

Cooperative effect of CH...O bonds in models for biological systems

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Abstract

In order to calculate CH...O interactions appearing in biologically important systems, a preliminary study is performed for smaller models. MO bond indices I_{XHY} are calculated for dimers involving HCN, acetic acid, acetamide, glyoxal and formamide, as well as a ribose33-U35 pair appearing in tRNA^{Phe} and 3MU-U, also related to RNA. The distance dependence obeys the same pattern for I_{OHO} , I_{NHO} and I_{CHO} . It is shown that the negative I_{XHY} sign is related to the lengthening of the XH distance; the fluctuation of net charges for the involved atoms is related to the bond index. All results point at a definite cooperative effect.

Keywords: CH...O bonds – Models for biological systems – Cooperative effect in H-bonds – Charge fluctuation correlation – Three-center bond index

1. Introduction

Progress in experimental and theoretical techniques has led to reconsideration of the role played by the CH group in hydrogen bonds, most of them having oxygen as acceptor atom [1]. They appear to be particularly important in biological systems [2, 3]. Their involvement in cooperative effect has been often remarked [4], as well as their essential role in the stabilization of unusual pairs of nucleic acid bases [5] in tRNA anticodons [3].

Whether or not these CH...O links are to be considered effective hydrogen bonds seems now beyond question, after long-lasting polemics [6, 7]. As the C...O distances usually are longer than O...O or N...O H-bond distances, they are supposed to be weaker, but energy data are relatively scarce and, when available, difficult to compare. In berberine formate-succinic acid, striking C...O distances, of 3.082 and 3.178 Å have been recently found for CH...O bonds connecting pairs of cations and molecules of succinic acid [8]. Let us remark that, for the H-bonds in DNA base pairs, in order to obtain agreement between theoretical and experimental distances, the molecular environment (water, sugar, counterions) must be incorporated [9] in computationally heavy DFT calculations. Transferability of the geometry obtained for small systems must be taken with caution, as it has been found that the gas-phase O...O distance in OH...O elongates in crystals and proteins [10]. This could mean more significant CHO bonds. Even much less conventional H-bonds have been studied: besides dihydrogen bonds, dimers with carbon as an acceptor have been proposed [7].

Usual XH...Y bonds are concomitant of elongation in the XH bond, with a red shift in the corresponding stretching frequency. The CH...Y bonds may involve a contraction in the CH bond, with blue shift of the frequency; this has been found so

striking as to lead to the term “anti-hydrogen bond” [11]. Hobza [12] has also proposed a simple appealing H-index which discriminates between what he chose then to label as classical and improper H-bonding.

A molecular orbital (MO) three- center bond index has been proved to be most suitable in estimating hydrogen bonds [13], providing quantitative estimations for biological systems [14, 15, 16]. In this work, we shall explore its performance when dealing with the unusual CH...O bonds. Our mentioned applications have not yet taken into account an appealing feature of this index, namely that it relates the charge fluctuations in the involved atoms [17].

2. The hydrogen bond index

In MO calculations with non-orthogonal bases, the first-order density matrix \mathbf{P} for closed shell systems may be written as a mixed tensor [18]

$$2\Pi_a^b = 2\sum_i x_{ia} x^{ib} \quad (1)$$

x_{ia} (x^{ib}) being the covariant (contravariant) coefficients of the i -th MO and a (b) label atomic orbitals.

The idempotency of \mathbf{P} has led us to define a bond index I_{AB} for atoms A and B [18, 19], the generalization to non-orthogonal bases of the Wiberg bond index [20], which was devised for non-orthogonal bases:

$$I_{AB} = 4 \sum_{a \in A, b \in B} \Pi_a^b \Pi_b^a \quad (2)$$

I_{AB} matches chemical intuition for usual bonds, being close to 1, 2 and 3 for single, double and triple bonds respectively.

