



CBPF-CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Notas de Física

CBPF-NF-015/92

GROUP-GROUP BOND INDEX FOR MOLECULAR SYSTEMS

by

Mario GIAMBIAGI, Myriam S. de GIAMBIAGI

Kleber C. MUNDIM

ABSTRACT

The group-group bond index defined in the present work gives an adequate account for: conjugated systems and molecules with "secondary" bonds; hydrogen-bonded nucleotide base dimers and unusual weak bonded associations. A single number may thus render a reasonable qualitative idea of intra- and intermolecular binding. The index leads to a definition of molecular valence.

Key-words: Group-group index; Weak chemical bonds; Molecular valence.

1. Introduction

Despite being the cornerstone of the chemistry building, chemical bond is still an elusive subject. Pauling's textbook¹ is yet an obliged fundamental reference. For many years, the Lewis electron pair model fulfilled almost all requirements that chemists demanded. Apparent octet rule violations and the departure from Lewis structures are discussed in a thorough, dense work of 1977². The fifteen years elapsed since then have not settled the matter. Dunitz and Seiler's work³ questioned for the first time the commonplace according to which chemical bonding is manifested by an accumulation of charge in the internuclear region. Julg⁴ found a non-equivalence between the Lewis model and the quantum model. Deformation electronic densities are employed to illustrate bonding effects⁵; on the other hand, experimental techniques may determine, under strict non-routine conditions, charge distribution on a molecule⁶.

The concept of chemical bond may thus be faced from different viewpoints, leading to multifarious interpretations. Bader's topological theory of atoms in molecules⁷ has become most popular in recent years, and has stimulated fruitful discussions⁸. We ourselves have generalized Wiberg bond indices⁹ to non-orthogonal bases¹⁰. We have also defined a multicenter bond index starting from the first-order density matrix of closed-shell systems, which is able to distinguish between usual and strong hydrogen bonds¹¹.

We define here an index evaluating the bonding between atom-

ic groups within a molecule. In the same way that our bond index quantifies the electronic distribution along a bond¹⁰, the group-group index gives the extent of electronic distribution among the atoms belonging to the groups considered. The definition proposed fulfills the desired invariance properties^{12,13}.

A particular case is that when the system consists of two molecules; a molecular valence definition steps straightforwardly. According to that, an isolated molecule has zero valence, in contrast with another definition of molecular valence found in the literature (molecular valence is half the sum of atomic valences)^{14,15}. Our molecular valence depends on the other molecule, while the mentioned definition gives the same value whatever the nature of the other molecule or group interacting with it.

The group-group bond index is applied here to some cases which may illustrate its utility: a) typical hydrocarbons, their derivatives and two nitrogen oxides, to verify whether the results agree with chemical expectation; b) dimers of bases appearing in nucleic acids, to see if there is a suitable fit to experimental data; c) two extreme examples of weak bonding, for a comparison with the topological theory applications of Ref.8. Molecular valence is discussed in b).

2. Group-Group Index

Our formulae shall be applied to closed-shell systems, for which the first-order density matrix is a mixed tensor, once covariant and once contravariant, when dealing with non-orthogonal bases¹²:

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

x_{ia} (x^{ib}) are the covariant (contravariant) coefficients of the i -th occupied molecular orbital (MO). Variance indices (i has no variance¹²) are raised or lowered through the overlap matrix between atomic orbitals ϕ

$$S_{ab} = (\phi_a, \phi_b) \quad (2)$$

and its inverse

$$S^{ab} = (S^{-1})^{ab} \quad . \quad (3)$$

S defines thus a metric, as recognized in the early Chirgwin-Coulson paper^{16,17}.

The tensor in (1) is represented by a matrix. Invariants related to chemical intuitive concepts are built through appropriate contraction of products between tensors. The Mulliken charge q_A of atom A in a molecule is given by^{17,18}:

$$q = 2 \sum_{a \in A} \Pi_a^a \quad . \quad (4)$$

The idempotency of the Π matrix permits the definition of bond indices I_{AB} between atoms A and B ^{10,12}

-4-

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \quad . \quad (5)$$

These indices are the generalization of Wiberg indices⁹ to non-orthogonal bases. Valence V_A is defined as¹⁹⁻²¹

$$V_A = \sum_{A=B} I_{AB} \quad . \quad (6)$$

The atomic charge q_A is susceptible of partition into self-charge and active charge^{10,12,22}.

$$q_A = (I_{AA} + V_A) / 2 \quad (7)$$

with an obvious meaning for I_{AA} , i.e. definition (5) when $A=B$. Although q_A is the Mulliken charge, the partition of eq.(7) is of course different from the classical Mulliken atom and bond population.

If a group G within a molecule is defined as $G = \{A_1, A_2, \dots, A_L\}$ we have found worthwhile to introduce the group valence V_G ¹³

$$V_G = \sum_{\substack{A \in G \\ B \notin G}} I_{AB} \quad ; \quad (8)$$

that is, the sum of the bond indices between atoms inside and atoms outside the group. Quantitative meaning is thus given to a chemically intuitive magnitude, i.e. the valence of a functional group.

