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Influence of Solvents on the Properties of Chemical Compounds

I. Determination of the Conformational Structure of Biphenyl, Butadiene, Benzaldehyde, Propionaldehyde, Furfural and Formamide by Means of a Continuum Model

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Based on Sinanoğlu's solvent theory in connection with a method for the calculation of the molecular volume given by Beveridge a modified continuum model is suggested. The model is tested by the determination of the conformational structure of the title compounds. The predictions obtained by this model are in good agreement with the experimentally determined data.

Key words: Solvent effects – Theoretical conformational analysis

1. Introduction

In recent years, powerful quantum chemical methods have been developed for predicting the conformational structure of isolated molecules ("free space approximation"). Now, some efforts are undertaken to reflect the experimentally observed differences between the most stable conformations of solvated molecules and those in the gas phase. The complexity of the theories applied ranges from simple correlations of the approximated molecular volumes with the free energy of solvation [1] to quantum chemical calculations on simulated associations of a single solute with some solvent molecules within the *ab initio* "supermolecule" framework [2]. Within some of these formalisms, the statistical nature of the solvation process is considered [3].

Among the various procedures, the "continuum model" [4–8] represents a useful step towards a theoretical calculation of solvent effects. The main advantage of this method is to provide an estimation of solvent effects on the molecular geometries without having the need for information about the explicit relative solvent-solute intermolecular geometry.

Thus, lengthy geometry optimizations [9] are avoided. Moreover, the results of this formalism are independent of the errors of the quantum chemical methods applied to the isolated molecule. Because of the limits of the approximations upon which the continuum models are based, it seems to be necessary to examine the significance of the calculated energy contributions by a comparsion with the experimental data of medium-sized molecules.

2. Method

The basis of our calculations is Sinanoğlu's solvent effect theory [4-6, 8, 10]. Some modifications concern the evaluation of the dispersion part of the solvent energy.

The total energy of a molecule under the influence of a solvent can be written as

$$E_{\text{tot}} = E_g + E_s. \tag{1}$$

E_g - energy of the isolated molecule, evaluated by means of a quantum chemical method
E_s - change of the energy of the solute under the influence of a solvent.
E_s is the sum of three contributions:

$$E_s = E_e + E_d + E_c \tag{2}$$

E_e - electrostatic interaction energy of the permanent and induced dipole moments of the solute with the solvent continuum.
E_d - dispersion energy part.
E_c - cavity energy.

In Eq. (2) the part of the reduction energy expressing the reduction of the free energies of interaction of the solute molecular groups due to the solvent has been neglected. It is considered to be relatively small and approximately constant [10]. The three energy terms contributing to E_s are functions of the molecular geometry of the solute. Therefore the central concept of the model is the determination of the volume of the spherical cavity that has to be created to insert a single solute into the solvent continuum [7]. Around the solute a rectangular solid is described. Its dimensions in the direction of the principle axes are given by the extrema of the x, y and z values of the atomic Cartesian coordinates plus 2 Å in each direction. The axes of the coordinate system placed at the centre of gravity of the molecule are parallel to those of the moment of inertia tensor of the molecule. An effective molecular solute cavity radius a is defined by equating the volume V_a of the rectangular solid and the volume of the sphere, so that

$$a = (3V_a/4\pi)^{1/3} = (V_a/4.189)^{1/3}. \tag{3}$$

2.1. Electrostatic Energy, E_e

For a molecule with a permanent electrostatic dipole moment μ_a Onsager's theory [11] provides an estimate of the resulting dipole moment m_a, placed at the centre of the spherical cavity, and of the reaction field E_R at the position of m_a. The equation

$$E_R = \frac{2(\epsilon_b - 1)}{2\epsilon_b + 1} \cdot \frac{m_a}{a^3} \tag{4}$$

is valid with

$$m_a = \mu_a + \alpha E_R, \tag{5}$$

where ϵ_b is the dielectric constant of the solvent and α is the polarizability of the dipole μ_a. Now, with μ_a in Debyes and a in Å Eq. (4) yields for the electrostatic energy[1] [12, 13]:

$$E_e = -14.39 \frac{\mu_a^2}{a^3} \cdot \frac{p}{(1 - 2D_a p)} \quad \text{[kcal/mole]}. \tag{6}$$

$$p = (\epsilon_b - 1)/(2\epsilon_b + 1)$$

$$D_a = (n_a^2 - 1)/(n_a^2 + 2)$$

n_a: refractive index of molecule a.