Three-center (3c) bond indices I_{ABC} may be similarly defined [13]:

$$I_{ABC} = 8 \sum_{a \in A, b \in B, c \in C} \Pi_a^b \Pi_b^c \Pi_c^a \quad (3)$$

as well as indices involving more centers. The Mulliken atomic charge q_A may be partitioned into self-charge ($I_{AA}/2$) and active charge

$$q_A = 1/2 \left(I_{AA} + \sum_{B \neq A} I_{AB} \right) = 1/2 (I_{AA} + V_A) \quad (4)$$

V_A denoting the valence of A [21, 22]. This partition is different from Mulliken's, being related to the second order density matrix [23]. The bond indices I_{AB} and valence V_A have been extended to open shells [24] and, most recently, in terms of 'fuzzy' atoms [25]. They issue naturally from the exchange contribution to condensed diatomic density [26].

Similarly to eq. (4), any bond index may be written in terms of higher-order bond indices [27], e.g.

$$I_{AB} = 1/2 \sum_C I_{ABC} \quad (5)$$

Both I_{AB} and overlap population suffer from equipartition of the bond charge.

However, formula (5) provides a way to circumvent this drawback [28], through

$$I_{AB} = 1/2 (I_{AAB} + I_{ABB}) + 1/2 \sum_{C \neq A, B} I_{ABC} \quad (6)$$

We have shown in Ref. [28] that I_{AAB} and I_{ABB} fulfil the expectations. As to the 3c-index, its sign has deserved much attention. Sannigrahi and Kar [27] claimed that only positive values are to be accepted. Kar and Marcos [29] associated positive values to

two-electron 3c bonds and negative ones to four-electron 3c bonds. We ourselves [17] pointed to another direction, the correlation between the fluctuations of the charges in each atom from their average values, with no *a priori* distinction between positive and negative values:

$$I_{ABC}/2 = \langle (\mathbf{q}_A - \langle \mathbf{q}_A \rangle) (\mathbf{q}_B - \langle \mathbf{q}_B \rangle) (\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \rangle \quad (7)$$

Where \mathbf{q}_A denotes the charge operator and $\langle \mathbf{q}_A \rangle = q_A$.

In hydrogen bonds XH...Y we may write eq. (6) as

$$I_{XH} = \frac{1}{2} (I_{XXH} + I_{XHH}) + \frac{1}{2} I_{XHY} \quad (8)$$

for, unless XH is involved in more than one H-bond, any other 3c-index including XH will be negligible.

We have always found negative values for I_{XHY} (Ref. [16] and Refs. therein). Eq. (8) shows that thus, lowering the I_{XH} value, it correctly parallels the lengthening of the XH distance in usual hydrogen bonds. The results in the present work give negative values for all the indices involving CH; in nearly all of them, the corresponding distance lengthens.

Preliminary calculations for the di-hydrogen system FH...H'Li yield negative values for I_{FHLi} and similar positive values for $I_{FH'Li}$. Accordingly, the FH distance lengthens while the H'Li distance shortens in the dimer.

We shall see that the results for the electronic charges of the atoms involved in a hydrogen bond enlighten the meaning of Eq. (7). In XH...O bonds, hydrogen becomes appreciably more acidic and oxygen appreciably more basic than they are in the corresponding isolated molecules, or also compared with hydrogen or oxygen atoms in similar groups of the same molecule, not involved in H-bonds. Net charges for X = C,

on the other hand, suffer much lesser variation. Let us underline that the acceptor oxygen in the water dimer behaves in similar way, its charge fluctuating much less than the donor's.

3. Results and discussion

The geometries of all the calculated systems have been optimised using the Hartree-Fock method with the 6-31G* basis from the Gauss98 package [30]. The I_{XHY} indices are calculated through the PM3 Hamiltonian of the MOPAC package [31]. The net charges reported issue also from the MOPAC-PM3 calculation. This approximation has been shown to serve very well our purposes for modelling fairly large biological systems [14, 16]. Although it is desirable to corroborate them through other *ab initio* calculations (which are under way in our laboratory), recent much more sophisticated results for typical small systems have shown that the basis has unexpectedly little influence on bond indices [25]. There is a most recent study of 3c-two electron bonds based on three-particle density matrices beyond the Hartree-Fock level [32]; the influence of correlation is carefully studied for some selected molecules, requiring much additional effort. Let us underline that we work at the Hartree-Fock level, where exchange is the only recognized correlation; the size of the biological systems which we intend to study further makes absolutely forbidden, and possibly nonsensical for the moment, to deal with more advanced calculations.