The natural, straightforward extension of formula (5) is now the group-group bond index I_{GG} ,

-5-

$$I_{GG'} = \sum_{\substack{A \in G \\ B \in G'}} I_{AB} \quad (9)$$

G and G' being two groups of atoms in the system. In a diatomic molecule we have

$$V_A = V_B = I_{AB} \quad (10)$$

Similarly, if the system in question is divided into two groups, we shall have

$$V_G = V_{G'} = I_{GG'} \quad (11)$$

If G, G' are molecules, (11) defines a molecular valence. In the following sections, we shall apply definition (9) to different kinds of chemical systems. Needless to underline, formulae (6), (8) and (9) refer to every pair of atoms in the system, including both effective and formal bonds.

3. Results and discussion

Throughout our calculations, we have used the PM3 Hamiltonian²³; unless stated, geometry has been optimized starting from the experimental data of Ref.24. For some of our examples, we have also used the IEH approximation²⁵.

a) Sample conjugated systems; "secondary" bonds

The first set of molecules chosen to apply the above formulae consists of some hydrocarbons and related derivatives, to-

gether with N_2O_4 and N_2O_5 ; we shall thus see if the results meet chemical expectations and how "secondary" bonds (involved in (9)) affect the $G_n G_m$ index. Among a host of numerical results we have chosen to comment on a few typical molecules.

The $G_1 G_2$ index higher than 1 (actually, 1.144) for methylbenzene (see Fig.1) is of course due to hyperconjugation. Adding a second methyl, as in 1,4-dimethylbenzene, has no influence on the $G_1 G_2$ index. Looking at the results for methylbenzene and nitrobenzene ($I_{G_1 G_2} = 1.085$), together with other values not shown here, we may say that the extra-nuclear substituent has small influence on $I_{G_1 G_2}$ for molecules of the type phenyl-X. Nitrobenzene has an expressive $I_{G_2 G_3}$ value (0.144) due to secondary $C_1 O$ contributions, with $I = 0.046$. The comparison between naphthalene and quinoline indicates that an intranuclear N substitution has also little influence on the various $I_{G_n G_m}$.

In anthracene (Fig.1), $I_{G_1 G_2}$ shows a significant value (0.267), although G_1 and G_2 are not adjacent. The "secondary" 11-13 bond contributes heavily (0.064) to that value; the 1-14 contribution (0.015) also deserves to be mentioned.

The $G_1 G_2$ index of phenantrene, 1.290, is consistent with the knowledge that the bond linking both groups is almost a single one. Taking a glance at the mesomeric structures, this bond contributes only with 1/5 to a double bond. On the other hand,

-7-

$I_{G_3G_4}$ is 3.250, due to the 9-10 bond, which appears as a double bond in 4 of the 5 mesomeric structures (Ref.1, p.199). The corresponding I_{AB} values agree of course with this: $I_{12,13} = 1.104$; $I_{9,10} = 1.730$. Both $I_{G_1G_2}$ and $I_{G_3G_4}$ involve secondary bonds contributions, as $I_{45} = 0.016$ and $I_{11,14} = 0.035$.

In N_2O_4 (Fig.1), I_{NN} being small (0.530) - the experimental distance²⁴ is long, 1.64 Å - it does not furnish an appropriate description of the molecular building. Instead, the G_1G_2 index value (1.008) is much more convincing regarding the existence of the molecule, including small O-O contributions ($I_{45} = I_{36} = 0.020$) and the much more important "secondary" N-O bonds ($I_{13} = I_{14} = I_{25} = I_{26} = 0.097$). The high $I_{G_3G_4}$ value (3.409) is mostly due to the amount of double character in the N-O effective bonds ($I_{15} = 1.563$)²⁶. The index describing the interaction between a single oxygen and the other three, $I_{G_5G_6}$, is noteworthy (0.276). Increased-valence structures have been shown to be essential to the valence-bond description of this molecule²⁷. Let us remember¹² that the small I_{45} value agrees with the prediction that this bond between the *cis* oxygens is not strong enough as to lock the system into the planar conformation²⁸.

Similarly, in N_2O_5 , although the experimental O_1N_3 distance is relatively small (1.30 Å)²⁴, $I_{13} = 0.517$. Again, the G_1G_2 value of 0.858 renders a better idea of the molecule, due to the "secondary" bonds such as O_1O_4 ($I = 0.055$) and N_3O_6 ($I = 0.035$); there are also contributions as O_4O_7 ($I = 0.018$). A brief spann-

ing of Harcourt's hard work about increased-valence structures involving "long bonds" or "secondary" bonds is given by Refs. 27,29,30 backwards to Refs.26,31,32.

Despite the "secondary" bonds contribution, the valence of oxygen in N_2O_4 and N_2O_5 has PM3 values lower than the classical value of 2. In the IEH approximation, nevertheless, "secondary" bonds lead regularly to an increased V_0 , higher than $2^{12,20,33}$.

(b) Hydrogen-bonded nucleotide base dimers

Quantum chemistry has dedicated countless works to the interaction energy of the bases related to the nucleic acids structure. For a typical couple of works made 25 years ago, see Refs.34,35; there is of course a lot of former work. Interaction has been studied both for hydrogen-bonded and for stacked configurations³⁶.