2.2. Cavity Energy, E_c

The energy required to create a spherical cavity with radius a in the solvent is given by

$$E_c = \gamma_b \cdot k_b(b/a) \cdot A \cdot \left(1 - \frac{\partial \ln \gamma_b}{\partial \ln T} - 2/3 \mathcal{A}_b T\right), \tag{7}$$

where $k_b(b/a)$ is a function of the relative radii of the solute a and the solvent b. $k_b(b/a)$ transforms the macroscopic surface tension γ_b to microscopic dimensions. The following relation is used:

$$k_b(b/a) = 1 + (b/a)^2 (k_b(1) - 1) \tag{8}$$

with

$k_b(1)$ - microscopic cavity factor,
$A = 4\pi a^2$ - surface of the spherical cavity,
b - radius of the solvent molecules,
$\mathcal{A}_b$ - thermal expansion coefficient of the solvent
and T - absolute temperature.

The cavity factor $k_b(1)$ is estimated from empirical solubility data. For non-polar liquids $k_b(1)$ is less than 1.0, for polar liquids it exceeds this value (Table 1) [10]. In both cases the interpolation to $k_b(b/a)$ ensures the expected asymptotic behaviour for $b/a \to 0$.

2.3. Dispersion Energy, E_d

This contribution to the total solvation energy is evaluated by summation over the discrete solvation layers which surround the molecule a:

$$E_d = \sum_{n=1}^{\infty} v_{ab}^{\text{eff}}(r_n) Z_n. \tag{9}$$

Z_n - number of solvent molecules in the nth layer (Appendix)
r_n - radius of the nth solvation layer (Appendix)
v_{ab}^{eff} - effective intermolecular potential in the solvent.

Compared with the widely used integration over a continuous distribution of solvent molecules the summation (9) needs no calibration constants [9] for correcting the deviations

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[1] Beveridge *et al.* [7] use the expression $E_a = -m_a E_R$ instead of Eq. (6). However, such an expression does not account for the induction of E_R by m_a and for the energy needed to enlarge the dipole moment of the solute from μ_a to m_a [12, 13].

of the integration of potential energy functions [9, 14] from summations of type (9). The effective interaction potential, v_{ab}^{eff}, defined by Sinanoğlu, is given by

$$v_{ab}^{\mathrm{eff}}(r) = v_{ab}^{\mathrm{K}}(r) \cdot B_{ab}(r) \tag{10}$$

v_{ab}^{K} is the Kihara-type potential and describes the gas phase intermolecular potential between molecules a (solute) and b (solvent). B_{ab} gives an estimate of the reduction of the intermolecular interaction due to the liquid environment. In the present case, v_{ab}^{eff} is of the form:

$$v_{ab}^{\mathrm{eff}}(r) = -(\epsilon_0/x^6)\{2 - \Delta' D_b' L_{ab}' - 1/x^6\} \tag{11}$$

with the following conventions:

$x = (r - l_{ab})/(r_{ab}^0 - l_{ab})$,
r_{ab}^0 - equilibrium distance between solute a and solvent b,
$l_{ab} = (l_a + l_b)/2$,
l_a, l_b - core diameter of a and b,
$D_b' \approx D_b/(1 + D_b)$,
$D_b = (n_b^2 - 1)/(n_b^2 + 2)$,
$\Delta' \approx 3/4$,
$L_{ab}' \approx L_{ab}$ dimensionless function of r, a and b [4],
ϵ_0 - potential energy minimum

The equilibrium distance r_{ab}^0 is evaluated by

$$r_{ab}^0 = (r_{aa}^0 + r_{bb}^0)/2 = (a + b)/\beta \quad (\beta \approx 1.15) \tag{12}$$

from the equilibrium distances r_{aa}^0, r_{bb}^0 of the pure liquids. β is an empirical constant [5]. Danon and Pitzer [15] have given a semiempirical relation between the Kihara core diameter l_a (average over all orientations of the molecule a) and the acentric factor ω_a of a molecule:

$$\frac{3l_a}{r_{aa}^0 - l_a} = 7\omega_a + 0.24. \tag{13}$$

This leads to the expression

$$l_a = \frac{2a}{\beta} \cdot \frac{0.24 + 7\omega_a}{3.24 + 7\omega_a}. \tag{14}$$

If the Kihara potential [15]

$$v_{ab}^{\mathrm{K}} = \epsilon_0^{\mathrm{K}}(1/x^{12} - 2/x^6), \tag{15}$$

which is used in (10), is required to have the asymptotic behaviour for large r given by the London term $-C_{ab}/r_{ab}^6$, with C_{ab} calculated theoretically according to

$$C_{ab} = 3/2\,\frac{\delta_a \cdot \delta_b}{\delta_a + \delta_b} \cdot \alpha_a \cdot \alpha_b, \tag{16}$$

