Russian Chemical Reviews **62** (7) 625 – 636 1993
© 1993 Russian Academy of Sciences and Turpion Ltd

UDC 541.67 + 541.124

Influence of the polarity of the medium on the electronic structure and energetics of molecules in solutions

I P Gol'dshtein, E S Petrov

Contents

I.	Introduction	625
II.	Theoretical approaches to the problem	625
III.	Changes in the electronic structure, energetics, and physicochemical properties of molecules under the influence of a polar medium	627
IV.	Molecular and ionic forms of H complexes in media with different dielectric permittivities	631
V.	Electronic structure of salts in media with different polarities	633
VI.	Conclusions	635

Abstract. Recent data on the effect of the polarity of the medium on the state of solute molecules having different types of chemical bond are reviewed. The changes in electronic structure and in the energetics of the molecules are discussed, and their influence on the physicochemical properties and role of the molecules in various liquid-phase processes (tautomeric and con-formational transformations, nucleophilic substitution, proton transfer) is examined. Special attention is paid to the new concept of preferential stabilisation of molecular and of ionic forms of salts and of complexes with intermolecular hydrogen bonds in media of different polarity. The bibliography includes 98 references.

I. Introduction

The influence of the medium on the state and properties of substances in solution (a problem first formulated towards the end of the last century) continues to stimulate the interest of research workers, because the properties of the solvent play a substantial (and often a dominant) role in the thermodynamics and kinetics of many important liquid-phase processes. Various aspects of the effects of solvation on the energetics and dynamics of these processes, the role of structural changes in the solvent, and the influence of the solvent on the reaction kinetics and on the physicochemical characteristics of dissolved substances have been discussed in several reviews and monographs.[1-13] However, like many of the original papers, the review literature fails (in our view) to give due weight to the influence of solvation on the electronic and the geometrical structure of the solute molecules. Thus, recent studies have shown that the transfer of molecules from the gas phase to a strongly solvating medium can result in marked structural changes, due to electron donor–acceptor (EDA) interactions between the solvent and the solute molecules (specific solvation) or to the polarising effect of the medium (nonspecific solvation).

Both experimental and calculated results suggest that the role of nonspecific solvation in the structural change of dissolved molecules can be as important as the role of specific solvation. Thus, in a very polar solvent a substantial charge separation can take place in easily polarisable molecules, leading to a transition to the ionic state. Furthermore the interaction with the polar medium also affects the electronic structure of the molecular complexes produced by the EDA interaction. As has been reported,[14-21] an increase in the dielectric permittivity (ε) of the medium increases the intermolecular charge transfer in these complexes, which can lead to the creation of ionic forms in specifically solvating media with a high value of ε. Large changes in the relative acidity and basicity of compounds, in the rates of (electron or proton) charge transfer reactions, and shifts in the tautomeric and other equilibria are also possible.

The aim of the present review was to highlight the general features of changes in the electronic and the geometrical structure of molecules under the influence of a polar medium and to show how these changes are reflected in the physicochemical properties of the molecules (such as dipole moments, spectral characteristics, etc.), in their solvation energy, and in their ionisation in solutions, and also in processes which are controlled by these properties.

II. Theoretical approaches to the problem

The rapid developments in theoretical methods of studying solvation effects during the last two decades[1-4] created a much wider understanding of the nature of changes stimulated in various systems by the presence of a solvent. However, even the most recent theoretical studies[1, 2] have not allowed adequately for the polarising effect of the medium on the electronic structure of molecules and of molecular complexes in solution. Three basically different approaches can be identified among the computational methods used in studies of solvation processes: statistical calculations by the Monte Carlo method (MC) and by molecular dynamics (MD), quantum-chemical calculations on the molecule to be solvated and on its nearest-neighbour solvent molecules (treated as a single super-molecule), and lastly calculations in the continuum approximation, in which the solute molecule is treated as surrounded by a continuous medium with a known value of ε. The polarising effect of the medium is usually ignored in the MC and MD methods, which treat the solvated molecule as a geometrically rigid species with an invariant electronic structure, whereas in the super-molecule approach no allowance is made for the influence of the whole volume of the polar solvent on intermolecular charge transfer.

Simkin and Sheikhet have described the theoretical methods of calculating the solvation effects, and have compared their

I P Gol'dshtein, E S Petrov Complex Catalysis Laboratory, Ya Karpov Physicochemical Research Institute, ul. Obukha 10, 103064 Moscow. Fax (7-095) 975 24 50

Received 18 January 1993
Uspekhi Khimii **62** (7) 667 – 679 (1993); translated by J I Carasso

prospects when applied to various aspects of the problem, in a recently published monograph[2] as well as in earlier reviews.[3, 4] As they clearly state,[4] no one method can be classified as 'good' or 'bad': the most important consideration is that the method should be adequately matched to the problem of interest.

Since the structure of the solvent and the mobility of its molecules in the solvation shell can be analysed only by the MC and MD methods, whereas the supermolecular approach is better suited to studies of specific solvation, in the absence of specific solvation it is more rational to use quantum-chemical calculations (which allow for the effect of the medium in the continuum approximation) in studies of the effect of the polarity of the medium on the electronic structure of solute molecules.

The distribution of electron density and the energy of a molecule immersed in a dielectric continuum are calculated by the Schrödinger equation in one of its approximations, defining the Hamiltonian of the molecule immersed in the medium as

$$\hat{H} = \hat{H}_0 + \hat{U}; \tag{1}$$

$\hat{H}_0$ is the Hamiltonian of the molecule in a vacuum and $\hat{U}$ is an operator describing the interaction of the molecule with the medium.

Eqn (1) provides the foundations of a wide range of methods of calculation, described in the review literature[2-4, 22-24] as well as in the original papers.[25-46] Therefore we shall only dwell on the most significant differences between the methods adopted in these approaches to construct the operator $\hat{U}$, since our further discussion requires the differences to be explicitly stated. The operator $\hat{U}$ is usually expressed in terms of the classical Born, Onsager, and Kirkwood theories of the electrostatic interaction between charged or polar particles and the medium. The Born equation (2) (E_B) and the Onsager equation (3) (E_{Ons}) are the most frequently used:

$$E_B = \frac{\varepsilon - 1}{2\varepsilon} \frac{q_i q_j}{r_{ij}}, \tag{2}$$

where q_i, q_j, and r_{ij} are (respectively) the charges on the interacting particles and the distance between them, and

$$E_{Ons} = \frac{\varepsilon - 1}{2\varepsilon + 1} \frac{\mu^2}{a^3}, \tag{3}$$

where μ is the dipole moment of the solute molecule, and a is the radius of the cavity which this molecule produces in the solvent.

Eqn (2), derived by Born in order to calculate the interaction energy of ions in a solution, found an interesting application in Klopman's solvaton model,[25] which provided a new impetus for the development of quantum-chemical methods of calculation allowing for the effect of the medium. In this model each atom A of a molecule immersed in the medium is conjugated with a solvaton C, at a distance r_{AC} and having a charge q_C equal to the charge of the atom A (Z_A) but of opposite sign. It is assumed that the solvatons do not mutually interact, and that the energy of the interaction between the atom and the solvaton is described by Eqn (2) in the form

$$E = \frac{\varepsilon - 1}{2\varepsilon} \frac{q_C Z_A}{r_{AC}}. \tag{4}$$

In this case the operator $\hat{U}$ becomes

$$\hat{U} = \frac{\varepsilon - 1}{2\varepsilon} \left[\sum_{C=1}^{N} \sum_{i=1}^{M} \frac{q_C}{r_{Ci}} - \sum_{C=1}^{N} \sum_{A=1}^{M} \frac{q_C Z_A}{r_{AC}} \right], \tag{5}$$

where N and M are the numbers of atoms and of electrons in the molecule respectively. Various modifications of the solvaton model[26-29] converge towards the ideas underlying the models of molecular perturbation by point dipoles[36] and of 'virtual charges'.[37-39]

An essentially different approach to the construction of the operator $\hat{U}$ was used by Tapia and coworkers,[38-42] who developed the self-consistent reactive field (SCRF) theory by analogy with Onsager's reactive field model. This approach allows not only for the effect of the polar medium on the molecule immersed in it (resulting in a redistribution of the charges in the molecule and therefore also in a change in the dipole moment), but also for the polarising interaction of this dipole with the surrounding medium, which produces the so-called 'reactive' Onsager field (R) in the medium. The quantum-chemical analogue of the classical electrostatic interaction energy ($E = -\mu R$) in the SCRF model is the operator $\hat{U}$, in the form

$$\hat{U} = -\hat{\mu} g \langle \Psi | \hat{\mu} | \Psi \rangle, \tag{6}$$

where $\hat{\mu}$ is the operator of the dipole moment vector, Ψ is the wave function of the molecule in a medium with a dielectric constant ε, and g is a tensor which defines the susceptibility of the reaction field, expressed [by analogy with Eqn (3)] as

$$g = \frac{\varepsilon - 1}{2\varepsilon + 1} \frac{2}{a^3}. \tag{7}$$

It is assumed that the molecule occupies a spherical cavity of radius a, within which ε is equal to 1.

The assumption of a spherical cavity seriously restricts the application of the SCRF model when the molecules of interest are asymmetric. In this case an improved Onsager model is used, in which the cavity produced by the molecule in the surrounding dielectric continuum has the same shape as the molecule.[30, 43-46] The molecule in its cavity is treated as a system of charges, defined by the distribution of electron density $\rho(x)$, which induce in the boundary surface S of the cavity the charges $\sigma(S)$ responsible for the reactive field.[44-46] Under these conditions the perturbation operator takes the form

$$\hat{U} = \sum_i q_i \int \frac{\sigma(S)}{r_i - S} \mathrm{d}S, \tag{8}$$

where q_i and r_i are the charge and the position of the ith particle respectively. The density of the surface charges $\sigma(S)$ is determined by the polarisation of the inner (P_+) and of the outer (P_-) boundary surface of the cavity:

$$\sigma(S) = P_+ \boldsymbol{n} + P_- \boldsymbol{n}, \tag{9}$$

where $\boldsymbol{n}$ is a unit vector perpendicular to the boundary surface at the point S. The polarisation vector is related to the ε value for the medium by the Maxwell relation

$$P = \frac{1}{4\pi}(\varepsilon - 1)E. \tag{10}$$

The electric field E is determined by the electrostatic potential Φ generated by the distributions $\rho(x)$ and $\sigma(S)$:

$$\Phi(r) = \int \frac{\rho(x)}{r - x} \mathrm{d}x + \int \frac{\sigma(S)}{r - S} \mathrm{d}S. \tag{11}$$

Thus in the SCRF model proposed by Miertuš[30] and subsequently developed by Hochi[44-46] and by Bazilevskii[47] the reactive field is created by the charges induced by the molecule in the surrounding dielectric, and the interaction of the molecule with the dielectric is described by its interaction with these charges. This approach brings the SCRF model close to the solvaton or virtual charges model described above.