Our main interest consists of bond indices which may be compared with calculations as those mentioned above and, most importantly, with the few experimental data available³⁷. We have focused our attention on hydrogen bond indices for the Watson-Crick pairs³⁸ and on the hydrogen bonded systems originating the tertiary structures of yeast tRNA^{Phe39}. We apply definition (9) to selected hydrogen-bonded base dimers (Figs. 2 and 3). Calculations have been carried out through the IEH approximation, which has proven useful in our previous works about hy-

drogen-bonded biological systems³⁸⁻⁴¹, and also with the PM3 method²³. As in Refs.38,39, geometries are taken from Ref.1, chaps.8 and 12. As any semiempirical method, PM3 performs well for certain magnitudes and not so well for other ones⁴². Several objections have been raised regarding PM3 (actually, regarding all the MNDO family) *energetic* aspects for hydrogen bonds^{43,44}. However, scarce attention seems to have been paid to PM3 *hydrogen bond indices*, notwithstanding they are usual outputs of standard programs.

For such large systems as those studied in this section, *ab initio* calculations are still too expensive and time-consuming, even reduced to medium-size basis of dubious efficiency: an ever-increasing basis might not be a sure prescription for obtaining better results^{45,46}. We have reported our inter-group indices in Table 1; this single number may be related to the experimental binding energy. Although the experimental results refer to methylated bases, the methyl influence on these indices is very small. The Table shows that T and U are almost interchangeable in our case: in Ref.47 interaction energies for methylated and nonmethylated base pairs differ in less than 2%. Experimental facts about DNA methylation are elusive⁴⁸.

Our C.C dimer is different from that shown in Refs.47,49, and also from those considered in Ref.50. The present dimer, the same as Ref.39, appears in crystalline cytosine monohydrate⁵¹. The experimental results indicate stronger association for C.C

than A.U or A.T; both PM3 and IEH agree on ranking this dimer among the strongly associated ones, as the other calculations mentioned^{47,49}.

PM3 and IEH indices are mutually consistent and both are consistent with experiment; IEH indices are approximately twice PM3 indices (we had found a similar relation for IEH and CNDO hydrogen-bond indices⁴¹). In table 2 we have reported some quotients between IEH, PM3 and experimental values; the agreement is quite satisfactory, IEH performing better than PM3. Let us note that for the dimers studied in this section we have found no significant "secondary" bonds, unlike what happens in Ref. 47. In short, the group-group bond index for these dimers, involving in a single number the two or three hydrogen bonds together with weaker interactions, allows a satisfactory comparison with experiment.

Let us now compare the sequence obeyed by our indices with sequences of theoretical interaction energies (actually, the absolute value of this magnitude). In Ref.49, Hobza and Sandorfy use *ab initio* calculations with a minimal basis set, taking into account basis set superposition errors and an empirical dispersion energy; their geometries of G, C, T and A are optimized, intramolecular geometry is frozen and only intermolecular coordinates optimized, ensuring coplanarity. In Ref.47, the authors perform a calculation with optimized potentials for liquid simulations (OPLS) functions; again, the geometry used for the

monomers is an optimized one. The sequences obtained are ranged as follows

49	GC >GG >CC >AC >GT >AT >AA >TT
47	GC >GG >CC >GT >AT >AC >TT >AA
this work, PM3	GT >GC >CC >GG >AC >AA >AT >TT
this work, IEH	GC >GG >GT >CC >AC >AA >AT >TT

We have picked the dimers paired such as ours from Refs.47,49 (except for CC, as explained above); similarly, in our pairs we have left out those involving U. It is seen that, as expected, three of the four sequences predict that GC is the strongest association; three out of four sequences (not the same as before) agree on pointing out TT as the weakest dimer. The accord obtained is satisfactory enough. Let us remark that the IEH results, despite the inherent naïvety of this method, are as satisfactory as those of the much more sophisticated treatments of Refs.47,49, and apparently better than PM3.

Let us now turn our attention to molecular valence. We mentioned in the introduction that our valence for an isolated molecule is zero, while the valence of a molecule interacting with another one depends on the nature of the second molecule, according to formula (11). The dimers of Fig.3 lead to the following IEH valence ranges

A(0.20-0.27); U,T(0.14-0.28); C(0.27-0.32); G(0.20-0.32)

The PM3 values are roughly half the above values.

As a matter of fact, in Ref.15 molecular valence V_M is de-

defined as $V_M = (\sum_A V_A)/2$; V_M increases with the number of atoms in the molecule. For example, G in the G.T dimer would have a valence of 21.59.

Another illustrative example is provided by carbon monoxide. Ref.15 gives that V_{CO} is 2.49(CI level) or 2.60(SCF level). CNDO/2 values for the carbonyl group in typical aldehydes, ketones and acids range from 1.97 to 2.28¹³. IEH values for this group in transition metal complexes (Ref.12 and unpublished results) vary between 1.50 for the equatorial carbonyl in iron pentacarbonyl up to 2.87 for the equatorial carbonyl in cobalt tetracarbonyl hydride. In the G.T dimer there are three carbonyl groups; both IEH and PM3 results predict that V_{CO} increases if the oxygen of the group enters a hydrogen bond.