δ_a, δ_b - mean excitation energies of the molecules
α_a α_b - polarizabilities

the potential minimum ϵ_0^{K} is given by

$$\epsilon_0^{\mathrm{K}} = \frac{C_{ab}}{2(r_{ab}^0 - l_{ab})^6}. \tag{17}$$

Using a Lennard-Jones-type intermolecular potential that arises from (17) by choosing $l_{ab} = 0$, one gets

$$\epsilon_0^{\mathrm{LJ}} = \frac{C_{ab}}{2(r_{ab}^0)^6}\,. \tag{18}$$

In all cases where l_{ab} deviates considerably from zero, differences between ϵ_0^{LJ} and ϵ_0^{K} occur [17]. Thus, an energy of approximately 8 kcal/mole results for the gas phase CCl_4-CCl_4 interaction at the potential minimum if (17) is used together with data given by Sinanoğlu [4, 6]. This value exceeds by far the empirically fitted Lennard-Jones parameter ϵ_0^{LJ} ($\approx$0.7 kcal/mole [14, 16])[2].

Because the main contribution to the dispersion energy of the solute comes from the first solvation layers, the calculation requires a good estimate of the potential energy minimum ϵ_0 rather than the correct asymptotic behaviour. The estimate of ϵ_0 was therefore taken from an extrapolation of the theoretical dispersion energy $-C_{ab}/r^6$ to the equilibrium distance r_{ab}^0.

Considering

$$\alpha_a = D_a \cdot a^3,$$

ϵ_0 is a function of the molecular dimensions [10] and is given by

$$\epsilon_0 = \frac{27}{32\pi^2} \cdot \frac{\delta_a \cdot \delta_b}{\delta_a + \delta_b} \cdot D_a D_b V_a V_b / (r_{ab}^0)^6. \tag{19}$$

The mean excitation energies δ_a and δ_b are evaluated according to [5] from

$$\delta_{a(b)} = \mu \cdot I_{a(b)} \tag{20}$$

with $\mu \approx 1.35$. I represents the ionization potential of the solute and the solvent, respectively.

Table 1. Data for the pure solvents (taken from: Landolt-Börnstein: Zahlenwerte und Funktionen, 6. Auflage)

Parameter	Tetra	Cyclohexane	*n*-Heptane	Water	Dimension
ϵ_b	2.23	2.01	1.92	77.81	
$\kappa_b(1)$	0.629	0.621	0.687	1.277	
T	300°	300°	300°	300°	°K
$\gamma_b\ (T)$	25.90	24.14	19.60	71.69	dyn/cm
$-\frac{\partial \ln \gamma_b}{\partial \ln T}$	1.459	1.491	1.531	0.657	
$\mathscr{A}_b$	1.22	1.20	1.25	0.257	10^{-3} grd^{-1}
b	3.37	3.51	3.88	1.93	Å
$\omega_b{}^a$	0.255	0.262	0.348	0.023	
I_b	11.46	10.30	10.20	12.60	eV
α_b	10.50	10.87	13.61	1.456	$Å^3$

[a] Non-polar part.

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[2] In good accordance with the empirically fitted ϵ_0^{LJ} mentioned above a calculation of the gas phase CCl_4-CCl_4 potential minimum by means of the atom polarizability method in the parametrization of Scheraga [18] with $R_w(\mathrm{Cl}) = 2.12$ Å yields $r_{ab}^0 = 5.7$ Å and $\epsilon_0 = -0.95$ kcal/mole [19].

The cavity radii of the various solvents examined were evaluated from the number density ρ_b of the pure liquid. For the radius b the following equation is valid:

$$b = \left(\frac{3}{4\pi\rho_b}\right)^{1/3}. \tag{21}$$

The corresponding ionization potentials I_b and polarizabilities α_b were taken from experimental data (Table 1). The ionization potentials I_a and the acentric factor ω_a of the solute were assumed to have the mean values 10 eV and 0.25, respectively. The refractive indices of all molecules examined are taken from standard handbooks [20, 21].

3. Results and Discussion

To test the described continuum model we examined the changes of the conformational structure under the influence of several solvents in the compounds biphenyl (1), butadiene (2), benzaldehyde (3), propionaldehyde (4), furfural (5), and formamide (6). The basic structure of all molecules is given in Fig. 1. The selected group of compounds contains members with no dipole moment in all conformations (biphenyl), very small or no dipole moments of the various molecular arrangements (butadiene), with a distinct dipole moment but relatively small changes of its value during the rotation by an angle θ (benzaldehyde, propionaldeyhde) and, lastly, molecules with a distinct dipole moment and considerable changes of it during the rotation process (furfural, formamide).

The energies for the isolated molecules were taken from both *ab initio* and our own NDDO calculations. Both procedures provide at least a qualitatively correct description of the potential curves for all compounds examined by rotation about the essential single bond.