Eqns (1)-(11) show that the Hamiltonian (1), in which the perturbation operator allows for the electrostatic interaction with the medium, can be used to solve the Schrödinger equation for an arbitrary value of ε. This allows the quantum-chemical calculations to be used to determine the electronic structure and the geometry of the molecules, and their physicochemical parameters, as a function of the ε value for the medium. As in the case of isolated molecules, these calculations have been carried out in both nonempirical[30-35] and semiempirical variants.[27-29, 45-49] In spite of the great sensitivity of the calculated results to the method used in the approximate solution of the Schrödinger equation and to the model chosen for the effect of the medium this approach usually gives a correct description of the general trends seen in the changes in electronic structure and in the properties and the

Table 1. Quantum-chemical calculations of the changes in total energy (ΔE) and in free energy (ΔF/kJ mol^{-1}) and dipole moments (μ/D) of the molecules resulting from the transfer from a vacuum ($\varepsilon = 1$, μ_1) to a medium with $\varepsilon = 80$ (μ_{80}).[45]

Compound	Calculated parameter	SCRF method			Virtual charges method	
		CNDO/2	INDO	STO-3G	4-31G	CNDO/2
H_2O	$-\Delta E$	34.0	39.4	–	42.8	366.0
	$-\Delta F$	16.5	19.4	–	21.4	105.2
	μ_1	2.1	2.14	–	2.69	2.10
	μ_{80}	2.19	2.24	–	2.86	3.07
H_2CO	$-\Delta E$	30.3	28.6	51.5	36.4	565.5
	$-\Delta F$	14.2	8.8	22.4	21.2	123.2
	μ_1	1.95	2.15	1.52	3.06	1.95
	μ_{80}	2.24	2.46	2.09	3.48	4.95
H_2NCHO	$-\Delta E$	72.2	74.6	–	70.7	911.0
	$-\Delta F$	33.3	29.3	–	33.0	257.7
	μ_1	3.68	3.90	–	–	3.68
	μ_{80}	4.30	4.57	–	–	7.26
$H_3N^+CH_2COO^-$	$-\Delta E$	540.1	535.9	–	–	2745.8
	$-\Delta F$	254.3	244.0	245.5	233.4	939.1
	μ_1	13.16	12.82	11.97	13.13	13.16
	μ_{80}	14.68	14.58	13.72	15.48	17.94

energetics of the molecules under the influence of a polar medium, and (as will be shown below) they are acceptably consistent with experimental data. The good agreement between calculations by different methods is shown in Table 1, where changes in the total energy (ΔE) and in the Helmholtz free energy (ΔF) of various molecules when transferred from a vacuum or from a gas phase to a medium with $\varepsilon = 80$ are compared.

The difference between the total energies of a molecule calculated for a medium with a given value of ε (E) and for a vacuum (E_0) can be used as a measure of the stabilisation energy experienced by the molecule in the polar medium as a result of electrostatic interactions.

III. Changes in the electronic structure, energetics, and physicochemical properties of molecules under the influence of a polar medium

Quantum-chemical calculations followed by an analysis of the Mulliken populations of the orbitals show that when a molecule is transferred from the gas phase ($\varepsilon = 1$) to a solution ($\varepsilon > 1$) the charges on almost all its atoms change by an amount which is greater, the greater the ε value of the medium. The most substantial changes are seen in easily polarisable bonds. Thus, in the case of the C=O bond in some carbonyl compounds (Table 2) it was established that a change in ε from 1 to 80 markedly

Table 2. Charges on the atoms (q), bond populations (P), and dipole moments (μ/D) of molecules in media with different ε.

1. $H-\underset{\underset{O}{\|}}{C}-NH_2$ (INDO–solvatons[48])

Parameter	$\varepsilon=1$	$\varepsilon=4$	$\varepsilon=20$	$\varepsilon=80$
q(O)	−0.408	−0.425	−0.441	−0.446
q(C)	+0.504	+0.521	+0.536	+0.550
q(N)	−0.260	−0.270	−0.280	−0.283
μ	3.90	4.02	4.12	4.15

2. $H^1-\underset{\underset{O}{\|}}{C^1}-N\begin{matrix}C^2H_3\\C^3H_3\end{matrix}$ (CNDO/2–solvatons[28])

Parameter	$\varepsilon=1$	$\varepsilon=2$	$\varepsilon=5$	$\varepsilon=40$
q(O)	−0.282	−0.316	−0.344	−0.355
q(C^1)	+0.231	+0.297	+0.306	+0.324
q(N)	−0.323	−0.264	−0.129	+0.114
q(C^2)	−0.323	−0.531	−0.894	−1.443
q(C^3)	−0.317	−0.525	−0.887	−1.429
q(H^1)	+0.069	+0.022	−0.008	−0.009
P(O–C^1)	1.197	1.197	1.193	1.185
$P$$C^1$–N)	0.900	0.914	0.940	0.976
P(C^2–N)	0.745	0.742	0.736	0.729
P(C^3–N)	0.745	0.743	0.739	0.732
P(C^1–H^1)	0.670	0.668	0.655	0.648
μ	2.69	2.89	3.30	3.89

3. $H_3C^4-C^3H=C^2H-\underset{\underset{H}{|}}{C^1}=O$ (INDO–SCRF[46])

Parameter	$\varepsilon=1$	$\varepsilon=2$	$\varepsilon=80$
q(O)	−0.2950	−0.3226	−0.3606
q(C^1)	+0.3159	+0.3324	+0.3557
q(C^2)	−0.0921	−0.0963	−0.1021
q(C^3)	+0.0509	+0.0603	+0.0753
q(C^4)	+0.0040	+0.0041	+0.0050

4. $O=N^1-N^2\begin{matrix}C^1H_3\\C^2H_3\end{matrix}$ (CNDO/2–solvatons[28])

Parameter	$\varepsilon=1$	$\varepsilon=2$	$\varepsilon=5$	$\varepsilon=40$
q (O)	−0.139	−0.150	−0.161	−0.169
q (N^1)	−0.026	−0.039	−0.095	−0.190
q (N^2)	−0.139	−0.126	+0.178	+0.465
q (C^1)	−0.360	−0.638	−1.110	−1.731
q (C^2)	−0.369	−0.646	−1.115	−1.728
P (O–N^1)	1.016	1.013	1.005	0.992
P (N^1–N^2)	0.860	0.871	0.889	0.908
P (N^2–C^1)	0.735	0.735	0.727	0.711
P (N^2–C^2)	0.751	0.750	0.744	0.730
μ	2.97	3.08	3.48	4.06

Table 3. Effect of ε for the medium on the electronic characteristics and the geometrical parameters of benzophenone (CNDO/S–VC method).[50]

ε	$-q_O$	μ/D	$r_{C=O}$/Å	r_{C-C}/Å[a]
1	0.438	4.68	1.214	1.504
2	0.550	5.68	1.223	1.494
3	0.642	6.46	1.233	1.491
4	0.717	7.06	1.242	1.485
35	1.015	–	1.300	1.460

[a] The distances between the carbon atom of the CO group and the neighbouring C atoms of the benzene rings are quoted.

increases the electron density on the O atoms and lowers it on the C atoms. In particular, polarisation of the C=O bond in dimethylformamide lowers its population, whereas the population of the neighbouring C–N bond increases: the lengths of these bonds are altered,[50, 51] and the dipole moment of the molecule shows a large increase. In *N*-nitrosodimethylamine changes in electron density on the O, N^1, and N^2 atoms lower the population of the $N^1=O$ bond and increase that of the N^1-N^2 bond in proportion to the ε value of the medium. Similar results were obtained for benzophenone, showing that an increase in ε stretches the C=O bond and shortens the C–C bond between the carbon atoms of the carbonyl group and the benzene rings (Table 3). Thus the polarisation of the surrounding medium affects the geometry of the molecule by causing a redistribution of charge in the molecule.

The changes in the charges of the individual atoms of the molecule caused by an increase in ε are also reflected by the screening parameters (σ) of the nuclei, which are correlated with the chemical shifts (δ) in the NMR spectra. For example, the decrease in electron density (Δ*q*) on the C^1, C^3, and C^4 carbon atoms of crotonaldehyde (see Table 2) caused by increasing ε for the medium from 1 to 80 results in a deshielding (Δσ) of the nuclei of these atoms, which is consistent with the shift of the corresponding ^{13}C NMR signals (Δδ) towards weak fields on going from pentane (ε = 1.8) to DMSO (ε = 49.6), whereas an increase in the negative charge on the C^2 atom corresponds to a shift of the ^{13}C NMR signal towards strong fields.[46]

An extensive experimental and theoretical study[52–54] of the effect of the polarity of the medium on the screening parameters and on the ^{14}N NMR chemical shifts in nitrogen compounds with chemical bonds of different types involving the N atom has been reported. It was shown, in particular, that the change from a nonpolar medium (ε < 2) to a polar medium increases the screening of the nitrogen nuclei in nitriles, whereas the opposite effect (deshielding) is found in compounds where the N atom is attached to an O atom or to a C=S group, in complete agreement with the changes in electron density on the nitrogen atoms in these compounds. Both effects increase with the ε value of the medium (Table 4).

