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REMARKS CONCERNING THE EFFECT OF ENVIRONMENT ON THE PROPERTIES OF CC AND CO BONDS

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Abstract—The purpose of this paper is to present, in a simple way, some results recently obtained at the "Centre de Mécanique Ondulatoire Appliquée" in studying the effect of environment on CC and CO bonds.

RELATION BETWEEN NOTATION AND LENGTH OF AROMATIC CC BONDS

THE effect of the environment of a bond can be divided into two classes:

(a) that which comes from nearest neighbours,
(b) that which comes from other parts of the molecule.

The latter is only important if the molecule contains delocalized bonds, arising either from conjugation or hyperconjugation.

The effects of the neighbourhood of the bond are very often classified as follow:

(1) Influence of the number and the organization of electrons surrounding the cores of the atoms of the bond (roughly the hybridization effect).
(2) Effect due to the charges of other cores surrounding the bond (inductive effect).
(3) Interaction between non-bonded atoms.

Until now it has not been possible to aportion satisfactorily the role of each individual effect.

Following Pauling, Mulliken and others it has become customary to explain in terms of conjugation and hyperconjugation the various CC bondlength which are found in molecules containing delocalized bonds.

More recently Dewar and Schmeising[1] have found that all evidence for the existence of appreciable effects of π-electron resonance in the ground states of conjugated and hyperconjugated molecules is inconclusive and that all observed effects can be explained as a result of differences in hybridization in carbon σ bond orbitals. Mulliken[2] has discussed Dewar's arguments and has shown that if the effect of resonance is probably not as great as has been usually supposed, it is nonetheless, not entirely negligible.

On the other hand Bartell[3] believes that the interaction between non-bonded atoms (which is the most neglected factor) gives promise of becoming one of the most important. He has shown that if a plausible set of potential functions describing interactions between non-bonded atoms are used, carbon–carbon bond lengths in non-aromatic hydrocarbons can be closely computed without invoking hybridization, conjugation or hyperconjugation.

However, Wilson[4] has strong objections against this point of view.

In such a confused situation it has seemed desirable to reconsider the notion of

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[1] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron* 5, 166 (1959).
[2] R. S. Mulliken, *Tetrahedron* 6, 68 (1959).
[3] L. S. Bartell, *J. Chem. Phys.* 32, 827 (1960).
[4] This symposium: E. B. Wilson, Jr., *Tetrahedron* 17, 191 (1962).

"bond notation" introduced several years ago[6] to represent the effect of environment on the length of an aromatic CC bond. It will be perhaps useful to recall that in an alternant conjugated hydrocarbon "bond notation" has been given to the set of the types of the CC bonds adjacent to a given bond; a bond type refers to the number of CC bonds which are adjacent to a given bond.

Fig. 1 shows, for example, the types of the CC bonds in naphthalene.

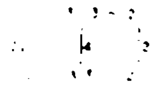

FIG. 1.

From this figure, it is obvious that, for example, the notation of the central bond will be (3,3,3,3) and that the notation of an $\alpha - \beta$ bond will be (2,3).

It has been shown[6] that both from the theoretical and from the experimental point of view the length of a CC bond only depends on its notation at least in a first approximation.

TABLE 1

Notation	Bond length (Å)
(2,3)	1·382 ± 0·019
(2,2)	1·397 ± 0·013
(2,4,4)	1·390 ± 0·010
(2,3,4)	1·425 ± 0·025
(3,3,3,3)	1·415 ± 0·021

TABLE 2

Notation	Bond length (Å)					
	B	N	A	C		V
(2,3)		1·364	1·368	1·361	1·376	1·369 ± 0·008
(2,2)	1·397	1·415	1·419	1·392		1·405 ± 0·014
(2,4,4)				1·405	1·423	1·414 ± 0·009
(2,3,4)		1·421	1·436	1·427	1·418	1·427 ± 0·009
(3,3,3,3)		1·418	1·428			1·423 ± 0·005

B = benzene, N = naphthalene, A = anthracene, C = chrysene, V = central value

Using experimental measurements made before 1955 the lengths that can be associated with some bond notations are given in Table 1.[6] The r.m.s. deviation from the central values is 0·016 Å.

Since that time important refinements have been introduced[7] in the experimental evaluation of bond length, and Table 2 gives the new lengths associated to the same set of bond notations.

The r.m.s. deviation is now only 0·009 Å and shows that the bonds possessing the same notation have the same length, the deviation from that rule being of the order of magnitude of the experimental uncertainty.

[6] C. Vroelant and R. Daudel, *Bull Soc. Chim. Fr* 16, 36 (1949). See also R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry, Methods and Applications* p. 128 *Interscience*, New York (1959).

[7] R. Daudel, *Advanc. Chem. Phys.* 1, 177 (1958).

It is of interest to note that the use of bond notation to predict bond lengths is as precise as the calculations based on MO or VB theory. Cruickshank and Sparks[7] have shown that recent X-ray results for the bond lengths in some alternant hydrocarbons agree to about 0·01 Å with MO and VB theories.