We have thus shown that molecular valence such as we are led to formulate in this work is qualitatively different from the previously known definition. Perhaps the present viewpoint is more flexible.

(c) Weak bonds in a covalent complex and in an ionic pair

Let us now calculate our index for two distinct examples of recognized weak intermolecular bonds⁸, which have been thoroughly analysed from the viewpoint of Bader's topological bond theory⁵²⁻⁵⁴. Our index, a single number, contains less detailed information than that furnished by topological bond theory.

However, the simplicity of the calculations may advocate it.

As in Ref.8, the first example is the benzene-tetracyanoethylene (TCNE) complex (Fig.4a). The IEH calculation has not converged for this system. We have used classical geometric data for benzene and PM3 optimized data for TCNE. We have not succeeded in optimizing the complex (Cioslowski et al.⁸ do not optimize it either). Optimization should not yield a qualitatively different description, as it may be seen in Table 3 for the second example. Our GG' PM3 index for the benzene-TCNE complex is 0.0200; this is almost covalent in character, as benzene conveys a slightly positive charge of 0.005. It is not clear for us that this should be described as a charge-transfer complex⁴¹; its dipole moment is 0.27 Debyes. As in Ref.8, the highest intermolecular weak bonds are those connecting the ethylenic TCNE carbons and the 1,4-carbons of benzene, for which $I_{cc} = 0.0013$.

Let us now see how the GG' index behaves for an ionic complex, again taken from Ref.8, the guanidinium-cyanofornide pair (Fig.4b and Table 3). We have supposed the C_{3v} geometry of Ref. 55 and submitted it to PM3 optimization. Other starting geometries and optimization itself, do not yield any qualitative differences in the quantities obtained. We have carried out IEH calculations with the PM3 geometries (with and without optimization); they are consistent with the results mentioned in the previous section, i.e. these are indeed weak bonds, much weaker

than hydrogen bonds. Ionic charges for guanidinium and for cyanofornide are ± 0.99 differing, for each calculation, only in the third decimal place. All indices are somewhat higher with optimized geometries. Table 3 shows that "secondary" intermolecular bonds partly differ from those predicted in Ref.8. The most expressive of these bonds links C_{guanid} with cyanofornide's C^* (see Fig.4b); instead, the weak bonds connecting amino nitrogens to C^* are for us higher than the bonds between the nitrogen atoms of the cyano and the amino groups, described in Ref.8 as unusual highly curved bonds. Finally, the PM3 group-group bond index for this ionic complex is lower than the index for the first complex; this is to be expected, for we have seen that the benzene-TCNE complex is rather covalent in character.

The role of groups within a wider framework is the very heart of chemistry. Interactions, usually in the fluid phase, may be considered "... 'weak' in the sense that the interacting systems retain their individuality, at least in good approximation"⁵⁶. This quotation of the first page in the last chapter of a capital book poses the question under the clearest possible form. The antisymmetrized product of "group functions" suggested there may be formulated in terms of the Grassmann algebra and the Slater determinant written as block-determinants according to the groups⁵⁷. We are now working towards this direction.

4. Conclusions

- The proposed definition of a group-group bond index allows quantifying structural features in agreement with chemical expectation.

- In some of the cases considered, "secondary" bonds contribute significantly to the group-group index.

- Results for dimers of the hydrogen-bonded bases appearing in nucleic acids are in close correlation with the few experimental interaction energies. The IEH approximation seems to perform better than PM3.

- Weak bonds in a covalent complex and in an ionic pair are correctly depicted.

- The molecular valence introduced here leads to reasonable values.

Figure Captions

Fig. 1 (a) Groups taken into account in methylbenzene, nitrobenzene and 1,4-dimethylbenzene. G_3 may contain either three hydrogen atoms (for methylbenzene) or two oxygens (for nitrobenzene).

(b) Groups involved in the discussion of anthracene and phenantrene.

(c) Groups considered for N_2O_4 and N_2O_5 .

Fig. 2. The nucleotide bases.

Fig. 3. Pairs calculated in this work, with the geometry of Ref.39. The points represent oxygen atoms, M is methyl group.

Fig. 4 (a) Benzene-TCNE complex. The distance between both molecules is chosen to be 3.0 \AA^B .

(b) Guanidinium-cyanofornide complex. We have drawn each fragment as planar; actually, there is a slight distortion.

The distance $C_{\text{guanid}}-C_{\text{cyano}}$ is supposed to be 3.252 \AA^{055} .