The results of quantum-chemical calculations are satisfactorily consistent with experimental data on the ^{14}N NMR chemical shifts, which are described by the relation[52–54]

$$\delta = \delta_0 + S(\pi^* + d\delta) + a\alpha + b\beta , \quad (12)$$

where δ and δ_0 are the ^{14}N NMR chemical shifts (relative to nitromethane) of the experimental compound in this solvent and in the standard (ε ~ 2) respectively; *S*, *a*, and *b* are parameters which characterise the polarisability, the proton-donor, and the electron-donor strength of the compound, π*, α, and β are parameters which characterise the polarising strength and the proton-donor and electron-donor strength of the medium respectively,[55] dδ is a correction for polychlorinated (δ = 0.5) and for aromatic solvents (δ = 1). Comparing the *S* values for the compounds shown in Table 4 shows that both theory and experiment suggest a large increase in the screening of the N nuclei as a result of the polarisation of the C=N bond in nitriles (compounds 1–4), whereas in *tert*-butyl nitrite (compound 5) the most marked effect is the deshielding of the nitrogen nuclei caused by the polarisation of the N=O bonds.

Good agreement between calculations by the CNDO/2–solvaton method and experiment (^{29}Si NMR) has been reported[56] for the chlorosilane series. The changes in the deshielding parameter (σ) and the shift of the ^{29}Si NMR signals towards weaker fields relative to TMS are described by the equation

$$\delta(-\sigma) = A\frac{\varepsilon - 1}{2\varepsilon} + B . \quad (13)$$

The agreement between calculated and experimental values of *A* in Eqn (13) is acceptably good.[56]

The observed deshielding of the nuclei as ε for the medium is increased can be attributed to the polarisation of the Si–Cl bonds, the effect decreasing in the following sequence: Me_3SiCl (μ = 2.09) > Me_2SiCl_2 (μ = 1.89) > $MeSiCl_3$ (μ = 1.87) > $SiCl_4$ (μ = 0); Me_2HSiCl (μ = 1.8) > $MeHSiCl_2$ (μ = 1.7) > $HSiCl_3$ (μ = 1.0) > $SiCl_4$ (μ = 0). Obviously, these effects are related to the decreases in the same sequence of the μ values for these compounds and to the consequent strengthening of the electrostatic interaction of the molecules with the polar medium.

The results of the quantum-chemical calculations show that the polarising effect of the medium and the associated redistribution of the charges in the molecule usually result in an increase in the dipole moments and therefore also in the ε values of the medium (Tables 1 and 2). Experimental data on the μ values of molecules in a series of solvents with different ε values point to the same conclusion. For example, in a molecule such as triphenylchloromethane (Ph_3CCl), which contains the covalent (in a nonpolar medium) but easily polarisable C–Cl bond the μ value increases from 1.9 to 12.2 D when ε for the solvent is increased from 2 to 65 (Table 5).

The change in electronic structure produced by the polarising effect of the solvent strongly influences the energy characteristics of the molecules. An analysis of the data in Tables 1, 2, 6, and 7 identifies the three most important types of change in the

Table 4. Changes in the screening parameters (Δσ) of the N nuclei produced by increasing the ε value of the medium from 2 to ε_i (INDO/S–solvatons method).[52–54]

Compound	Δσ					*S*
	$\varepsilon_i = 4$	$\varepsilon_i = 10$	$\varepsilon_i = 20$	$\varepsilon_i = 40$	$\varepsilon_i = 80$	
1. MeCN	1.68	2.46	2.57	2.63	–	8.81
2. EtCN	1.76	2.69	2.83	2.85	–	8.75
3. Pr^iCN	1.79	2.77	3.05	3.49	–	8.59
4. Bu^tCN	2.06	3.14	3.49	3.53	–	8.72
5. $Bu^tO-N=O$	−12.30	−15.89	−16.88	−17.34	−17.53	−9.88
6. $MeO-NO_2$	−3.18	−5.02	−5.65	−5.87	−6.14	−3.75
7. $MeN=C=S$	−2.2	−3.2	−3.3	−3.4	−3.7	−7.36
8. $Bu^tN=NBu^t$	−0.31	−0.49	−0.55	−0.58	−0.60	0

Table 5. Results of a dielectrometric and calorimetric study of triphenylchloromethane in solvents of different solvating power.[57]

Solvent	Solvent			Ph_3CCl			
	ε	DN	δ^2	μ	$-\Delta H_s$	ΔE_{cav}	$-\Delta E_{int}$
1. Tetrachloromethane	2.23	0	308.8	1.9	98.6	68.3	166.9
2. Chlorobenzene	5.62	1.2	370.4	2.54	98.0	82.0	180.0
3. Dichloromethane	8.93	1.6	403.2	3.79	93.0	89.2	182.2
4. 1,2-Dichloroethane	10.38	0.1	409.7	4.22	97.0	90.7	187.7
5. Isobutyl methyl ketone	14.6	–	306.7	5.27	105.7	67.9	173.6
6. Acetone	20.7	17.0	389.8	6.52	100.3	86.3	186.6
7. Hexamethylphosphorotriamide	29.6	38.8	334.1	8.42	124.7	73.9	198.6
8. Nitrobenzene	34.89	4.4	512.4	8.84	106.4	113.4	219.8
9. Acetonitrile	36.7	14.1	603.2	8.85	97.8	133.5	231.3
10. Nitromethane	36.7	2.7	664.6	9.0	88.7	147.1	235.8
11. Propene carbonate	65.1	15.1	555.5	12.2	104.5	122.9	227.4

Notes. DN is the Gutmann donor number of the solvent;[58] δ^2 is the cohesion energy density of the solvent;[59] μ/D is the dipole moment of Ph_3CCl; ΔH_s/kJ mol^{-1} is the solvation enthalpy of Ph_3CCl; ΔE_{cav}/kJ mol^{-1} is the energy of formation of a cavity; ΔE_{int}/kJ mol^{-1} is the energy of interaction of Ph_3CCl with the solvent.

energetics of molecules induced by an increase in the polarity of the medium:

1. A decrease in the energy of the molecule (E), and therefore in its stabilisation energy (E_{st}), resulting from the transfer of the molecule from the gas to the solution.

2. A change in the energy of the highest occupied (n, π) and the lowest unoccupied (π^*) MO, and therefore in the energies of the singlet $n-\pi^*$ and $\pi-\pi^*$ transitions.

3. An increase in the barriers to internal rotation round the bonds (C–N in amides, N^1-N^2 in nitrosamines), whose population increases.

These changes have a marked effect on the physicochemical characteristics of molecules and of processes involving those molecules in solutions.

The stabilisation energy of molecules in polar media (Table 1) is higher for molecules with a high intrinsic dipole moment. The parameter μ increases with the ε value of the medium, with a corresponding increase in the stabilisation energy of the molecule. This justifies the conclusion that the stabilisation energy in polar media is strongly dependent on the dipole–dipole interaction between the solute and the solvent molecules, and that this contribution increases with the polarities of both the participants. The same conclusion follows directly from Onsager's classical reactive field model in conjunction with Eqn (3), and is confirmed by Monte-Carlo modelling[60] of the dependence of the electrostatic interaction energy of solute molecules with the medium (ΔE_{int}) on their dipole moment.

Neither the lack of dependence of the enthalpy of solvation (ΔH_s) on μ for the solute molecules[61] nor the lack of a definite dependence of ΔH_s on μ and ε for the solvent (Table 5) can be interpreted as proof of the absence of a stabilising effect from dipole–dipole interaction. We must allow for the energy used to cut out the cavity (ΔE_{cav}), which makes a substantial endothermic contribution to ΔH_s. By introducing the correction $\Delta E_{cav} = \delta^2 V$ (where δ is Hildebrand's parameter and V is the molar volume of the solute) we can present the data in Table 5 as a linear dependence of ΔE_{int} on the μ value of the solute (Fig. 1). It is noteworthy that the solvents under study give two almost parallel straight lines, of which the lower corresponds to the solvents 5–7 and 11 (which according to their Gutmann donor numbers have the strongest specific solvation power). A possible explanation is the failure to allow for the contribution to ΔH_s from the reorganisation of the solvent associated with the creation of solvation shells in the calculation of ΔE_{int} from ΔH_s. In the case of specific solvation, which is accompanied by the formation of more rigid shells, this reorganisation requires a more substantial

Table 7. Energy (E_{MO}) of the molecular n, π, π^* orbitals and singlet transitions ($\Delta E_{n\to\pi^*}$ and $\Delta E_{\pi\to\pi^*}$) of *N,N*-dimethylformamide and *N*-nitrosodimethylamine in media with different ε values.[28]

ε	E_{MO}/a.u.			$\Delta E_{n\to\pi^*}$/eV	$\Delta E_{\pi\to\pi^*}$/eV
	n	π	π^*		
			A. $O=\overset{H}{\overset{\vert}{C}}-NMe_2$		
1	−0.4290	−0.4257	0.1744	5.892	10.616
2	−0.4140	−0.4077	0.1895	5.981	10.505
5	−0.3887	−0.3780	0.2103	5.916	10.260
40	−0.3504	−0.3354	0.2393	5.604	9.906
			B. $O=N-NMe_2$		
1	−0.4546	−0.4854	0.1613	3.535	10.714
2	−0.4314	−0.4655	0.1839	3.522	10.635
5	−0.4001	−0.4359	0.2123	3.507	10.397
40	−0.3647	−0.4016	0.2448	3.413	10.139

Table 6. Effect of the polarity of the medium (ε) on the physicochemical characteristics of *N,N*-dimethylformamide and *N*-nitrosodimethylamine in solution.[28]

ε	Me_2NCHO				Me_2NNO			
	$-E$	μ	ΔE_{C-N}	$\Delta\mu$	$-E$	μ	ΔE_{N-N}	$\Delta\mu$
1	53.22	2.69	33.0	−0.51	57.79	2.97	75.6	−0.45
2	53.31	2.89	32.9	−0.53	57.91	3.08	66.3	−0.51
5	53.40	3.30	55.5	−0.62	58.05	3.48	81.2	−0.66
40	53.53	3.89	94.4	−0.78	58.22	4.06	105.9	−0.88

Notes. E(a.u.) is the total energy of the molecule; ΔE/kJ mol^{-1} is the barrier to rotation round the C–N or N–N bond, ; $\Delta\mu$/D is the change in dipole moment caused by the change from the planar to the nonplanar form (i.e. by a 90° rotation).