3.1 *Small dimers with water and with HCN*

Let us compare indices and energies for small dimers involving the CH...O bond. Energies may be subject to comparison only when resulting from the same type of calculation or experiment, otherwise the uncertainties may be larger than the effect

intended to measure. Thus, let us report the energies from a study on the influence of hybridization and substitution on the properties of the CH...O bond [33]. The most sophisticated bases including electron correlation and BSSE (basis set superposition error) do not yield qualitative differences in the binding energies ΔE . We report in Table 1 Scheiner and co-workers' results [33] for ΔE using the 6-31G* basis, together with our calculated magnitudes; the distance corresponds to a 6-31G* calculation, while charges and 3c-index to PM3. As expected, sp hybridization leads to stronger H-bond than sp² hybridization. As for sp³, ethane does not bind to water.

Literature about dimers involving HCN affords perhaps the best known examples of small systems with recognized CH...O bonds (see Table 2). Among them, the dimer with water has been extensively studied, with a disturbing range of different results [34]. Gutowsky et al [34] report a most thorough discussion of experimental data, pointing at a strong hydrogen bond limiting the floppiness of HCN and a C...O distance of 3.1521 Å. Our optimised geometry gives 3.149 Å and the corresponding I_{CHO} index is -0.0060. A detailed calculation of several systems at different degrees of sophistication [33] gives similar distances and binding energies around 5 kcal/mol, which appears to be overestimated.

The small system formaldehyde-HCN has been studied in Ref. [35]. Calculated interaction enthalpies are quite similar for semiempirical and *ab initio* methods, about -2.7 kcal/mol. The interpretation of rotational spectra gives a C...O distance of 3.271 Å [36], for which we obtain 3.221 Å; the I_{CHO} value of -0.0043 is consistent with the other systems studied here.

An experimental interpretation for the dimer of HCN and oxirane suggests inversion doubling in its rotational spectrum [36]; the predicted C...O distance is particularly short (3.035 Å) and agrees with the one we obtain, of 3.166 Å.

3.2 Acetic acid and acrylic acid dimers

The crystal structure of acetic acid is known to exhibit a dimer with OH...O and CH...O bonds (Ref [6], chap. 10). An early estimation of 1.0 kcal/mol was proposed for the energy of the CH...O interaction [37]; it was inferred by comparison with a normal dimer with two OH...O bonds and it does not take into account any cooperative effect. The hydrogen of the OH group not involved in H-bonding appears to rotate in the dimer, moving away from the other oxygen (Fig. 1). This is related to this oxygen showing a decrement in its basicity instead of the usual increment (Table 3), relaxing its influence on the mentioned hydrogen. Let us remark that the acrylic acid dimer could behave similarly, but it does not, obeying the same pattern as the others in the Tables.

An acetic acid-acetamide dimer appears in a study of related hydrogen bonded pairs [38]. No et al [38] only take into account the OH...O bond of the dimer we are interested in. We expected a remark about CH...O contact which, however, the authors do not mention. Indeed, our results indicate such a possibility, on the same footing as the other ones in the Tables.

The last system in Table 3 has two equivalent weak CHO bonds. Their importance is underlined in a study of the role played by CH...O (carbonyl) interactions in the packing features of carboxylic acids crystal structures by X-ray diffraction analysis [37].

3.3 Formamide dimers

Formamide is usually studied as the simplest model for the peptide bond and as a first step towards biological systems. Besides the formamide dimers themselves, glyoxal affords another appropriate instance when building this kind of pattern. We have formed the possible dimers between glyoxal and formamide (see Fig. 2), as well as the usual closed and open formamide dimers (Ref. [6], p. 97); the closed dimer shows two non-equivalent CH...O bonds.

Table 4 shows that the charge fluctuations in the CH...O bond are even more appreciable than those of the previous Tables. The I_{XHY} values are consistent with the distances and with the previous results. Systems (1) and (2) are the only ones where the CH H-bond distances are slightly shorter in the dimers than in the corresponding monomers. As expected, I_{NHO} for the formamide NH...O bond appears to be lower in the open dimer (e) than in the closed one (d).