The consistent results of bond notation might be considered to be a proof of the effect of conjugation in determining the bond lengths in aromatic molecules, as the demonstration[5] of the relation between notation and length is based on resonance theory.

However the consistency may also be considered as only an empirical rule, a refinement in a sense of the law observed by Costain anf Stoicheff[8] that state that the C—C, C=C and C—H bond lengths increase linearly with increase in the number of adjacent bonds.

In conclusion we can say that, even in conjugated molecules, the length of a bond only depends on its environment but this includes a larger part of the molecule than in molecules containing only localized bonds.

This extension of the "effective" environment gives, in a sense, a measure of the conjugation effect. Refinements of the structures of many alternant hydrocarbons would be helpful to measure the generality of the above statements.

EFFECT OF ENVIRONMENT ON THE FORCE CONSTANT OF THE CARBONYL GROUP

As for bond distance, the force constant of a bond may also be considered as a measure of its strength. The force constant of a bond is correlated with its stretching vibration frequency which may be determined from the study of the corresponding infra-red spectrum. This is why chemists very commonly use infrared data to ascertain the effect of environment on a given bond. For example, the fact that the $\nu_{C=O}$ stretching frequency is 1775 cm^{-1} for cyclobutanone and about 1715 cm^{-1} for non-cyclic saturated ketones has been considered as evidence of the "unsaturated character" of small rings.

As Bratoz and Besnainou have shown, going directly from the stretching frequency to the structure of the C=O bond is dangerous. It is better to use the force constant as intermediate quantity.

Using Wilson's matrices, or more exactly a perturbation procedure[9] giving more intermediate results, Bratoz and Besnainou[10] have calculated the force constant of the C=O bond in various compounds, like saturated and unsaturated ketones, aldehydes, carbocylic acids, esters and quinones.

Table 3 gives some of their results.

TABLE 3. FORCE CONSTANTS (10^6 dyne/cm)

Saturated ketones	10—10·3
Unsaturated ketones	9—9·8
Halogenated ketones	10·3—10·9
Cyclobutanone	10·3
Orthoquinones	9·7—10·1
Paraquinones	9·5—9·9

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[7] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A **258**, 270 (1960).

[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

[9] S. Bratoz, *J. Chem. Phys.* **28**, 159 (1955).

[10] S. Bratoz and S. Besnainou, *J. Chim. Phys.* **56**, 555 (1959).

It is interesting to point out that the force constant in cyclobutanone has about the same value as that in non-cyclic saturated ketone. The use of the perturbation method has clearly shown that the increase of the frequency is mainly due to the fact that in cyclobutanone the angle between the C=O and the adjacent C–C bonds is smaller than in an ordinary ketone; this change of geometry increases the coupling between the C=O and the adjacent C–C vibrators. The change of $\nu_{C=O}$ is finally mainly due to a mechanical factor and not to an electronic one. Again, evidence of conjugation disappears.

The most striking effect of the environment shown by Table 3 is the low value ($9 \cdot 10^5$ dyne/cm)of the force constant in some unsaturated ketones and its high value ($10 \cdot 9$ 10^5 dyne/cm) in some halogenated ketones. To understand the origin of each variation observed on Table 3, Bratoz and Besnainou[11] have determined the π-electronic wave function corresponding to the various molecules concerned using the Pariser and Parr approximation and have given a general formula for the force constant of a bond in that approximation.

To represent the inductive effect of the adjacent atoms of the carbonyl group they have estimated the penetration integrals from the ionization energy of some free radicals. The other necessary parameters used are those of Sidman coming from the ultra-violet spectrum of formaldehyde.

Table 4 compares the force constants calculated using that way and those coming from the stretching frequencies.

TABLE 4. FORCE CONSTANTS (10^5 dyne/cm)

	From electronic wave function	From stretching frequencies
Acetone	10·29	10·3
Formaldehyde	10·58	10·8
Orthobenzoquinone	10·15	10·0
Parabenzoquinone	10·11	9·8

TABLE 5. EFFECT PRODUCING THE SHIFT OF $\nu_{C=O}$

	$\nu_{C=O}$(in cm^{-1})	
Saturated ketones	1706–1725	
Unsaturated ketones	1650–1750	mesomeric effect
Chlorinated ketones	1725–1765	inductive effect
Cyclobutanone	1775	coupling between vibrators
Saturated aldehydes	1720–1740	coupling between vibrators + inductive effect
Quinones	1660–1690	coupling between vibrators + mesomeric effect + inductive effect

The quantitative agreement obtained gives confidence in the final conclusions of the authors which are given in Table 5 and lists the effects on the $\nu_{C=O}$ stretching frequency due to various kind of environment.

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[11] S. Bratoz and S. Besnainou, *J. Chem. Phys.* 34, 1142 (1961). S. Besnainou, Thesis, Paris (1960).