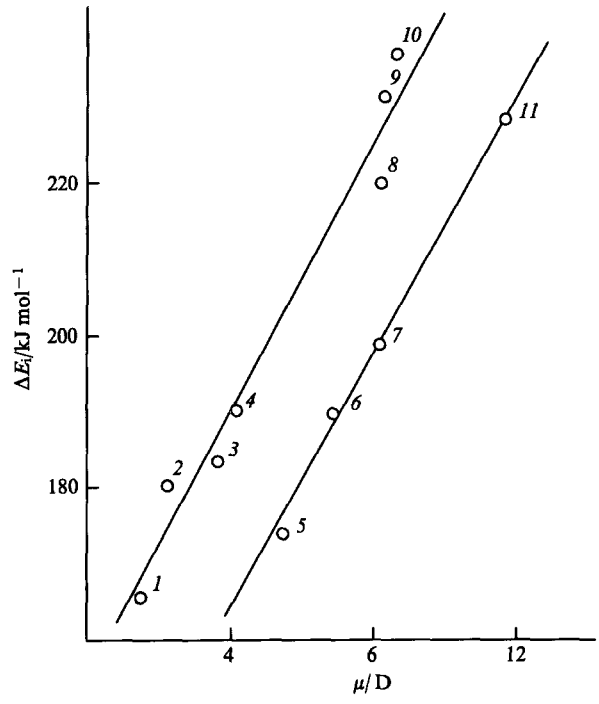


Figure 1. Plots of the interaction energy ΔE_{int} of triphenylchloromethane with the medium against its dipole moment for different ε values of the solvents (numbered as in Table 5).

consumption of energy than in nonspecific solvation. The important role of the formation of the cavity in solvation processes is also made clear by the reported[62] linear dependence

$$\ln \tau = a + b\Delta E_{cav}, \quad (14)$$

where τ is the dielectric relaxation time, which characterises the rotational mobility of the solute molecules.

Eqn (14) is consistent with the rotational diffusion model, in which the molecule can undergo discontinuous changes in its axis of rotation by overcoming a potential barrier equal to the cavity formation energy, i.e. by passing from one cavity into the next.

The dependence of the stabilisation energy of the molecules of the polar medium on their dipole moment is reflected by the nature of the dependence of ε for the solvent on the position of the absorption bands in the electronic spectra of the dissolved substances. Theoretical calculations[28, 48, 50] and experimental data[63-65] show that an increase in ε for the medium can either raise or lower the energy of the electronic transitions. CNDO/S calculations for benzophenone[50] have confirmed that the transition to the excited state can be accompanied by either an increase or a decrease in the dipole moment of the molecule (Table 8), as suggested by the experimental data.[65] Under these conditions the

Table 8. Dipole moments of benzophenone in the ground state (μ/D) and in excited states (μ^*/D) and energies (ΔE/eV) of the corresponding singlet transitions in media of different polarities.[50]

$f(\varepsilon)$[a]	μ	$\mu^*_{n\pi^*}$	$\mu^*_{\pi\pi^*}$	$\Delta E_{n\to\pi^*}$	$\Delta E_{\pi\to\pi^*}$
0	4.68	2.33	8.05	3.39	5.14
0.1	5.05	2.59	8.39	3.52	5.08
0.25	5.68	3.15	8.96	3.80	5.60
0.4	6.46	4.08	9.58	4.21	4.91
0.5	7.06	–	10.03	4.52	4.85

[a] $f(\varepsilon) = 1 - \varepsilon^{-1/2}$

energy of the $n-\pi^*$ transition increases, and that of the $\pi-\pi^*$ transition decreases, in keeping with data on the blue and the red shift of the corresponding spectral bands produced by an increase in ε for the solvent (Table 9). The increase in the $n-\pi^*$ transition energy calculated theoretically[43] agrees with the experimentally observed[64] blue shift of pyridine and of acetone: in the latter compound a decrease in the energy of the $\pi-\pi^*$ transition consistent with the red shift of the absorption band has also been reported.[48, 64] The change in the transition energy combined with a decrease in μ (shown schematically in Fig. 2) can be explained by postulating that when ε is increased the stabilisation of the ground state is more marked than that of the less polar excited state. The opposite state of affairs is observed when the transition involves an increase in μ during excitation.

The change in the electronic structure and in the energetics of molecules under the influence of a polar medium strongly affects the processes taking place in solutions, and in particular the tautomeric and conformational equilibria.[2, 48]

Low-barrier intramolecular proton transfer processes (prototropic tautomerism) have attracted wide interest because of their dominant role in many important processes such as the activity of living cells. An example of this type of tautomerism can be found in the keto–enol equilibria between 2-pyridone and 2-hydroxypyridine, or between uracil and 4-hydroxyuracil. The equilibrium constants of these processes, which determine the concentration ratio of the keto and the hydroxy form, can vary by several orders of magnitude when the system is transferred from the gas phase to a strongly polar solvent.[2, 48] This shift in the equilibrium is largely due to the preferential stabilisation by the polar medium of the tautomeric form having the higher dipole moment. For example, whereas in the pair of tautomers uracil and 4-hydroxyuracil, which have similar μ values in the gas phase, the uracil (keto form) is predominant, in aqueous solutions we find mainly 4-hydroxyuracil, which is not observed in the gas phase.[66] This is because the increase in μ, and therefore the decrease in E in media of high polarity is more marked for the hydroxy form than for uracil, and this form becomes the more stable when $\varepsilon > 8$ (see Table 10).

Table 9. Absorption bands (in nm) in the electronic spectra of benzophenone and energies (in eV) of the corresponding transitions in solvents of different polarities.[50]

Solvent	ε	$f(\varepsilon, n)$[a]	$n\to\pi$		$\pi\to\pi^*$	
			λ	ΔE	λ	ΔE
Hexane	–	0.0	364	3.57	259	5.01
Cyclohexane	1.87	0.002	363	3.58	260	4.99
Diethyl ether	3.89	0.317	360	3.60	261	4.98
Chloroform	4.55	0.289	352	3.68	–	–
Acetonitrile	36.6	0.711	355	3.66	262	4.95
Methanol	30.7	0.707	347	3.74	264	4.91
Water	76.6	0.775	337	3.85	270	4.81

[a] $f(\varepsilon, n) = (\varepsilon-1)/(\varepsilon-2) - (n^2-1)/(n^2+2)$.

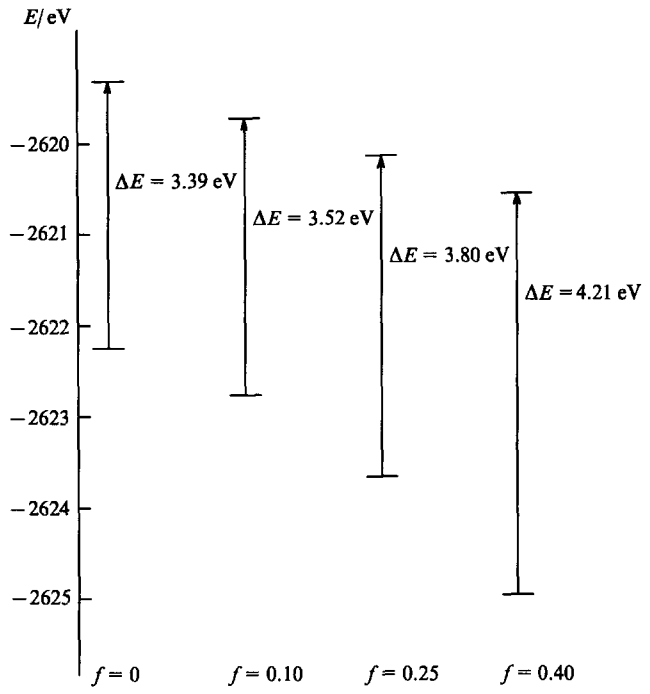


Figure 2. Changes in the energies of the ground and the excited states of benzophenone corresponding to the $n \rightarrow \pi^*$ transition, and energies of this transition as a function of the polarity of the solvent (f values, see Table 8).

The effect of a polar medium on the conformational equilibria is associated with a change in the energy of the barriers opposing the interconversion of the isomers. Thus, the conversion of *N,N*-dimethylformamide and *N*-nitrosodimethylamine from the planar to the nonplanar form (by a 90° rotation) requires surmounting barriers to internal rotation round the C–N and N^1–N^2 bonds whose height increases with the ε value of the medium. This may be due to two possible factors: the stabilisation of the more polar, planar conformer and the increased population (Table 2) of the bonds round which the rotation takes place. The difference between the dipole moments ($\Delta\mu$) of the planar and the nonplanar form increases with the ε value of the medium (see Table 6), and this effect should be accompanied by a relative stabilisation of the first form and a shift of the equilibrium towards it. An increase in the height of the barriers to internal rotation with increase in ε for the medium has been established also for formamide on the basis of INDO and CNDO/2 calculations, allowing for the effect of the medium in the solvaton formalism.[48, 67] The calculated results are acceptably consistent with the experimental determination of the barrier to internal rotation round the C–N bond in amides.[48, 68–70] For example, the barriers to rotation in formamide found by NMR increase from 70 to 80 kJ mol^{-1} when the compound is transferred from a nonpolar solvent (ε = 2) to water (ε = 80), whereas the calculated values increase from 87 to 90–100 kJ mol^{-1} when ε increases from 1 to 40 (see Ref. 48).

Table 10. Dipole moments and total energies (E/a.u.) of uracil and 4-hydroxyuracil in media of different polarities (INDO-solvatons method[48]).