Recently, a systematic study of the formamide-methanol dimer has been accomplished [39], using *ab initio*, MP2 and five DFT methods with different basis sets; all magnitudes in this work, unlike others, are fairly dependent on the basis. One of the structures involves a relatively weak CH...O bond. The reported interaction energies do not seem comparable with our results.

3.4 Two sample biological systems

An interesting dimer between the ribose of the nucleotide at position 33 and uracil at position 35 appears in tRNA anticodons of aspartic acid and lysine (Fig. 3). This tandem H-bond (Ref. [6], p. 40) is considered hydrogen bond disorder, the HH separation being just above the limit of 2.4 Å. The C...O distance is 3.369 Å, the O...O one 2.933 Å. While $I_{\text{OHO}} = -0.0114$, the I_{CHO} value of -0.00085 is more

puzzling. The hydrogen charge variation in the CH...O bond corresponds indeed to a H-bond (see Table 5).

We have also calculated the pseudo Watson-Crick pair between a 3-methyl-uracil and a uracil (Fig. 3), which was suggested to play a role in *in vitro* transcription and ribosome binding [40]. The bridge distances in this Ref. are predicted to be 2.77 Å for N...O and 3.23 Å for C...O; we obtain 2.775 Å and 3.362 Å respectively. Although the C...O distance is close to that found in the previous dimer, and carbon having here an unfavourable sp^3 hybridization, we obtain an appreciably higher index $I_{CHO} = -0.0036$ ($I_{OHO} = -0.0152$). In the methyl group, the net hydrogen charge goes from 0.0800 to 0.1055 in the bridge, while the other hydrogens are practically unaltered; this is more significant than the corresponding one for $C(sp^2)$ in the methylene-water dimer. Similarly, the hydrogen in the NH...O bridge goes from 0.1090 to 0.1634, in agreement with the results for the formamide dimers.

Hobza et al. [41] have studied two other uracil dimers involving a CH...O and a NH...O contact. One (UU-C) is referred to as the Calcutta pair and the other one (UU7) cannot occur in nucleic acids, involving a position not accessible to H-bonding. UU7 is predicted to have a C...O distance of 3.257 Å and UU-C 3.236 Å; the N...O distances are respectively 2.860 Å and 2.913 Å. These calculations are of MP2/6-31G** level, the distances of MP2 optimizations being shorter than the HF ones. Thus, our relatively simple calculations are as well consistent with the Popelier H-bond criterion of increment in the net hydrogen charge, the other criteria following topological analysis [42].

3.5 The system trinitromethane-dioxane

Structure analysis of the recrystallization of trinitromethane from dioxane has led to a surprising adduct where two $(\text{O}_2\text{N})_3\text{CH}$ molecules are linked by $\text{CH}\dots\text{O}$ bonds to dioxane [43]. The corresponding distances of 2.937 Å are the shortest ones that we have found in the literature. The results that we have obtained for this system (Table 6) are equally intriguing.

We have calculated the monomers trinitromethane and dioxane, the dimer with one $\text{CH}\dots\text{O}$ bond and the trimer found in experiment (Fig. 4). All of them with the PM3 Hamiltonian (reported in Ref. [43] as reproducing the experimental $\text{CH}\dots\text{O}$ distance), the 6-31G* and the 6-31G** basis. This enlargement of the hydrogen basis produces negligible differences in our results. The PM3 optimization yields for trinitromethane a CH distance of 1.1314 Å, which appears too long. In the dimer it becomes 1.1711 and 1.1678 Å in the trimer. The corresponding 6-31G* values are 1.0726, 1.0786 and 1.0772 Å respectively, the differences being much lower but the trend is the same. The symmetry of the trimer in the 6-31G* basis appears as broken in the PM3 results; this seems to be an artifact of the calculation.

The I_{CHO} bond index, the net charges in oxygen and the bonding hydrogen, together with the $\text{C}\dots\text{O}$ distances, show likewise effects in the dimer when compared with the trimer (Table 6). Thus, it evinces no cooperative effect whatsoever. This system deserves therefore a much more detailed study.