-17-

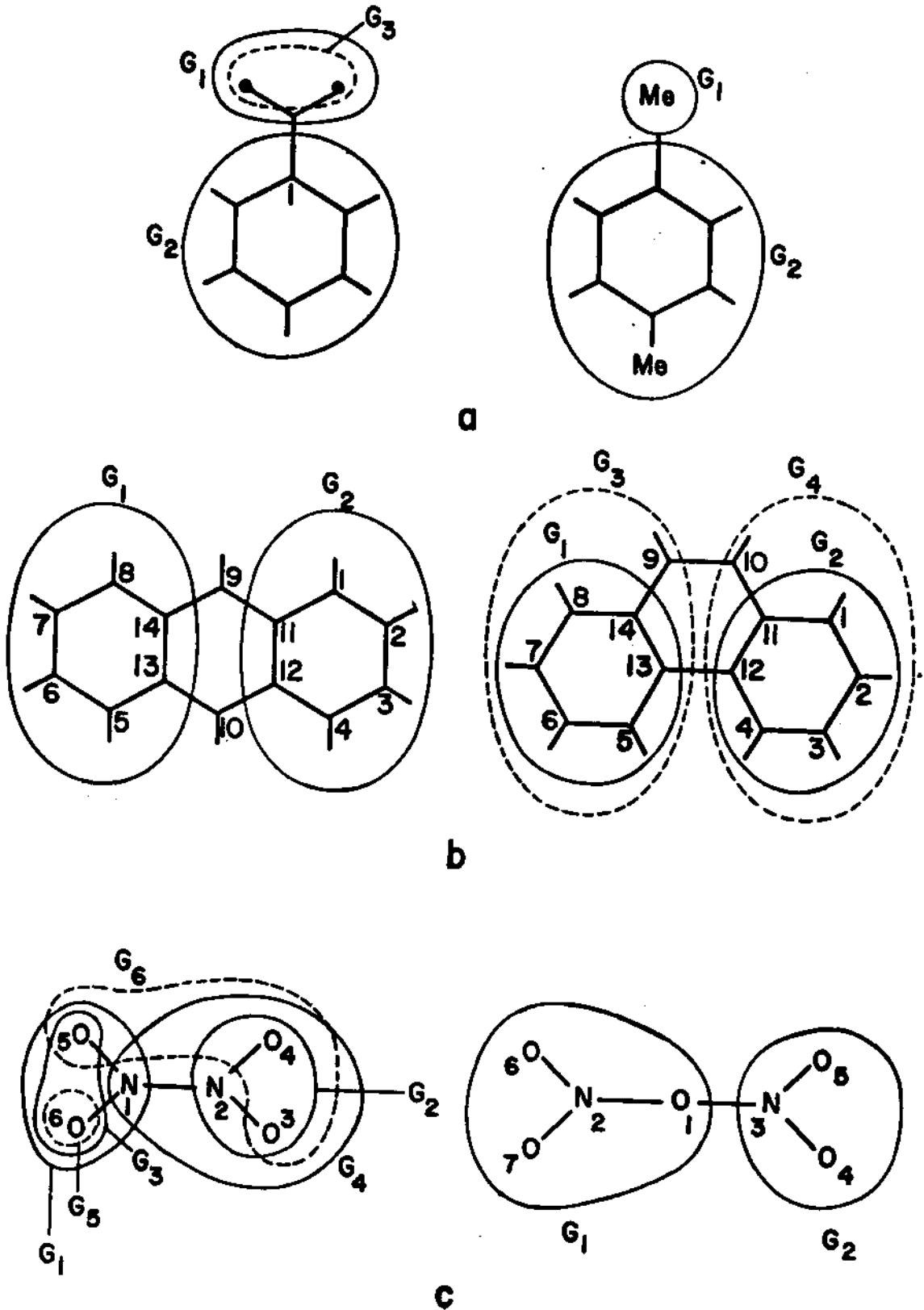
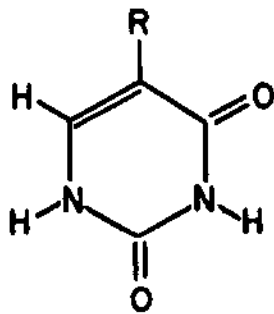
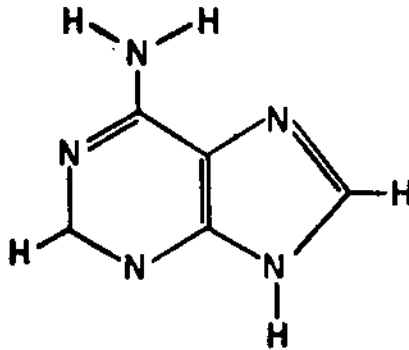


Fig. 1

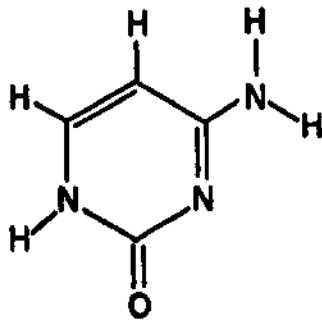
-18-



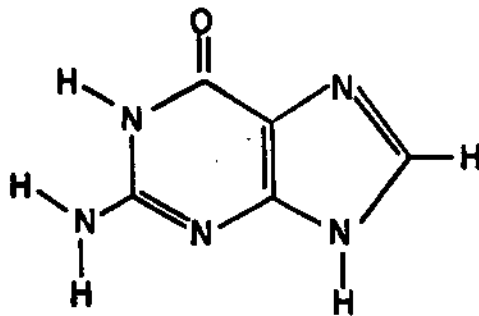
T (R=CH₃) and **U** (R=H)