ε	Uracil		4-Hydroxyuracil	
	μ	$-E$	μ	$-E$
1	4.26	86.45815	4.61	86.45140
8	4.46	86.48542	4.78	86.49878
80	4.55	86.49794	4.86	86.52064

IV. Molecular and ionic forms of H complexes in media with different dielectric permittivities

Compounds which are easily polarised in solutions include complexes with an intermolecular hydrogen bond, formed by acids AH and bases B and existing in a molecular (AH · B) or an ionic form (A^-HB^+). In the molecular form we observe intermolecular charge transfer from the B molecule to the AH molecule, acting as electron n-donor and σ-acceptor respectively,[71–74] whereas in the ionic form proton transfer from the AH to the B molecule takes place, with formation of an ion pair. Problems concerning the role of charge transfer in the stabilisation of the molecular forms of H complexes and the role of the effect of the polarity of the medium on the transfer of a proton and on the formation of ionic forms have been widely discussed in the literature on the nature of the hydrogen bond. The many theoretical and experimental approaches aimed at solving these problems have been examined in depth in a series of recently published monographs and reviews.[14, 16, 75–81]

There are two fundamentally different ways of describing the hydrogen bond. According to the first[14, 75, 76, 80] the molecular forms of H complexes are stabilised only through the electrostatic interaction of the component molecules, and the substantial increase in the dipole moment resulting from the formation of the H complexes is attributed to the equilibrium between the low-polarity molecular form and the high-polarity ionic form:

$$AH + B \rightleftarrows AH \cdot B \rightleftarrows A^-HB^+ . \qquad (15)$$

According to the second concept of the hydrogen bond,[71–74] based on the EDA interaction between the AH and the B molecule, the increase in μ accompanying the formation of the H complexes is due to the intermolecular charge transfer or to the shift of electron density from B to AH. Evidence in favour of this interpretation is provided by the experimentally[71, 72] and theoretically well established[73, 74] linear relationship between the energy (ΔE_c) or enthalpy (ΔH_c) of formation of the H complexes and the extent of the charge transfer (Δq_{ct}) in low-polarity media. However, as regards the equilibrium (15), the ionic forms have never been observed in the gas phase or in low polarity media.[17] The erroneous conclusions stipulating the presence of this equilibrium are often based on the observation of two minima on the potential curves. However, in amine–hydrogen halide systems in a vacuum it has been shown that two minima can be obtained on the potential curve even in very strict nonempirical calculations if no allowance is made for the electronic correlations or for the dispersion interaction of the component molecules.[82–84] Allowance for electron correlations results in the merging of the two minima into a single, wide minimum, corresponding to the molecular form of the H complex. Zundel and coworkers have shown[16, 85, 86] that the second minimum experimentally found on the potential curves of AH · B systems is due to the polarising effect of the solvent.

Quantum-chemical calculations on systems with H bonds, allowing for the solvent,[15, 19, 21, 87–89] have shown that changing from the gas phase to a polar medium has a marked effect on the shape of the potential curves, consistent with the change in electronic and geometrical structure resulting from complex formation. As shown by the increase in the μ value for the H complexes, and as in the case of individual molecules, the charge separation under the influence of the medium is greatest in media with the highest dielectric permittivity. For example, the dipole moment of the complex $Bu_3N \cdot HCl$ increases from 8 to 13 D as ε for the medium is increased from 2.3 to 35, the μ and ε values being related by the expression[19]

$$\mu = 13.6 - \frac{12.7}{\varepsilon} \quad (r = 0.985) . \qquad (16)$$

The intermolecular charge transfer (Δq_{ct}) calculated for μ = 8 D and the enthalpy of formation of the complex $Bu_3N \cdot HCl$ in benzene (ε = 2.3) satisfy the linear relation between ΔH_c^0 and Δq_{ct}

which characterises the EDA complexes.[72] The value 8 D agrees well with the μ value (7.2 D) calculated by the CNDO/2 method for the model complex $Me_3N \cdot HCl$ in the gas phase, which gives only one minimum on the potential curve (for $\varepsilon = 1$, Fig. 3*a*). In the same figure we show the potential curves calculated with allowance for the effect of the medium by the solvaton model. Under these conditions a second minimum appears on the potential curves: it corresponds to the ionic form, and its depth increases with the ε value for the medium. The calculations for the molecular and the ionic form of the complex indicate large differences between their geometric (and their charge) characteristics (Table 11). The N–Cl distance in the molecular form is much shorter than in the ionic form. Whereas the binding of the HCl molecule in the $Me_3N \cdot HCl$ complex lengthens the H–Cl bond by only 0.14 Å the H–Cl distance in the ionised complex reaches 2.3 Å. Essentially this implies the breaking of the H–Cl bond, as shown by the decrease in its population (P_{H-Cl}) almost to zero. The intermolecular distance N...H in the molecular complex is 0.2 Å longer than the corresponding distance in the ionic form, whose value is close to the length of the N–H bond in the Me_3NH^+ ion. The binding Me_3N and HCl molecules into a molecular complex lowers the population of the orbital of the unshared pair (P_{up}) on the N atom and increases P_{up} for the Cl atom (calculated as already described[90]) by an amount close to Δq_{ct}. This state of affairs is consistent with the normal behaviour of molecular H complexes with charge transfer from the unshared pair (UP) of the hetero-atom in the donor molecule to the electronegative atom attached to the proton in the acid. The transition to the ionic form increases P_{up} for the Cl atom to a value corresponding to the formation of a Cl^- ion. As could have been expected in this type of complex,[90] the population of the N...H bond is substantially less than unity, but in the ionic form it is very close to unity. The same is true of the charge on the Cl atom (q_{Cl}). However, the q_{Cl} value in $Me_3NH^+Cl^-$ is less than unity by approximately 0.15, and the μ value (13.03 D) is smaller than the value calculated for the contact ion pair with unit charges on the cation and the anion (16.3 D for $r_{N-Cl} = 3.4$ Å). This suggests the presence of interionic charge transfer from the Cl^- anion to the Me_3NH^+ cation.[91, 92] We note that μ for the ionic form is close to the value given by Eqn (16) for $Bu_3N \cdot HCl$ with $\varepsilon \to \infty$.

Table 11. Parameters of the molecular and the ionic forms of the $Me_3N \cdot HCl$ complex and of their components, calculated by the CNDO/2 method.[19]

Parameter	$Me_3N \cdot HCl$	$Me_3NH^+Cl^-$	Me_3N	HCl	Me_3NH^+
r_{N-Cl}/Å	2.75	3.40	–	–	–
r_{N-H}/Å	1.31	1.10	–	–	1.08
r_{H-Cl}/Å	1.44	2.30	–	1.30	–
q_{Cl}	−0.42	−0.86	–	−0.09	–
P_{N-H}	0.24	0.85	–	–	–
P_{H-Cl}	0.70	0.05	–	0.99	–
P_{up} (N)	1.72	1.39	1.94	–	–
P_{up} (Cl)	1.42	1.91	–	1.09	–
μ/D	7.17	13.04	1.43	2.48	0.48
Δq_{ct}	0.27	–	–	–	–
$-\Delta E_c$/ kJ mol^{-1}	115	–	–	–	–

The results in Table 12 shows that the μ values of both the molecular and the ionic form of the H complex increase with the ε value of the medium: this is due mainly to an increase in the level of intermolecular charge transfer, and also to an increase in the level of charge separation.[90, 91] An increase in Δq_{ct} (and therefore in ΔH_c) for the complexes with a Y...H–X intermolecular hydrogen bond (where Y is the heteroatom with an UP in the B molecule and X is the electronegative atom bound to the H atom in the acid molecule) shortens the Y...H distances and lengthens the X–H bond. These changes in the geometry of the H complexes are observed also when the increase in Δq_{ct} is due to an increase in the polarity of the medium, as shown in particular by *ab initio*

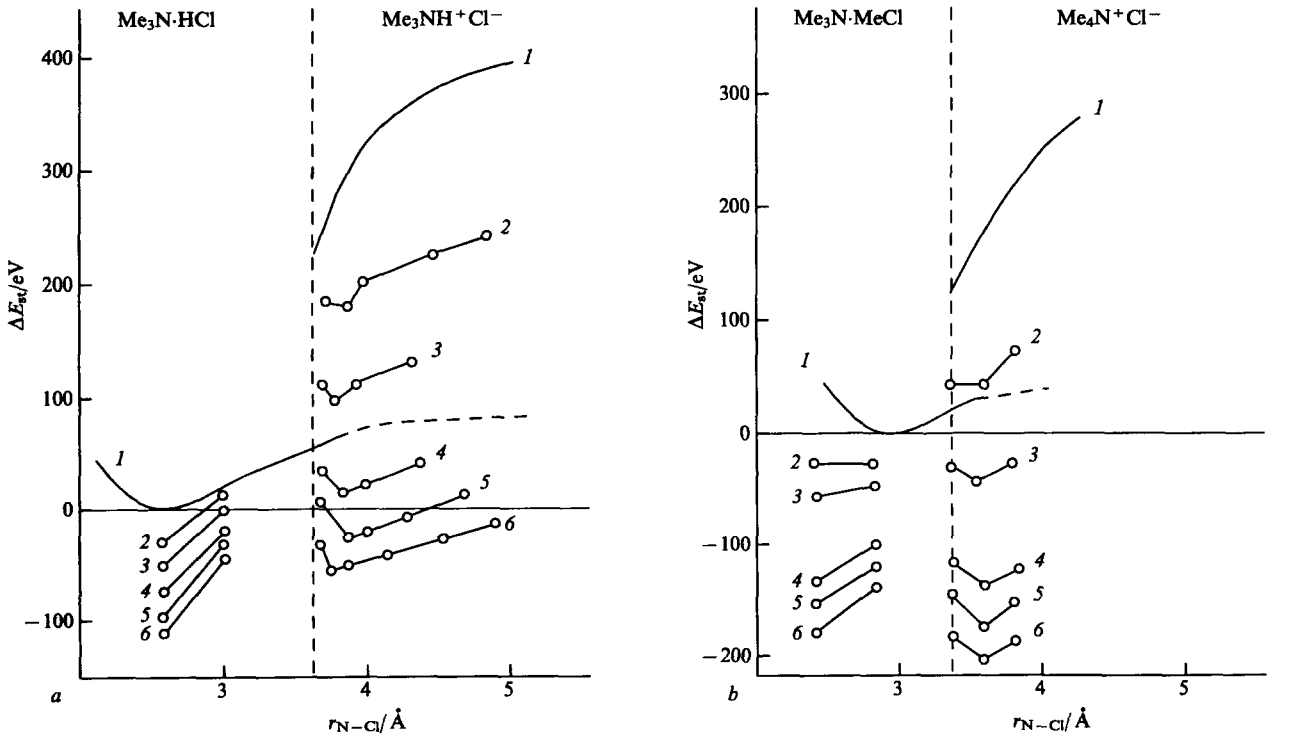


Figure 3. Plots of ΔE_{st} against r_{N-Cl} for Me_3NHCl (*a*) and Me_4NCl (*b*) in media with different ε: (*1*) 1; (*2*) 1.5; (*3*) 2.3; (*4*) 5.6; (*5*) 10; (*6*) 40.