4. Bond index distance and angular dependence

Figures 5 to 7 show the I_{XHY} dependence on the XY distance. It is seen that all of them have the same monotonous behaviour. I_{OHO} has been calculated with the water

dimer, I_{NHO} with the NH_4^+ - H_2O dimer, and I_{CHO} with the dimer HCN and water. It may be verified that the values of the Tables generally follow the predictions of the graphics, so that heavy calculations may be avoided.

5. Conclusions

- All the studied systems exhibit a tendency to maximize their possibility of forming hydrogen bonds, exploring for the purpose every available CH bond.
- The CHO bonds, however weak, manifest a cooperative effect regarding usual hydrogen bonds as well as other CHO bonds.
- In CHO bonds, hydrogen becomes more acidic and oxygen more basic than they are in the isolated monomers.
- The distance dependence of I_{CHO} is monotonous.

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Table 1 Bond indices I_{CHO} , net charges, C...O distances (Å) and binding energies (ΔE , in kcal/mol) for small molecules in complex with water

Molecule	HCN	HCCH	H ₂ CCH ₂
$-I_{\text{CHO}} \times 10^4$	60	44	10
Net H charge	0.2474 ^a 0.2231 ^b	0.2111 ^a 0.1920 ^b	0.0950 ^a 0.0770 ^b
Net O charge	-0.3758 ^a -0.3530 ^b	-0.3640 ^a	-0.3560 ^a
C...O distance	3.149	3.305	3.740
ΔE [33]	5.60	2.53	0.86

^a in dimer, ^b in monomer

Table 2 Bond indices I_{CHO} , net charges and C...O distances (Å) for complexes with HCN

Molecule	water	formaldehyde	oxirane
$-I_{\text{CHO}} \times 10^4$	60	43	47
Net H charge	0.2474 ^a 0.2231 ^b	0.2461 ^a	0.2444 ^a
Net O charge	-0.3758 ^a -0.3530 ^b	-0.3366 ^a -0.3050 ^b	-0.2945 ^a -0.2620 ^b
C...O distance	3.149	3.221	3.166

^a in dimer, ^b in monomer

Table 3 Bond indices I_{XHY} , net charges and H-bond distances (\AA) for the systems in Fig. 1.

system	XHY	$-I_{\text{XHY}} \times 10^4$	Net H charge	Net O charge	XY distance
(a)	CHO	32	0.1105 ^a 0.0709 ^b	-0.4223 ^a -0.3827 ^b	3.426
	OHO	162	0.2553 ^a 0.2179 ^b	-0.3644 ^a -0.3827 ^b	2.844
(b)	CHO	27	0.1033 ^a 0.0734 ^b	-0.4211 ^a -0.3827 ^b	3.484
	OHO	199	0.2636 ^a 0.2179 ^b	-0.4306 ^a -0.3876 ^b	2.804
(c)	CHO	17	0.1433 ^a 0.1198 ^b	-0.3993 ^a -0.3824 ^b	3.624

^a in dimer, ^b in monomer

Table 4 Bond indices , net charges and XY distances (Å) for the dimers with formamide in Fig. 2

System	XH...Y	$-I_{\text{XHY}} \times 10^4$	Net H charge	Net O charge	XY distance
(a)	CH...O	35.6	0.1016 ^a 0.0585 ^b	-0.4162 ^a -0.3895 ^b	3.390
	CH...O	12.6	0.0721 ^a 0.0485 ^b	-0.2829 ^a -0.2612 ^b	3.424
(b)	CH...O	35.9	0.1021 ^a 0.0585 ^b	-0.4208 ^a -0.3895 ^b	3.243
	NH...O	74.1	0.0884 ^a 0.0624 ^b	-0.2956 ^a -0.2612 ^b	3.126
(c)	CH...O	40	0.1055 ^a 0.0585 ^b	-0.4226 ^a -0.3895 ^b	3.398
	NH...O	62.9	0.0888 ^a 0.0624 ^b	-0.2907 ^a -0.2612 ^b	3.156
(d)	NH...O	155	0.1161 ^a 0.0624 ^b	-0.4444 ^a -0.3895 ^b	2.991
(e)	NH...O	59.6	0.1104 ^a 0.0624 ^b	-0.4240 ^a -0.3895 ^b	3.070