A



C



G

Fig. 2

-19-

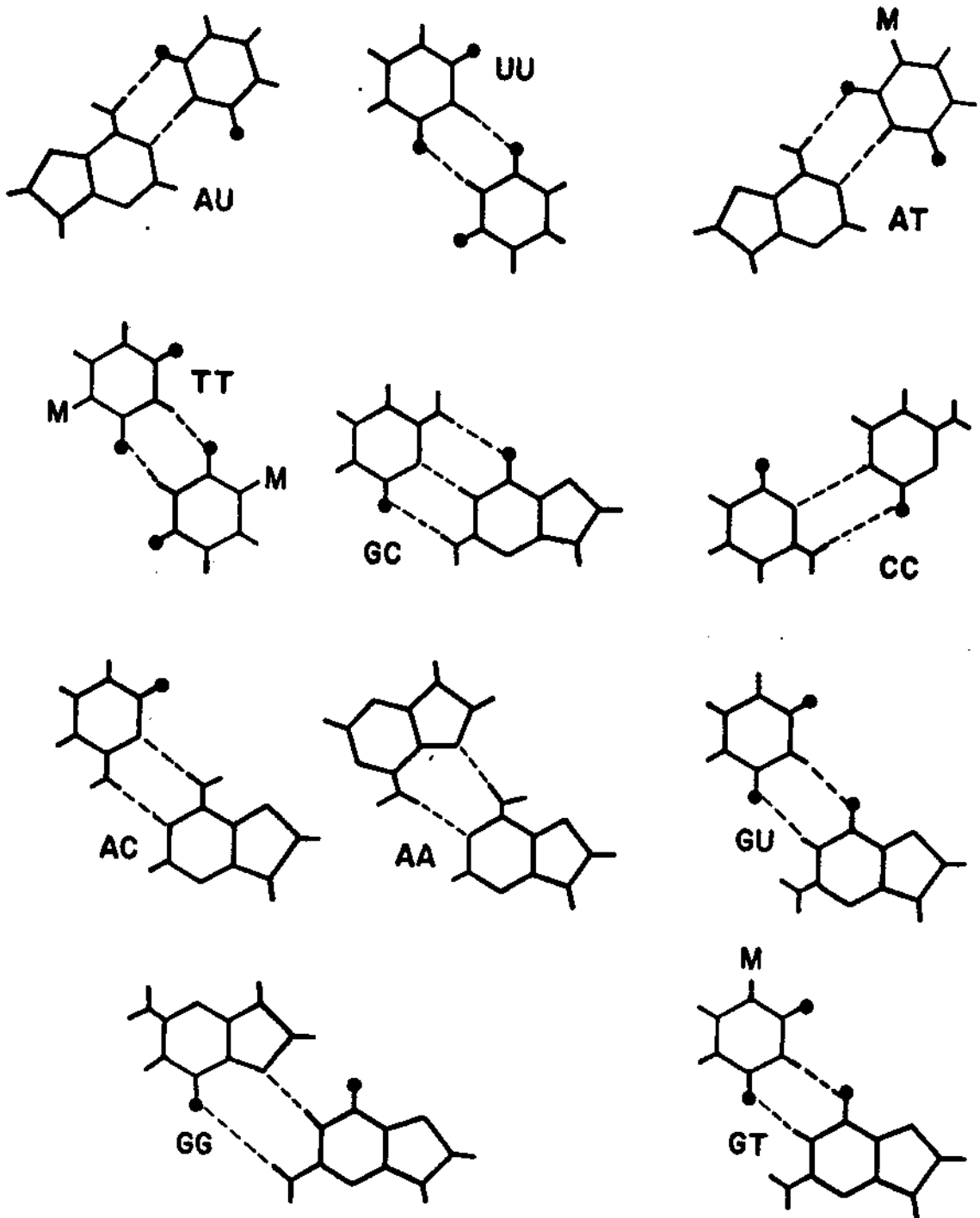
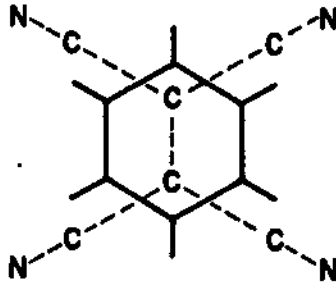
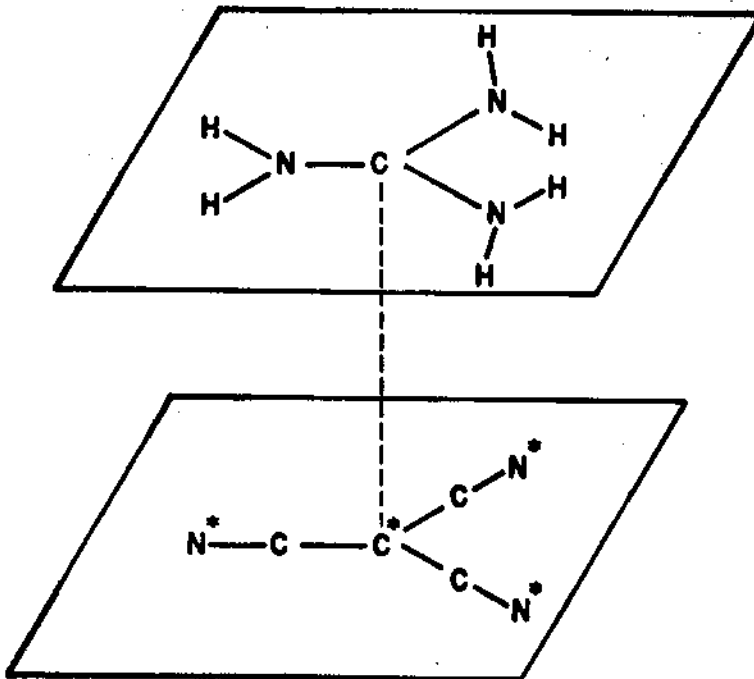


