ATTI ACCADEMIA NAZIONALE DEI LINCEI

CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

RENDICONTI

VICTOR GUTMANN

Structural variability: a Donor-Acceptor approach

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **68** (1980), n.2, p. 117–122.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1980_8_68_2_117_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1980.

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Structural variability: a Donor-Acceptor approach.*

Nota di VIKTOR GUTMANN (*), presentata (**) dal Socio G. SARTORI.

RIASSUNTO. — Variazioni strutturali dovute ad interazioni intermolecolari possono venir descritte dalle cosidette regole di variazione della lunghezza di legame. Parametri empirici del solvente cioè il numero di donatore e di accettore servono per caratterizzare le interazioni soluto-solvente. Sono state trovate numerose relazioni tra i parametri empirici del solvente da una parte, e dall'altra i parametri termodinamici strutturali e cinetici.

1. GENERAL CONSIDERATIONS

The Donor-Acceptor Concept was originally suggested by G. N. Lewis as a solvent-independent acid-base concept [1, 2]. Its electronic description is widely applied in the fields of organic and coordination chemistry. However, the structural consequences have not been recognized fully, since the changes in the relative positions of the nuclei as connected with changes in electron densities have not been given proper attention.

As a result of systematic investigations in non-aqueous solutions an extension of the donor-acceptor concept has been developed, which is applicable to molecular interactions ranging from solid state physics to biochemistry [3]. The extension is based on well-known facts and in agreement with quantum-chemical results. It stresses the molecular structural changes due to changes in molecular environment rather than the structure of a molecule as such (under ideal gas-like conditions) and establishes relations between structural changes on the one side and changes in thermodynamic and kinetic parameters on the other.

Any molecular interaction leads to a rearrangement of the charge density pattern. One of the interacting molecules may be considered as a donor of electrons and the other one as an acceptor of electrons. In the course of a typical donor-acceptor interaction

$$\underset{\text{donor}}{C - D} \longrightarrow \underset{\text{acceptor}}{A - B}$$

the charge density rearrangement is considered as due to contributions of charge transfer from the donor to the acceptor unit and of polarization effects, which cannot be separated unambiguously [3, 4].

The extent of charge transfer from an ammonia molecule to a fluorine molecule has been calculated as 0.0483 electron [5]. The $F_{(1)}$-acceptor atom

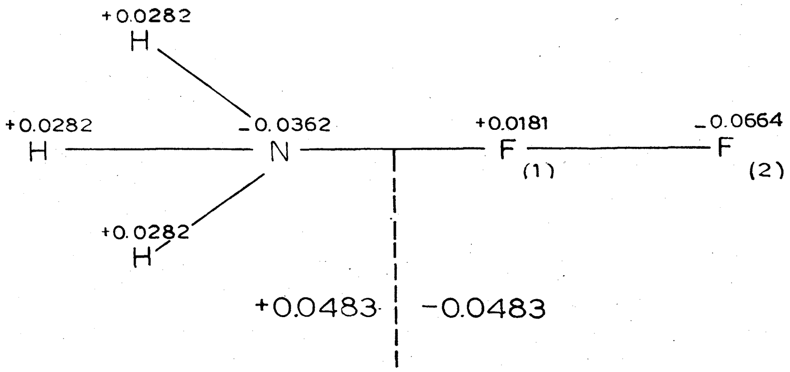
---

(*) Institute of Inorganic Chemistry, The Technical University of Vienna–Austria.

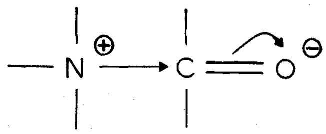
(**) Nella seduta del 9 febbraio 1980.

acquires a small increase in positive net-charge, as all of the electron charge transferred to the acceptor unit is passed on to other areas of the acceptor unit including part of the electron density originally situated at the $F_{(1)}$-acceptor atom, i.e. in this case to the $F_{(2)}$-atom. This has been described as the *spillover effect of negative charge from the acceptor atom* [3, 4].

The original loss of negative charge at the N-donor atom of the ammonia molecule is overcompensated by the induced attraction of negative charge from the hydrogen atoms. The increase in negative net-charge at the donor atom has been termed *pile-up effect* [3, 4]. By both of the said effects the polarities of the bonds adjacent to the sites of the intermolecular interaction are lengthened, i.e. all of the N-H-bonds and F-F-bond in the considered interaction [4].

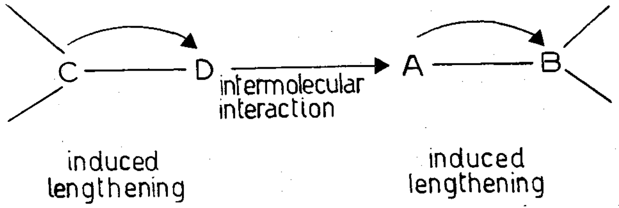


Thus the increase in positive charge, usually assigned to the donor atom, e.g.



in therefore not in agreement with the facts.