^a in dimer, ^b in monomer

Table 5 Bond indices I_{XHY} , net charges and XY distances (Å) for two biological systems (Fig. 3)

System	XH...Y	$-I_{\text{XHY}} \times 10^4$	Net H charge	Net O charge	XY distance
	OH...O	114	0.2238 ^a 0.1891 ^b	-0.3726 ^a -0.3434 ^b	2.933
Rib33-U35					
	CH...O	8.5	0.1621 ^a 0.1447 ^b	-0.3463 ^a -0.3078 ^b	3.369
	CH...O	36	0.1055 ^a 0.0800 ^b	-0.4154 ^a -0.3980 ^b	3.362
MU-U					
	NH...O	152	0.1634 ^a 0.1090 ^b	-0.4370 ^a -0.4070 ^b	2.775

^a in dimer, ^b in monomer

Table 6 Net charges, H-bond distances (Å) and bond indices I_{CHO} for the trinitromethane-dioxane system (Fig. 4)

	PM3	6-31G*
<i>Monomers</i>		
$(\text{O}_2\text{N})_3\text{CH}$		
Net H charge	0.1907	0.2102
CH distance	1.1314	1.0726
<i>Dioxane</i>		
Net O charge	-0.2562	-0.2496
<i>Dimer</i>		
Net H charge	0.2509	0.2434
Net O charge	-0.2943	-0.3027
C...O distance	2.9284	3.0437
CH distance	1.1711	1.0786
I_{CHO}	-0.0325	-0.0101
<i>Trimer</i>		
Net H charge	0.2498 0.2450	0.2391
Net O charge	-0.2891 -0.2909	-0.2974
C...O distance	2.9339	3.0606
CH distance	1.1678	1.0772
I_{CHO}	-0.0295 -0.0291	-0.0080

Figure captions

Fig. 1 Dimers with acetic acid and acrylic acid. (a) acetic acid dimer; (b) acetic acid-acetamide; (c) dimer of acrylic acid.

Fig. 2 Dimers with formamide. (a) (b) (c) glyoxal-formamide; (d) (e) formamide dimer.

Fig. 3 Biological systems. (a) Rib33-U35; (b) 3MU-U.

Fig. 4 Trinitromethane-dioxane.

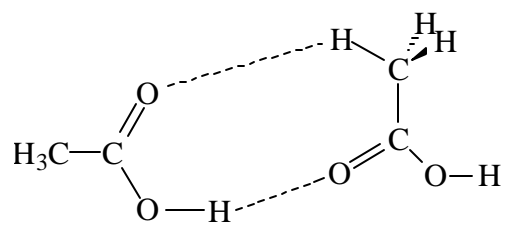
Fig. 5 $|I_{\text{OHO}}|$ as a function of the O...O distance (Å).

Fig. 6 $|I_{\text{NHO}}|$ as a function of the N...O distance (Å).

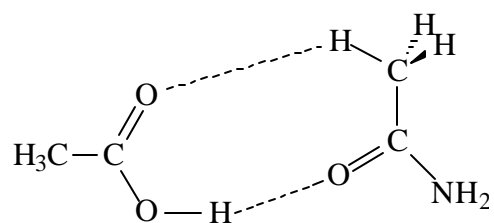
Fig. 7 $|I_{\text{CHO}}|$ as a function of the C...O distance (Å).

Figure 1

(a)



(b)



(c)