Table 12. Dipole moments (μ/D), charges on the Cl atoms (q_{Cl}), stabilisation energies (ΔE_{st}/kJ mol^{-1}) of the molecular and the ionic forms of the complex of Me_3N with HCl contributed by the medium, and energies of interaction with the medium (ΔE_{int}) as a function of ε (CNDO/2 and CNDO/2–solvatons methods[19]).

ε	$Me_3N{\cdot}HCl$ (r_{N-Cl} = 2.75 Å)			$Me_3NH^+Cl^-$ (r_{N-Cl} = 3.4 Å)			
	μ	$-q_{Cl}$	$\Delta E_{st} - \Delta E_{int}$	μ	$-q_{Cl}$	ΔE_{st}	E_{int}
1	7.17	0.42	0	13.04	0.78	–	–
2.3	6.78	0.52	−40	14.25	0.90	118	−165
5.6	7.34	0.57	−74	14.68	0.93	24	−237
10	–	–	–	14.77	0.94	−3	−280
20	7.34	0.58	−97	14.83	0.94	−26	−309
40	7.39	0.59	−99	14.86	0.94	−36	−319

calculations[21] allowing for the effect of the medium in the SCRF formalism for the $Me_nH_{3-n}N{\cdot}HX$ series of model complexes, where X = F, Cl, or Br, and n = 0–3.[21] In the gas phase the energy of formation of these complexes (ΔE_c) increases with n in the series Br > Cl > F. The N–H distances decrease in the same sequence, and the H–X bonds become longer. However, even in the most stable complexes (n = 3, X = Br, Cl) the r_{N-H} lengths do not reach the very low values found in the $Me_nH_{4-n}N^+$ cations.

Allowing for the polarising effect of the medium shortens r_{N-H} and lengthens r_{H-X} in all the complexes by an amount which increases with ε for the medium. Conversion of the molecular complexes into the ionic form $Me_nH_{4-n}N^+X^-$ was observed only for X = Cl or Br and in media of relatively high polarity (ε > 10), the $Me_nH_{3-n}N{\cdot}HCl$ complexes giving the ionic form less readily than their HBr analogues. An analysis of the potential curves (Fig. 3) shows that the change from the gas phase to a polar medium stabilises the ionic form only when ε > 10. This effect is caused by the need to expend energy in rearranging the molecular structure into an ionic structure (mainly, in breaking the H–X bond). These energies are quite substantial: for example, 283 kJ mol^{-1} for $Me_3N{\cdot}HCl$.[19] The total stabilisation energy (ΔE_{st}) resulting from the change from the gas to a solution can be expressed as the sum of terms for the rearrangement (ΔE_r) and for the interaction with the medium (ΔE_{int}):

$$\Delta E_{st} = \Delta E_r + \Delta E_{int} . \quad (17)$$

The energy of the electrostatic interaction with the medium is higher for the more polar ionic form of the complex than for the molecular form, but in both forms $-\Delta E_{int}$ increases with the ε value of the medium as it does in the individual molecules (Table 12). The lack of stabilisation of the ionic forms in media with ε < 10 is due to the fact that in these cases $|\Delta E_r| > |\Delta E_{int}|$.

V. Electronic structure of salts in media with different polarities

Studies of the simplest members of this class of compounds, such as the alkali metal halides and the tetra-alkylammonium salts,[19, 90–93] have shown that in the gas phase and in nonpolar solvents their dipole moments are much lower and their interionic distances are much shorter than the values expected for ion pairs (Table 13). An attempt to explain these differences by the mutual polarisation of ions model[94] was unsuccessful, as can be seen by comparing the experimental values of the dipole moments observed in the gas phase (Table 13) with those calculated for the ion pairs (μ_{ip}) by the equation

$$\mu_{ip} = er^3\left[1 - \frac{r(\alpha_+ + \alpha_-) + 4\alpha_+\alpha_-}{r^6 - 4\alpha_+\alpha_-}\right] . \quad (18)$$

Mulliken's model, which treats the ion pairs as EDA complexes in which the anion acts as the electron donor and the cation as the electron acceptor,[95] proved more successful. This approach accounted for the decrease in μ for the ion pair in terms of the oppositely oriented dipole moment resulting from the interionic charge transfer, and the shortening of the bond between the ions was ascribed to the additional stabilisation of the pair.

Calculations on the LiCl and Me_4NCl molecules by CNDO/2 method (in a vacuum) with full optimisation of the geometry showed[90] that in both compounds the charges on the Cl atoms (q_{Cl}) are close to 0.5 of a unit charge, and the dipole moments and interionic distances are much lower than those expected for ion pairs. Under these conditions the distance between the C and Cl atoms in Me_4NCl (Table 14) is almost equal to the sum of their covalent radii (0.99 Å for Cl and 0.77 Å for C), and the N–C distance exceeds the sum of the covalent radii of C and N (1.47 Å)

Table 13. Dipole moments (μ_r/D) and interatomic distances (r_r/Å) of the alkali metal halides measured in the gas phase, and values of these parameters expected for contact ion pairs (μ_{ip}, r_{ip}).[93]

Compound	μ_r/D	r_r/Å	$\mu_{ip} = er_r$	$r_{ip} = r_+ + r_-$	$\mu_{ip} = er_{ip}$	μ_{ip}[a]
1. LiF	6.30	1.56	7.49	2.01	9.65	7.97
2. LiCl	7.12	2.02	9.70	2.57	12.34	10.51
3. LiBr	7.27	2.17	10.42	2.75	13.20	11.38
4. LiI	7.43	2.39	11.48	3.02	14.50	12.62
5. NaF	8.16	1.93	9.27	2.31	11.09	9.70
6. NaCl	9.00	2.36	11.34	2.81	13.49	12.00
7. NaBr	9.12	2.50	12.01	2.98	14.30	12.77
8. NaI	9.24	2.71	13.02	3.23	15.50	13.87
9. KF	8.6	2.17	10.42	2.66	12.77	10.85
10. KCl	10.27	2.67	12.82	3.14	15.07	13.44
11. KBr	10.41	2.82	13.54	3.29	15.79	14.21
12. KI	8.5	3.05	14.65	3.53	16.94	14.16

[a] Calculated by Eqn (18).

Table 14. Parameters of the molecular and the ionic forms of the Me_4NCl complex, of the Me_3N and MeCl molecules, and of the Me_4N^+ cation (CNDO/2 method).[19]

Parameter	Me_4NCl	$Me_4N^+Cl^-$	Me_3N	MeCl	Me_4N^+
r_{N-Cl}/Å	3.40	3.80	–	–	–
r_{N-C}/Å	1.63	1.50	1.41	–	1.43
r_{C-Cl}/Å	1.77	2.30	–	1.68	–
HCH angle[a]/deg	120	107	–	110.9	107.3
q_{Cl}	−0.46	−0.91	–	−0.14	–
P_{N-C}	0.55	0.74	–	–	–
P_{C-Cl}	0.76	0.09	–	0.98	–
P_{up} (N)	1.66	1.36	1.94	–	–
P_{up} (Cl)	1.37	1.99	–	1.05	–
μ/D	8.64	15.2	1.43	3.06	–
q_{ct}	0.274	–	–	–	–
$-\Delta E_c$/kJ mol^{-1}	28	–	–	–	–
$-\Delta E_c$[b]/kJ mol^{-1}	141	–	–	–	–

[a] The quoted angle is for the C atom directly attached to the Cl atom.
[b] Energy of the rearrangement of MeCl during the formation of a complex with Me_3N.

by only 0.16 Å. All these observations indicate a molecular (rather than an ionic) structure for the compounds in the gas phase and in nonpolar solvents.

The R_4NX compounds are electronic analogues of the $R_3N \cdot HX$ H complexes. In particular, the potential curves for Me_3NHCl and Me_4NCl (Fig. 3) are identical. Both gas-phase curves show a single minimum which in the case of Me_4NCl can be assigned to the molecular $Me_3N \cdot MeCl$ $n\sigma$ complex, with the alkyl halide acting (like HCl) as a σ acceptor. The geometric and the charge characteristics of the N–C and C–Cl bonds, calculated by the CNDO/2 method in a vacuum with full optimisation of the geometry of Me_4NCl (Fig. 3*b*, minimum on curve *1*), are also consistent with the EDA interpretation of the N...C–Cl bond and with the assumed analogy of this bond with the N...H–Cl bond in $Me_3N \cdot HCl$. Comparing the data in Tables 11 and 14 shows that the C–Cl (or H–Cl) bonds in the σ-acceptor molecules MeCl (or HCl) are only slightly stretched by the formation of molecular complexes with Me_3N, and that their population, though decreased, remains close to 1, whereas the population of intermolecular N–C and N–H is substantially less than 1. In the ionic structures the geometric and the charge characteristics of the N–C, C–Cl, N–H, and H–Cl bonds are markedly different. The C–Cl and H–Cl bonds are effectively broken, as shown by their elongation to 2.3 Å and by the decrease of their population to practically zero. Under these conditions the N–C and N–H bonds are shortened to values close to the r_{N-C} or r_{N-H} distances in the cations Me_4N^+ or Me_3NH^+ respectively.