The *first bond length variation rule* of the extended donor-acceptor approach expresses the observed inverse relationship between intermolecular and intramolecular bond lengths adjacent to the sites of interaction [3, 4].

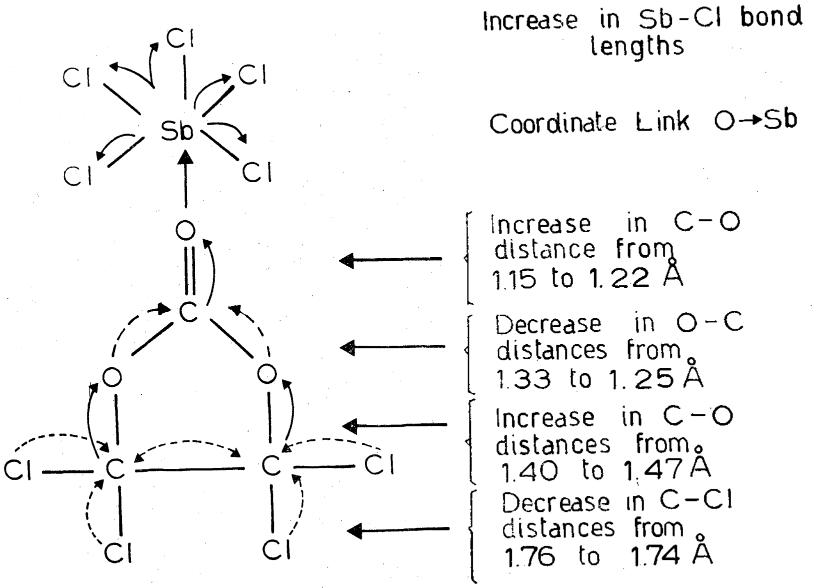


The increase in bond length is represented by a fully bent arrow connecting the bonded nuclei and pointing in the direction of the electron shift induced by the intermolecular interaction. Examples have been given elsewhere [3, 6].

Subsequent changes in bond lengths are induced throughout the molecules and expressed by the *second bond length variation rule* of the extended donor-acceptor concept: A bond is lengthened when negative charge is shifted from the more electropositive to the more electronegative atom and it is shortened when it is shifted from the more electronegative to the more electropositive atom. A decrease in bond length is denoted by a dashed arrow pointing in the direction of the electron shift.

Such cooperative effects are not confined to adduct formation and indeed, they result from any molecular rearrangement because a new structure pattern is developed for the whole system under consideration.

The structural variability of a given molecule in different molecular environments, for example in different solvents, is reflected in its *chemical variability*: Bond lengthening leads to decrease in energy required for heterolysis. Increase in negative net charge means increase in donor property (nucleophilic and/or reducing property), whereas increase in positive fractional charge means increase in acceptor property (electrophilic and/or oxidizing property).



2. EMPIRICAL SOLVENT PARAMETERS

According to the extended donor-acceptor approach two parameters are required for the characterization of a donor-acceptor interaction, namely one for the donor property and one for the acceptor property. The empirical parameters which have been found extremely useful are the donor number and the acceptor number.

TABLE I.

Donor and Acceptor Numbers for Selected Solvents.

SOLVENT	DN	AN	SOLVENT	DN	AN
Acetic Acid	—	52.9	Dimethylsulfoxide	29.8	19.3
Acetone	17.0	12.5	Dioxane	14.8	10.8
Acetonitrile	14.1	19.3	Ethanol	19.0	37.1
Acetylchloride	0.7	—	Ethylene Sulfite	15.3	—
Benzene	—	8.2	Hexamethylphosphoricamide	38.8	10.6
Benzonitrile	11.9	15.5	Methanol	20.0	41.3
Benzoylchloride	2.3	—	Nitrobenzene	4.4	14.8
Carbontetrachloride	—	8.6	Nitromethane	2.7	20.5
Chloroform	—	23.1	Propanol	18.0	33.5
Diethylether	19.2	3.9	Propylencarbonate	15.1	18.3
Dichloroethylenecarbonate	3.2	16.7	Pyridin	33.1	14.2
Diglyme	24.0	10.2	Tetrahydrofuran	20.0	8.0
Dimethylacetamide	27.3	13.6	Tributylphosphate	23.7	—
Dimethylformamide	24.0	16.0	Water	30	54.8

For a solvent-independent representation of the donor ability of a molecule the "*donor number*" or "*donicity*" (DN) is used [7]. It is defined as the molar enthalpy value for the reaction of the donor (D) with $SbCl_5$ as a reference acceptor in a 10^{-3}M solution of dichloroethane.

$$D + SbCl_5 \rightleftharpoons D \cdot SbCl_5 \quad : \quad DN \equiv -\Delta H_{D \cdot SbCl_5}$$