Fig. 3

-20-



a



b

Fig. 4

Table 1. Inter-group bond index for nucleic acids base pairs (see Fig.3), calculated with IEH and PM3 approximations.

Experimental binding energies are taken from Ref.37.

Base pair	IEH index	PM3 index	Bind.en.(kcal/mol)
A.U	0.2042	0.0948	14.5
U.U	0.1451	0.0704	9.5
A.T	0.2021	0.0927	13.0
T.T	0.1444	0.0703	9.0
G.C	0.3160	0.1599	21.0
C.C	0.2778	0.1564	16.0
A.C	0.2707	0.1259	
A.A	0.2113	0.1211	
G.U	0.2789	0.1617	
G.G	0.2869	0.1379	
G.T	0.2811	0.1619	

Table 2. Relations for inter-group indices of some dimers appearing in Fig.3.

	IEH	PM3	Exp
I(G.C)/I(A.T)	1.566	1.726	1.615
I(A.U)/I(A.T)	1.010	1.022	1.115
I(C.C)/I(A.T)	1.375	1.687	1.230
I(T.T)/I(A.T)	0.715	0.758	0.692
I(U.U)/I(A.T)	0.718	0.759	0.731

Table 3. Bond indices, GG' indices and dipole moment μ for the guanidinium-cyanoformide complex (see Fig.4b). PM3 results are respectively with(') and without(⁰) geometry optimization. The IEH calculations are carried out with the PM3 respective geometries.

	$I_{CC} \times 10^3$	$I_{NC} \times 10^3$	$I_{NN} \times 10^4$	$I(\text{guanid-cyano}) \times 10^2$	μ (Debyes)
PM3 ⁰	1.7	0.9	4	1.16	14.88
PM3'	2.2	1.0	4	1.26	15.04
IEH ⁰	2.9	1.1	6	2.24	15.52
IEH'	3.7	1.3	8	2.56	15.81

References

- 1 L. Pauling, *The Nature of the Chemical Bond*, Cornell, Ithaca, 1960.
- 2 T.A. Halgren, L.D. Brown, D.A. Kleier and W.L. Lipscomb, *J. Am. Chem. Soc.*, 1977, **99**, 6793 and references therein.
- 3 J.D. Dunitz and P. Seiler, *J. Am. Chem. Soc.*, 1983, **105**, 7056.
- 4 A. Julg, *Int. J. Quantum Chem.* 1984, **26**, 709.
- 5 W.H.E. Schwartz, P. Valtazanos and K. Ruedenberg, *Theor. Chim. Acta*, 1985, **68**, 671.
- 6 P. Coppens, *J. Phys. Chem.*, 1989, **93**, 7949.
- 7 R.F.W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9.
- 8 J. Cioslowski, S.T. Mixon and W.D. Edwards, *J. Am. Chem. Soc.*, 1991, **113**, 1083.
- 9 K. Wiberg, *Tetrahedron*, 1968, **24**, 1083.
- 10 M. Giambiagi, M.S. de Giambiagi, D.R. Grepel and C.D. Heymann, *J. Chim. Phys.*, 1975, **72**, 15.
- 11 M. Giambiagi, M.S. de Giambiagi and K.C. Mundim, *Struct. Chem.*, 1990, **1**, 423.
- 12 M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, *Z. Naturforsch.*, 1984, **39a**, 1259.
- 13 K.C. Mundim, M. Giambiagi and M.S. de Giambiagi, *Nvo. Cim.*, 1990, **12D**, 765.
- 14 M.S. Gopinathan, P. Siddarth and C. Ravimohan, *Theor. Chim. Acta*, 1986, **70**, 303.
- 15 P. Siddarth and M.S. Gopinathan, *Int. J. Quantum Chem.*, 1990, **37**, 685.