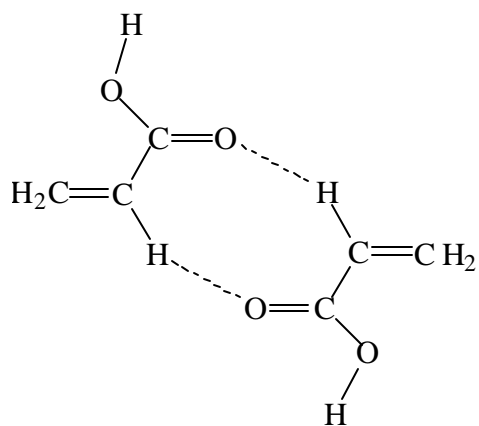


Figure 2

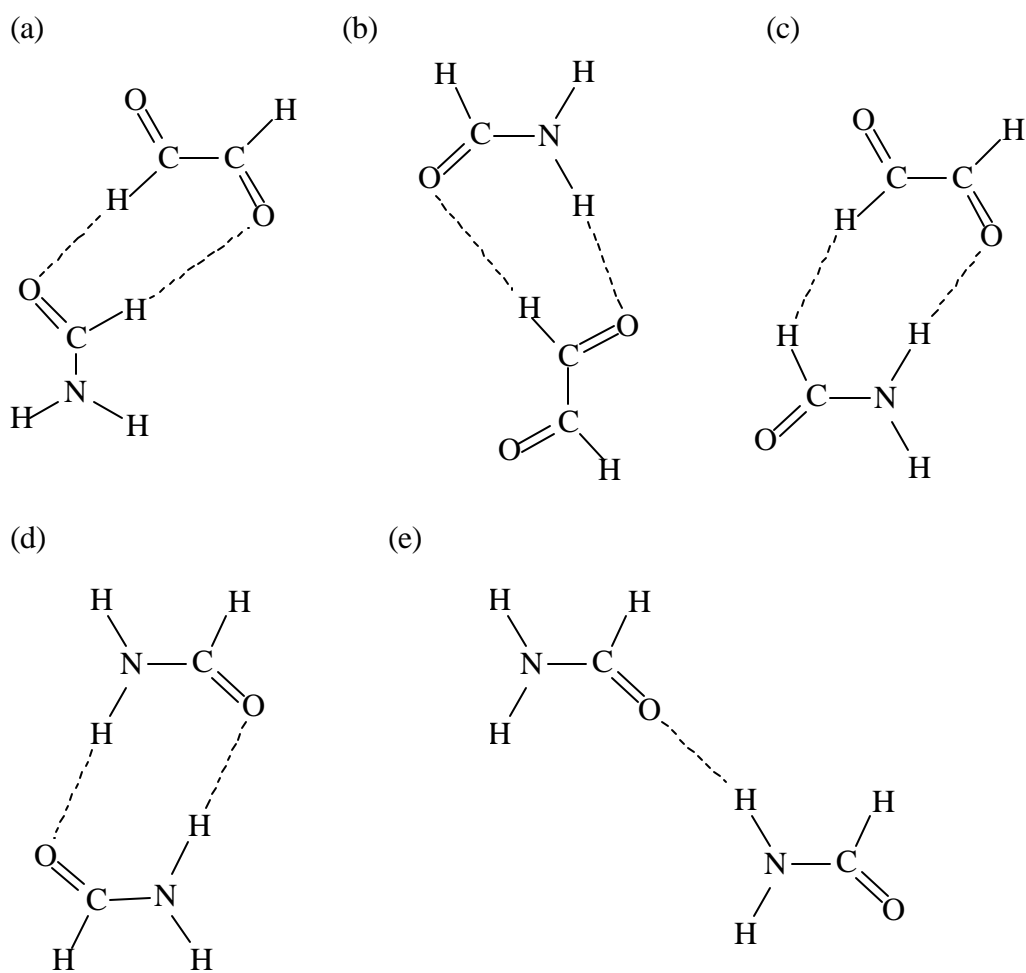
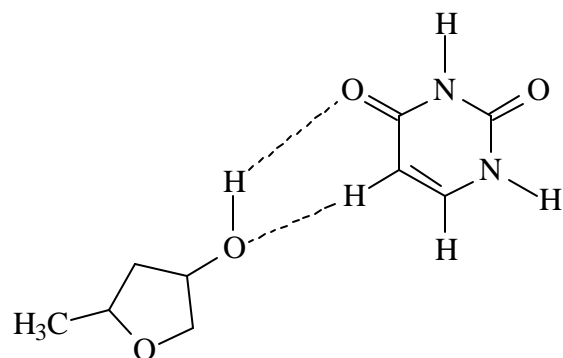


Figure 3 (a)



(b)