Since most aprotic solvents have similar acceptor properties, differences in donor numbers are found correlated with the following properties (*i*) change in ΔG for the respective interactions D → $SbCl_5$, (*ii*) ΔH for the interactions with hard and border line acceptors, (*iii*) the electron binding energies of Sb in quickly frozen solutions of $D.SbCl_5$ [8], (*iv*) the ^{29}Si NMR chemical shifts of silanols in the respective solvents [9], (*v*) the increase in O-H-bonding on aerosile [10] (*vi*) the ^{23}Na NMR chemical shift in $NaClO_4$ solutions in various solvents [11], (*vii*) the free enthalpies of various cations [12], such as K^{+}

(*viii*) the extent of ionization of a covalent substrate in the solvents [13], (*ix*) the polarographic half wave potential for a given cation [14], (*x*) the rate coefficient for the substitution of a coordinated solvent molecule [3, 15] (*xi*) the rate coefficient for the substitution of a non-solvent ligand molecule [3].

The second of the two important solvent parameters characterizes the acceptor or electrophilic property of a solvent. The *acceptor number* (*AN*) is deduced from ^{31}P NMR studies of triethylphosphine oxide in the respective solvent [16].

In order to emphasize the relationship between acceptor properties and their conjugate donor properties, the same substance, namely $SbCl_5$ has been used as a standard for both parameters, the $Et_3PO.SbCl_5$ adduct being assigned the acceptor number of 100. The acceptor number expresses the acceptor property of a given solvent relative to those of the reference acceptor.

The acceptor numbers are related [3] to (*i*) Grunwald's Y-values [17], (*ii*) Kosowers Z-values [18], (*iii*) Dimroth-Reichhardt's E_T-values [19], (*iv*) the free enthalpies of solvation of the chloride ion in different solvents [3, 20], (*v*) the half wave potentials for the polarographic reduction of hexacyanoferrate (III) [21], (*vi*) the ^{13}C NMR chemical shift in acetone dissolved in the respective solvents and hence to the C—O bond lengthening [16], (*vii*) the changes of C—O bond length in metal carbonyls dissolved in the solvents [22] (*viii*) the rate coefficients of S_N1 reactions, which are increased by increase in AN and (*ix*) the rate coefficients of S_N2 reactions, which are decreased by increase in AN [15]. The last two points are of great importance in choosing the proper solvent for substitution reactions in organic chemistry.

LITERATURE

[1] G. N. Lewis (1923) – *Valence and Structures of Atoms and Molecules*, «The Chemical Catolog Co.», New York.

[2] W. F. Luder and S. Zuffanti (1946) - *The Electronic Theory of Acids and Bases*, Wiley, New York.

[3] V. Gutmann (1978) – *The Donor-Acceptor Approach to Molecular Interactions*, « Plenum Press », New York – London.

[4] V. Gutmann (1977) – « Rev. Chim. Roum. », *22*; 679.

[5] L. A. Carreira and W. B. Person (1972) – « J. Am. Chem. Soc. », *94*, 1485.

[6] V. Gutmann (1979) – « Pure Appl. Chem. », *51*, 2197.

[7] V. Gutmann (1968) – *Coordination Chemistry in Non-Aqueous Solutions*, Springer Verlag, Wien–New York.

[8] K. Burger, E. Fluck, (1974) – « Inorg. Nucl. Chem. Letters », *10*, 171.

[9] E. A. Williams, J. Cargioli and R. W. Larochelle (1976) – « J. Organomet. Chem. », *108*, 153.

[10] W. Horill and H. Noller (1976) – « Z. physik. Chem. (Frankfurt) », *100*, 155.

[11] R. H. ERLICH and A. I. POPOV (1971) – « J. Am. Chem. Soc. », *93*, 5620.
[12] U. MAYER (1977) – «Mh. Chem.», *108*, 1479.
[13] V. GUTMANN and U. MAYER (1969) – «Mh. Chem.», *100*, 2048.
[14] V. GUTMANN and R. SCHMID (1969) – «Mh. Chem.», *100*, 2113.
[15] A. J. PARKER, U. MAYER, R. SCHMID and V. GUTMANN (1978) – « J. Org. Chem. », *43*, 1843.
[16] U. MAYER, V. GUTMANN and W. GERGER (1975) – «Mh. Chem.», *107*, 1275.
[17] E. GRUNWALD and S. WINSTEIN (1948) – « J. Am. Chem. Soc. », *70*, 846.
[18] E. M. KOSOWER (1958) – « J. Am. Chem. Soc. », *78*, 5700 (1956); *80*, 3253 (1958).
[19] K. DIMROTH, C. REICHHARDT, T. SIEPMANN and F. BOHLMANN (1963) – « Ann. », *661*, 1.
[20] E. ALEXANDER, A. J. PARKER, J. H. SHARP and W. E. WAGHORNE (1972) – « J. Am. Chem. Soc. », *94*, 1148.
[21] V. GUTMANN, G. GRITZNER and K. DANKSAGMÜLLER (1976) – « Inorg. Chim. Acta », *17*, 81.
[22] V. GUTMANN (1977) – «Mh. Chem.», *108*, 429.