- 16 B.H. Chirgwin and C.A. Coulson, *Proc. Roy. Soc. (London)*, 1950, **A201**, 196.
- 17 M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, *Theor. Chim. Acta*, 1985, **68**, 337.
- 18 I. Mayer, *Int. J. Quantum Chem.*, 1983, **23**, 341.
- 19 D.R. Armstrong, P.G. Perkins and J.J.P. Stewart, *J. Chem. Soc. (Dalton)*, 1983, p.838.
- 20 N.P. Borisova and S.G. Semenov, *Vestn. Leningr. Univ.*, 1973, **16**, 119.
- 21 K. Jug, in *Molecules in Physics, Chemistry and Biology, Vol. III*, ed. J. Maruani, Kluwer, 1989, pp. 149-170, and refs. therein.
- 22 C. Trindle, *J. Am. Chem. Soc.*, 1969, **91**, 219.
- 23 J.J.P. Stewart, *QCPE Bulletin* 1986, **6**, 91; Program 455, MOPAC 5.0.
- 24 L.E. Sutton, *Tables of Interatomic Distances*, Chem. Soc., London, 1958.
- 25 Program from P. Dibout, *QCPE*, 1973, **10**, 256.
- 26 R.D. Harcourt, *J. Mol. Struct.*, 1971, **8**, 11.
- 27 R.D. Harcourt, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1098.
- 28 C.H. Bibart and G.E. Ewing, *J. Chem. Phys.*, 1974, **61**, 1284.
- 29 R.D. Harcourt, *J. Mol. Struct. (Theochem)*, 1991, **229**, 39.
- 30 R.D. Harcourt, *J. Phys. Chem.*, 1991, **95**, 6916.
- 31 R.D. Harcourt, *J. Mol. Struct.*, 1971, **9**, 221.
- 32 R.D. Harcourt, *J. Am. Chem. Soc.*, 1978, **100**, 8060.

- 33 S. G. Semenov, in *Theory of Valence in Progress*, ed. V.I. Kuznetsov, MIR, Moscow, 1980, chap. 7.
- 34 B. Pullman, P. Claverie and J. Caillet, *Proc. Natl. Acad. Sci. USA*, 1966, 55, 904.
- 35 P. Claverie, B. Pullman and J. Caillet, *J. Theor. Biol.*, 1966, 12, 419.
- 36 See for example Z.G. Kudritskaya and V.I. Danilov, *J. Theor. Biol.*, 1976, 59, 303; also J. Langlet, P. Claverie, F. Caron and J. Boueve, *Int. J. Quantum Chem.*, 1981, 20, 299.
- 37 I.K. Yanson, A.B. Teplitsky and L.F. Sukhodub, *Biopolymers*, 1979, 18, 1149.
- 38 M. Giambiagi, M.S. de Giambiagi and W.B. Filho, *Chem. Phys. Lett.*, 1981, 78, 541.
- 39 M.S. de Giambiagi, M. Giambiagi and D.M.S. Esquivel, *Z. Naturforsch.*, 1983, 38c, 621.
- 40 M.S. de Giambiagi, M. Giambiagi and D.M.S. Esquivel, *Z. Naturforsch.*, 1982, 37a, 292.
- 41 M.S. de Giambiagi, M. Giambiagi and C.A. Chamarelli, *Nvo. Cim.*, 1984, 3D, 522.
- 42 See the polemics in M.J.S. Dewar, E.F. Healy, A.H. Holder and Y. Yuan, *J. Comp. Chem.*, 1990, 11, 541; J.J.P. Stewart, *J. Comp. Chem.*, 1990, 11, 543.
- 43 E.L. Coitiño and O.N. Ventura, *Folia Theor. Chim. Latina*, 1989, 17, 191.
- 44 M. Khalil, R.J. Woods, D.F. Weaver and V.H. Smith Jr., *J. Comp. Chem.*, 1991, 12, 584.

- 45 S. Huzinaga, M. Klobukowski, Z. Barandiaran and L. Seijo, *J. Chem. Phys.* , 1986, 84, 6315.
- 46 J. Simons, *J. Phys. Chem.* , 1991, 95, 1017.
- 47 J. Pranata, S.G. Wierschke and W.L. Jorgensen, *J. Am. Chem. Soc.* , 1991, 113, 2810.
- 48 C.Q. Liu, Y. Wang, J.F. Huang and H. Zhang, *J. Theor. Biol.* , 1991, 148, 145.
- 49 P. Hobza and C. Sandorfy, *J. Am. Chem. Soc.* , 1987, 109, 1302.
- 50 R. Czerminski, J.S. Kwiatkowski, W.P. Person and K. Szczepaniak, *J. Mol. Sctruct.* , 1989, 198, 297.
- 51 G.A. Jeffrey and Y. Kinoshita, *Acta Cryst.* , 1963, 16, 20.
- 52 R.F.W. Bader in *The Force Concept in Chemistry.* , ed. B.M. Deb, Van Nostrand, N. York, 1981, chap. 2.
- 53 R.F.W. Bader, T.S. Slee, D. Cremer and E. Kraka, *J. Am. Chem. Soc.* , 1983, 105, 5061.
- 54 R.F.W. Bader, R.J. Gillespie and P.J. Mac Dougall, *J. Am. Chem. Soc.* , 1988, 110, 7329.
- 55 J. Cioslowski and S.T. Mixon, *Chem. Phys. Lett.* , 1990, 170, 297.
- 56 R. McWeeny, *Methods of Molecular Quantum Mechanics*, Academic Press, 1989, chap. 14.
- 57 K.C. Mundim, Ph.D.Thesis, *Centro Brasileiro de Pesquisas Fisicas, Rio de Janeiro, Brasil, 1991.*