicates an increasing role of the charge transfer when the strength of the H-bond increases (Fig. 2). So, the charge transfer is only from 1/16 to 1/5 of the total atomic charge shifts TCS in all the five studied C–H...F bonds. This relationship varies

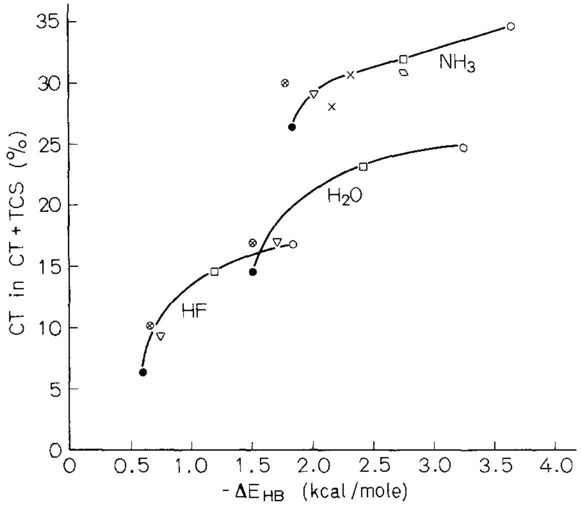


Fig. 2. Relationships between charge transfer and charge shift at fixed electron donor (HF, H_2O, NH_3). See also captions to Fig. 1

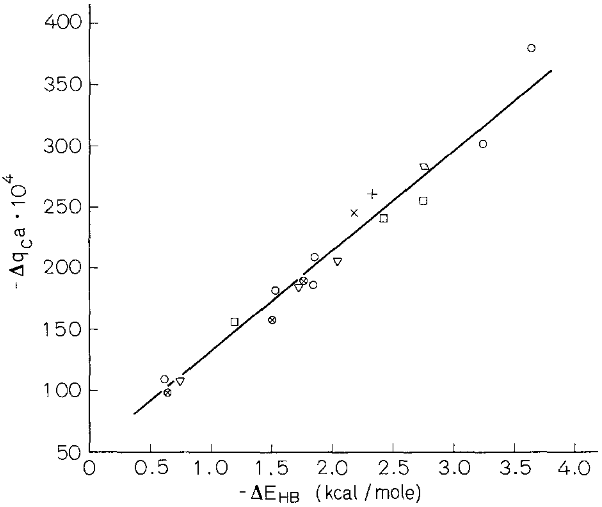


Fig. 3. A linear correlation between the H-bond energy and the charge change on the carbon of C–H-group upon H-bond formation. See also captions to Fig. 1

however from 1/3 to 1/2 for the more stable C–H...N bonds. All these relations become smaller when the charge transfer is referred to the total σ- and π-charge shift $TCS^{\sigma,\pi}$ (Table 5).

It is of interest to note that the considerable loss of electron density of the bridged hydrogen, which is a general feature of the H-bond, does not correlate with the bond energy. The sum of the charge changes on all the three atoms in the C–H...X bond correlates better but not sufficiently well. An excellent linear correlation, however, occurs between ΔE_{HB} and the change of electron density around the main acceptor atom C^a (Fig. 3). One may look for a possible explanation of this dependence in the greater and essential part of the charge transfer and charge shifts associated with the electron density gain on this atom.

A Positive Character of the Hydrogen in the Bond

Kollman and Allen [9] have connected the principal features of the hydrogen bond to the degree of positive character of the hydrogen in the bond. As can be seen from Table 6, there is no correlation between the hydrogen bond formation energy and the positive character of the hydrogen $\xi^{+}_{H_0}$, for the weak H-bonds studied here. For instance the CNDO/2 excess charges on the hydrogen in acetylene and formic acid are respectively +0.0624 and −0.0069, but the interesting point is that both the proton donors form with ammonia H-bonds with equal stability. It is clear that the criterion of Kollman and Allen is not appropriate for weak H-bonds formed by molecules with a positive character of a hydrogen near to zero or negative.

We consider as new and important for the understanding of the nature of the hydrogen bond the conclusion that molecules with negative character of a hydrogen, like benzene, formaldehyde, formic acid and especially formamide (Table 6) can also interact with electronegative atoms of other molecules and form H-bonds. This successful interaction emphasizes again the great importance of the charge shift for the weak hydrogen bonds.

The considerable replacement of charge from the bridged hydrogen to the internal part of the acceptor ($CS_H = 0.022–0.029$) causes the increase in the positive character of a hydrogen which additionally stabilizes the bond. The character of the hydrogen however remains in most cases near to zero. Rather peculiar in the light of the above is the system $NH_2CHO + NH_3$, where in spite of H-bond the hydrogen atom continues to have negative excess charge:

$$\begin{array}{ccc} \text{C} & \text{–H}\ldots & \text{N} \\ +0.324 & -0.013 & -0.211\,. \end{array}$$

Table 6. Excess charge and charge shift on the hydrogen in the C–H...NH_3 bonds[a,b]

Proton donor Quantities	HCN	C_2H_2	CH_4	C_2H_4	HCOOH	HCHO	C_6H_6	NH_2CHO
ξ_{H_0}	+ 747	+624	+112	+ 90	− 69	− 93	−109	−396
ξ_H	+1040	+854	+327	+329	+220	+190	+153	−131
CS_H	293	230	215	239	289	283	262	265
ΔE_{HB}	3.64	2.75	1.77	2.05	2.74	2.32	1.84	2.18

[a] ξ_{H_0} – in isolated proton donor, ξ_H – in H-bonded complex.
[b] ξ_{H_0}, ξ_H, CS – in atomic units $\times 10^4$.

The small electrostatic repulsion existing in this case between hydrogen and nitrogen is not essential, because of the greater attraction between carbon and nitrogen.

Some Remarks on the H-Bond Definition

The proton donors with negative or near to zero positive character of the hydrogen, which have been studied in this paper, demonstrate the great variety of possibilities for H-bond formation, a variety which is appreciably greater than is usually supposed.

A question arises: might all these cases be classified as hydrogen bonds? Some autors consider such interactions as weak hydrogen bonds, others prefer to speak about strong intermolecular forces [1a, 6]. According to our point of view, it is possible to speak about hydrogen bond if all the properties of this bond are available.

The following features of the hydrogen bond Y–H...X could be considered as essential:

1. Formation energy.
2. Decreased electron density along the bond [27].
3. Elongation (and eventually bending) of the Y–H bond.
4. Charge transfer through the bond.
5. Charge redistribution (especially on the proton donor fragment).

All C–H...X bonds examined in this paper show these features though to a lesser degree than the ordinary H-bonds. There are great differences in the strength of the proton donors but no difference in principle appears to exist between the hydrogen bond which these form and an ordinary H-bond.

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