The binding of the MeCl molecule in a complex with Me_3N is accompanied by an increase in the HCH bond angle from 111° to 120°, while the N–C–Cl fragment ion in the molecular complex adopts a trigonal bipyramidal structure with a planar CH_3 group, corresponding to sp^2 hybridisation of the C atom. This rearrangement of the MeCl molecule requires an energy expenditure of ~113 kJ mol^{-1}, which explains the much lower energy of formation of the $Me_3N \cdot MeCl$ complex (as compared with $Me_3N \cdot HCl$) for similar Δq_{ct} values of the two complexes. Applying a correction for the rearrangement energy gives similar values of ΔE_c (Tables 11 and 14). The conversion of the $Me_3N \cdot MeCl$ complex into the ionic form decreases the HCH angle in the methyl group to 107°, corresponding to the Me_4N^+ cation with a Walden inversion of the carbon tetrahedron relative to the methyl group in the free MeCl molecule.

As in the case of the $Me_3N \cdot HCl$ complex (Table 14) the dipole moments of the molecular and of the ionic form of Me_4NCl increase with the polarity of the medium (Table 15) as a result of the increase in the intermolecular charge transfer in the former and of the decrease in the interionic charge transfer in the latter. Corresponding increases in the energy of the electrostatic interaction with the medium take place: these are substantially higher for the more polar ionic form than for the molecular form. The energy of the rearrangement of the molecular structure $Me_3N \cdot MeCl$ into the ionic structure (151 kJ mol^{-1}) is substantially lower than for $Me_3N \cdot HCl$ (283 kJ mol^{-1}), and therefore the stabilising effect of the polar medium is higher in the former than in the latter (see Fig. 3). Whereas in Me_4NCl the minimum for the ionic form is deeper than that of the molecular form when $\varepsilon > 5.6$, in Me_3NHCl the effect is not observed even for $\varepsilon = 40$.[19] The validity of the theoretical predictions has been confirmed by a dielectrometric and conductimetric study of R_4NX (X = Cl or Br) and $R_3N \cdot HCl$.[19, 90, 91]

Studies of several organic chlorides and hexachloroantimonates[90, 91, 96–98] by the dielectrometry of conducting media method[92] showed that as ε for the solvent is increased from 2 to 10 the dipole moments of the salts rapidly increase to values of the same order as μ_{ip} for $\varepsilon = 35$, the dependence of μ on $1/\varepsilon$ taking the linear form

$$\mu = \mu_{ip} - \frac{A}{\varepsilon}. \qquad (19)$$

The parameter A characterises the sensitivity of the electronic structure of the given salt to the polarising effect of the medium. In the light of the theoretical ideas discussed above this type of dependence [Eqn (19)] can be explained by a transition from a molecular $n\sigma$ or $n\nu$ complex (a halogen complex of a metal with an n donor in Mulliken's terminology) to a complex with interionic charge transfer, followed by charge separation up to the formation of contact ion pairs with unit charges on the cation and the anion. Whereas the quaternary ammonium halides in nonpolar solvents have an $n\sigma$ complex structure the molecular

Table 15. Dipole moments (μ/D), charges on the Cl atoms, stabilisation energies (ΔE_{st}/kJ mol^{-1}) of the molecular and the ionic forms of the complex of Me_3N with MeCl provided by the medium, and energies of the interaction with the medium (ΔE_{int}) as a function of ε (CNDO/2-solvatons method[19]).

No.	ε	$Me_3N \cdot MeCl$ (r_{N-Cl} = 3.4 Å)			$Me_4N^+Cl^-$ (r_{N-Cl} = 3.8 Å)			
		μ	$-q_{Cl}$	$\Delta E_{st} \approx \Delta E_{int}$	μ	$-q_{Cl}$	ΔE_{st}	ΔE_{int}
1	1[a]	8.69	0.46	0	15.24	0.91	–	–
2	1.5	8.93	0.52	−28	16.21	0.95	46	−105
3	2.3	9.44	0.56	−58	16.59	0.97	−39	−190
4	5.6	10.65	0.64	−101	16.93	0.98	−141	−292
5	10	10.22	0.63	−123	17.02	0.99	−173	−324
6	20	10.35	0.64	−136	17.08	0.99	−194	−345
7	40	10.42	0.65	−143	17.11	0.99	−205	−356
8	80	10.45	0.65	−146	–	–	–	–

[a] Gas phase

form of the hexachloroantimonates is an $n\nu$ complex in which the intermolecular bond is formed by the UP of the Cl atom, bound to the cation, and the unoccupied sp^3d^2 orbital of the $SbCl_5$ molecule, known as a very strong V electron acceptor.[17, 58] The similarity of the electronic structure and of its changes under the influence of a polar medium which we have established for the salts and the H complexes offers the possibility of a unified treatment of the mechanism of two types of reaction: the bimolecular nucleophilic substitution (S_N2) and the proton transfer reaction in solutions, by the interaction of bases B with alkyl halides X–C in the first case and with bases A–H in the second:

$$X-C + B = C-B^+ + X^- , \quad (20)$$

$$A-H + B = H-B^+ + A^- . \quad (21)$$

In both these reactions two types of complex behave as intermediates: molecular (X–C...B or A–H...B) and ionic ($X^-...C-B^+$ or $A^-...H-B^+$). The reactions (20) and (21) produce a transition from molecular to ionic complexes by surmounting an activation barrier as the system moves along the reaction coordinate.[2]

Molecular complexes stable in the gas phase and in low-polarity solvents are formed by intermolecular charge transfer from the electron donor B to the electron acceptor (alkyl halide or acid). The complete transfer of an electron from the molecule B to the alkyl halide or acid, accompanied by the breaking of the X–C or A–H bond and by the addition of an alkyl radical or of a proton to the B molecule, leads to ionic complexes, stabilised mainly by the contribution from the interionic charge transfer. The formation of an ionic complex is a necessary precursor of the appearance of free ions.[87]

The conversion of a molecular complex into the ionic form is accomplished by using the energy of the interaction of the molecular complex with the polar solvent (ΔE_{int}), which increases with the ε value of the medium.

When ΔE_{int} exceeds ΔE_r the ionic complex becomes more stable than the molecular, the dissociation into free ions becomes possible. The dielectric permittivity (ε) of the solvent for which dissociation is possible depends on the properties of the system, as can be seen from the results of the experimental and theoretical study of the tri- and tetra-alkylammonium halides discussed above.

The important role of the polarising effect of the medium in controlling reactions such as (20) is underlined by a study of the interaction of various azoles with alkyl halides.[98] The stable products of this reaction in low-polarity solvents are molecular $n\sigma$ complexes, and in more polar solvents they are quaternary azolium salts. The quaternisation of azoles (like that of tertiary amines) during their interaction with alkyl halides is accompanied by Walden inversion of the tetrahedron of carbon atoms, which contributes to the formation of N–C bonds in the azolium cation. This is preceded by the formation of a molecular complex having a structure close to trigonal bipyramidal. Evidence for the EDA nature of the interaction of azoles with alkyl halides comes from the fact that only one of the several N atoms in the azole heterocycles acts as a reaction centre: it has n-donor properties, whose theoretically calculated indices for a series of azoles of different structure are linearly correlated with the logarithms of the rate constants of their interaction with methyl iodide in acetonitrile.

VI. Conclusions

The above discussion demonstrates the importance of effects from the polar medium in determining the distribution of electron density and the energetics of the molecules dissolved in the medium. Obviously, the mechanisms of liquid-phase processes cannot be described correctly without allowing for this effect.

The charge separation in the solute molecules and the stabilisation of their more polar forms under the influence of polar media are reflected in the changes of their physicochemical characteristics, which play an important role in many processes taking place in solutions. The shift of tautomeric or conformational equilibria towards the more polar forms and the increase in the rate constant of S_N2 or proton transfer reactions in solvents with a high dielectric permittivity are largely the result of an increase in the charge separation and in the stabilisation energy of the reacting molecules, of the intermediates, or of the reaction products. Processes involving the conversion of various compounds from the molecular into the ionic form take place at a reasonably high rate only in highly polar solvents, which induce an effective charge separation in the relevant molecules up to the formation of ion pairs.

Obviously, liquid-phase processes cannot be correctly described without allowing for these factors. We must therefore take careful note of the results and conclusions of theoretical studies of the mechanisms and kinetics of reactions in solutions which allow for solvation effects only in the approximation of structurally rigid reactant molecules.