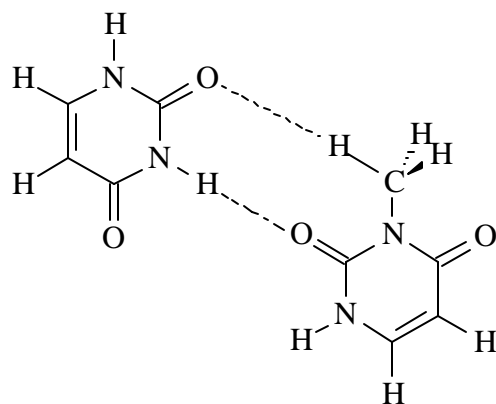


Figure 4

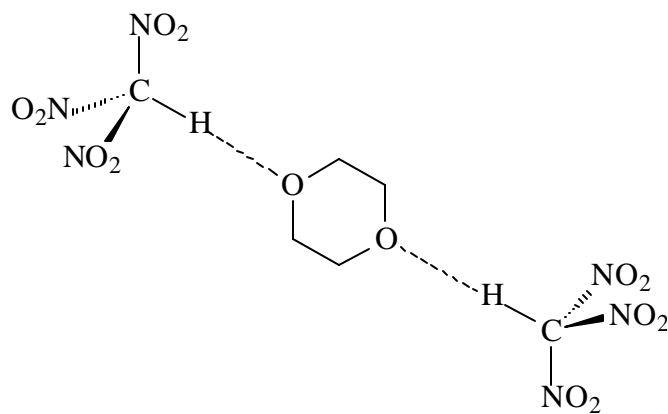


Fig. 5.

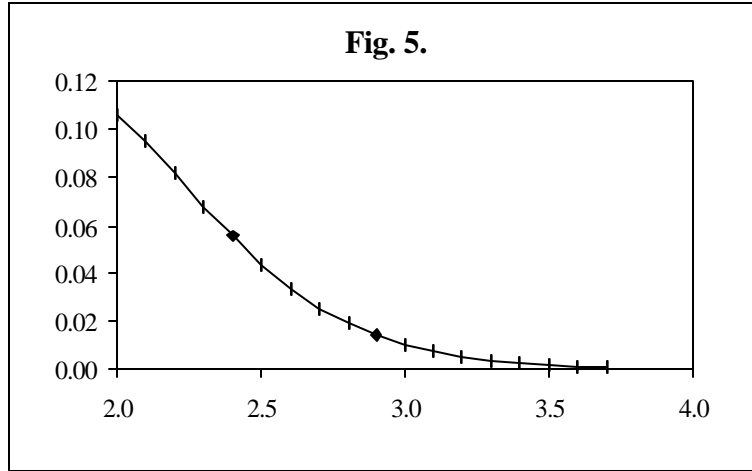


Fig. 6.

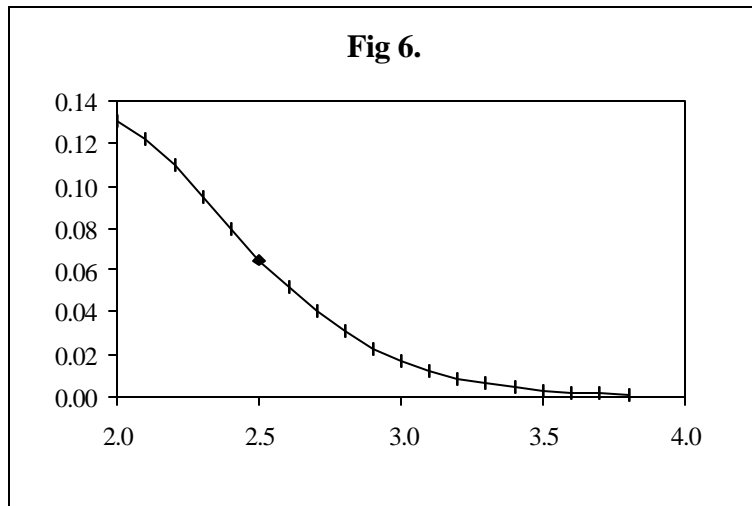


Fig. 7.