References

1. R R Dogonadze et al. (Eds) *The Chemical Physics of Solvation* Part A (Amsterdam: Elsevier, 1985)
2. B Ya Simkin, I I Sheikhet *Kvantovokhimicheskaya Statisticheskaya Teoriya Rastvorov* (Quantum-chemical Statistical Theory of Solutions) (Moscow: Khimiya, 1989)
3. B Ya Simkin, I I Sheikhet, in *Fizicheskaya Khimiya. Sovremennye Problemy* (Modern Problems in Physical Chemistry) (Ed. Y M Kolotyrkin) (Moscow: Khimiya, 1983) p. 148
4. B J Simkin, I I Sheikhet *J. Mol. Liquids* **27** 79 (1983)
5. N A Smirnova *Molekulyarnaya Teoriya Rastvorov* (Molecular Theory of Solutions) (Leningrad: Khimiya, 1987)
6. G A Krestov (Ed.) *Sovremennye Problemy Khimii Rastvorov* (Modern Problems in Solution Chemistry) (Moscow: Nauka, 1986)
7. G A Krestov (Ed.) *Rastvory Neelektrolitov v Zhidkostyakh* (Solutions of Nonelectrolytes in Liquids) (Moscow: Nauka, 1989)
8. G A Krestov (Ed.) *Kompleksoobrazovanie v Rastvorakh* (Complex Formation in Solutions) (Moscow: Nauka, 1989)
9. K Burger *Solvation, Ionic Reactions, and Complex Formation in Nonaqueous Solutions* (Translated into Russian) (Moscow: Mir, 1984)
10. B Bogchi *Adv. Rev. Phys. Chem.* **40** 115 (1989)
11. E M Kosower, E V Huppert *Ann. Rev. Phys. Chem.* **37** 127 (1986)
12. P F Barbara, W Jarerta *Acc. Chem. Res.* **21** 195 (1988)
13. E Arnett *J. Chem. Educ.* **62** 385 (1985)
14. H Ratajczak (Ed.) *Molecular Interactions* (New York: Wiley, 1980) Vol. 1
15. P Th Duijen, B T Thole, in *Quantum Theory of Chemical Reactions* (Eds R Daudel et al.) (Dordrecht: Reidel, 1983) Vol. 3, p. 85
16. R Daudel et al. (Eds) *Quantum Theory of Chemical Reactions* (Dordrecht: Reidel, 1983) Vol. 3
17. Z Powelka *Acta Univ. Wratisl.* **692** 5 (1986)
18. I P Gol'dshtein, I E Paleeva, S I Gryzlov, O V Braverman, T A Pestova, E N Gur'yanova *Zh. Fiz. Khim.* **62** 3333 (1988)
19. I P Gol'dshtein, O V Braverman, I A Abronin, A N Fedotov, E N Gur'yanova *Zh. Obshch. Khim.* **58** 138 (1988)
20. R Sahai, P C Paude, V Singh *Indian J. Chem. A* **18** 211 (1979)
21. J Y Kuring, S Scheiner *Int. J. Quantum Chem.* **14** 47 (1987)
22. I A Abronin, K Ya Burshtein, G M Zhidomirov *Zh. Strukt. Khim.* **21** 145 (1980)
23. L G Gorb, I A Abronin, N V Kharchevnikov, G M Zhidomirov *Zh. Fiz. Khim.* **58** 9 (1984)
24. K Vaiss, I A Abronin *Izv. Akad. Nauk SSSR, Ser. Khim.* 364 (1984)
25. G Klopman *Chem. Phys. Lett.* **1** 200 (1967)
26. G Klopman, P Andreozzi *Theor. Chim. Acta* **55** 77 (1980)
27. H A Jermer Jr *Theor. Chim. Acta* **35** 273 (1974)
28. H A Jermer Jr *Theor. Chim. Acta* **34** 145 (1974)
29. S Miertuš, O Kysel *Chem. Phys.* **21** 27 (1977)
30. S Miertuš, E Scroccj, J Tomasi *Chem. Phys.* **55** 177 (1981)
31. S Miertuš, J Tomasi *Chem. Phys.* **65** 239 (1982)
32. A Y Duben, S Miertuš *Chem. Phys. Lett.* **88** 395 (1982)
33. R Cimiraglia, S Miertuš, J Tomasi *Chem. Phys. Lett.* **80** 286 (1981)

34. R Bonaccorsi, R Cimiraglia, J Tomasi *J. Comput. Chem.* **4** 567 (1983)
35. R Bonaccorsi, P Palla, J Tomasi *J. Am. Chem. Soc.* **106** 1945 (1984)
36. K Ya Burshtein *J. Mol. Struct.* **153** 195 (1987)
37. R Constancial *Theor. Chim. Acta* **54** 123 (1980); **69** 505 (1986)
38. O Tapia, O Josciuski *Mol. Phys.* **29** 1653 (1975)
39. R Constancial, O Tapia *Theor. Chim. Acta* **48** 75 (1978)
40. O Tapia, B Silvi *J. Phys. Chem.* **84** 2646 (1980)
41. O Tapia, G Johannin *J. Chem. Phys.* **75** 3624 (1981)
42. J E Sanhuesa, O Tapia *J. Mol. Struct.* **89** 131 (1982)
43. J Langlet, P Claveric, J Cailett, A Pulman *J. Phys. Chem.* **92** 1617 (1988)
44. H Hochi, S Sacurai *J. Chem. Phys.* **87** 1107 (1987)
45. H Hochi, M Sacurai, R Chujo *J. Mol. Struct.* **180** 267 (1988)
46. M Sacurai, H Hochi, J Inoul, R Chujo. *Bull. Chem. Soc. Jpn.* **63** 1335 (1990)
47. M V Bazilevskii, D V Napolov, G E Chudinov *Khim. Fiz.* **11** 691 (1992)
48. M Saunders, G A Webb *J. Mol. Struct.* **158** 69 (1987)
49. H A Jermer *J. Chem. Phys.* **58** 3524 (1973)
50. A Botrel, F Corre, A Le Benze *Chem. Phys.* **75** 383 (1983)
51. F Corre *J. Mol. Struct.* **86** 69 (1981)
52. M Witanowski, W Sicinska, G Webb *Magn. Reson. Chem.* **27** 380 (1989)
53. M Witanowski, J Sitkowski, S Biernat, B Kamienski, B Hangin, G Webb *Magn. Reson. Chem.* **25** 729 (1987)
54. M Witanowski, J Sitkowski, S Biernat, L V Sudha, G A Webb *Magn. Reson. Chem.* **23** 748 (1985)
55. M J Kamlet, J L Abond, R W Taft *Prog. Org. Chem.* **13** 485 (1980)
56. T Takajama, J Ando, T Asacura *Bull. Chem. Soc. Jpn.* **62** 1233 (1989)
57. S I Gryznov, I P Gol'dshtein *Zh. Fiz. Khim.* **63** 1637 (1989)
58. V Gutmann *Co-ordination Chemistry in Nonaqueous Solutions* (Translated into Russian) (Moscow: Mir, 1971)
59. J H Hildebrand, R L Scott *The Solubility of Nonelectrolytes* (New York: Dover, 1964)
60. V N Levchuk, I I Sheikhet, B Ya Simkin, I V Dorogan *Zh. Strukt. Khim.* **3** 75 (1990)
61. B N Solomonov, A N Konovalov *Zh. Obshch. Khim.* **55** 2529 (1985)
62. A N Fedotov, E S Isaeva, I P Gol'dshtein *Zh. Fiz. Khim.* **65** 2501 (1991)
63. W L Dilling *J. Org. Chem.* **31** 1045 (1966)
64. H Suzuki *Electronic Absorption, Spectra and Geometry of Organic Molecules* (New York: Academic Press, 1967)
65. O Exner *Dipole Moments in Organic Chemistry* (Stuttgart: Thieme, 1975)
66. D Shugar, K Szczepaniak *Int. J. Quantum Chem.* **20** 573 (1981)
67. A J Duben, S Miertuš *Theor. Chim. Acta* **60** 327 (1981)
68. A Calzolari, F Conti, C Franconi *J. Chem. Soc. B* 555 (1970)
69. W E Stewart, T H Siddal *Chem. Rev.* **70** 577 (1970)
70. W T Raynes, V A Raza *Mol. Phys.* **20** 334 (1971)
71. I P Gol'dshtein, E N Gur'yanova, T I Perepelkova *Zh. Obshch. Khim.* **42** 2091 (1972)
72. I P Gol'dshtein, T I Perepelkova, E H Gur'yanova *Dokl. Akad. Nauk SSSR* **226** 91 (1976)
73. I P Gol'dshtein, E S Shcherbakova, I A Misurkin, E N Gur'yanova *Fiz. Molekul* 51 (1980)
74. A E Read, F Weinhold, L A Curtiss, D J Pochatko *J. Chem. Phys.* **84** 5687 (1986)
75. H Ratajczak, W J Orville-Thomas (Eds) *Molecular Interactions* (Translated into Russian) (Moscow: Mir, 1984)
76. N D Sokolov (Ed.) *Vodorodnaya Svyaz'* (The Hydrogen Bond) (Moscow: Nauka, 1981)
77. B Pullman, P Schuster (Eds) *Molecular Interactions from Diatomics to Biopolymers* (Translated into Russian) (Moscow: Mir, 1981)
78. L M Epshtein, A V Iogansen *Usp. Khim.* **59** 229 (1990) [*Russ. Chem. Rev.* **59** 134 (1990)]
79. Z Sobczyc *J. Mol. Struct.*, **177** 111 (1988)
80. A C Legon, D J Millen *Acc. Chem. Res.* **20** 39 (1987)
81. J Zipinski *J. Mol. Struct.* **201** 87 (1989)
82. Z Latajka, S Sakai, K Morokuma, H Ratajczak *Chem. Phys. Lett.* **110** 464 (1984)
83. Z Latajka, S Scheiner, H Ratajczak *Chem. Phys. Lett.* **35** 5 (1987)
84. A Breiz, A Karpfen, H Lischka, P Schuster *J. Chem. Phys.* **89** 337 (1984)
85. U Bohner, G Zundel *J. Phys. Chem.* **90** 964 (1986)
86. G Zundel, Y Fritsch, in *Chemical Physics of Solvation* Part B (Eds R R Dogonadze et al.) (Amsterdam: Elsevier, 1986) Ch. 2
87. S Miertuš, Y Bartos *Collect. Czech. Chem. Commun.* **48** 2308 (1980)
88. O Tapia, F M Stamato, J G Smeyers *J. Mol. Struct.* **123** 67 (1985)
89. J E Sanhueza, O Tapia *J. Mol. Struct.* **131** 131 (1982)
90. I P Gol'dshtein, A N Fedotov, I A Misurkin *Zh. Obshch. Khim.* **56** 40 (1986)
91. I P Gol'dshtein, O V Braverman, I A Misurkin, E N Gur'yanova *Dokl. Akad. Nauk SSSR* **284** 150 (1985)
92. I P Gol'dshtein, O V Braverman, Yu V Podgornyi *Zh. Obshch. Khim.* **55** 2720 (1985)
93. G E Grunwald, S Higsneith, J Ting-Po, in *Organic Reactions* Vol. 2 (Ed. M Szwarc) (New York: Wiley Interscience, 1974) p. 448
94. C J F Böttcher *Theory of Electric Polarization* (Amsterdam: Elsevier, 1952)
95. R S Mulliken, W B Person *Molecular Complexes* (New York: Wiley Interscience, 1969)
96. I P Gol'dshtein, S I Gryzlov, O V Braverman *Dokl. Akad. Nauk SSSR* **305** 890
97. S I Gryzlov, I P Gol'dshtein, O V Braverman *Zh. Obshch. Khim.* **60** 2529 (1990)
98. I P Gol'dshtein, L D Khamaganova, A N Fedotov *Zh. Fiz. Khim.* **65** 959 (1991)