3.1. Biphenyl

The experimentally determined torsion angles for biphenyl are 42° (gas phase [22]) and about 20° (*n*-heptane [23]). An *ab initio* study with optimization of the positions of the hydrogen atoms in the *ortho* positions and the distance between the two rings provides

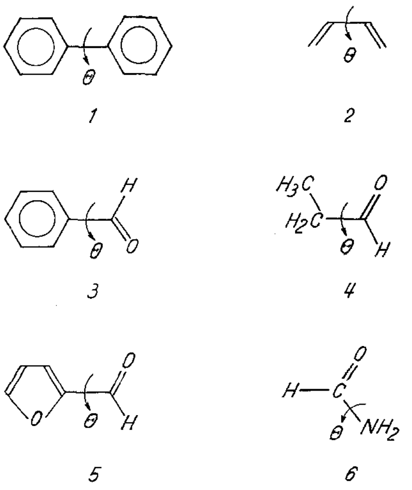

Fig. 1. Basic structures of the molecules examined. The given arrangements correspond to the torsion angle $\theta = 0°$

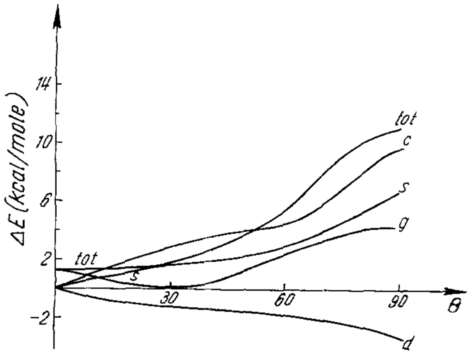

Fig. 2. Changes of the solvation energy and its contributions, the *ab initio* energy of the isolated molecule, and the total energy for biphenyl in the solvent *n*-heptane. The following abbreviations are valid in all figures: $c = \Delta E_c$, $d = \Delta E_d$, $e = \Delta E_e$, $g = \Delta E_g$, $s = \Delta E_s$, $\mathrm{tot} = \Delta E_g + \Delta E_s$

a torsion angle of 32° [24]. According to the NDDO method, the lowest energy was obtained for a non-planar conformation having a torsion angle of 45° [25]. No geometry optimization was performed in these cases, but the same molecular geometry was used as in the known CNDO/2 calculations [26]. We calculated the solvation energy for both molecular geometries. Biphenyl has no dipole moment in all conformations. Thus, there are only contributions of the cavity and dispersion energy. The corresponding curves are presented for the solvent *n*-heptane in Fig. 2. The change of the cavity energy overcompensates the change of the dispersion energy. Therefore, a destabilization of the twisted forms results. Relating the values of the solvation energy to the energies of the isolated molecule arising from *ab initio* calculations, we obtained the total potential curve also given in Fig. 2. In good agreement with experiment, this curve indicates that a decrease of the torsion angle occurs in solution. Based on the *ab initio* results the planar form is favoured. In connection with the NDDO results [25], the minimum is now at about 30°. However, the energy of the molecule is very insensitive by rotation around the formal single bond in a wide range of the torsion angle.

3.2. Butadiene

The question whether the second conformer in butadiene is planar *cis* or a gauche form was not answered satisfactorily for a long time. Recently published experimental data seem to indicate that the second conformer is gauche. The torsion angle may be about 20° [27]. These examinations were performed in the solvent carbon disulphide. *Ab initio* and NDDO calculations also yield a favouring of a gauche form [28, 29]. The torsion

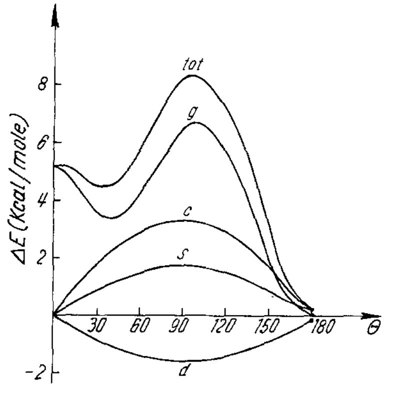

Fig. 3. Changes of the solvation energy and its contributions, the *ab initio* energy of the isolated molecule, and the total energy for butadiene in the solvent tetra (for abbreviations cf. Fig. 2)

angles are about 30-40°. Based on the experimentally determined molecular geometry [30], the energy differences between the planar *cis* and gauche form are 1.8 and 0.7 kcal/mole, respectively. A geometry optimization reduces the *ab initio* difference to 0.4 kcal/mole. For our calculations of the solvation energy the NDDO dipole moments were used. Due to the small dipole moments of the various conformations, the contribution of the electrostatic term can be practically neglected. Again the change of the cavity energy is of decisive importance for the total change of the solvation energy. Fig. 3 demonstrates the course of the solvation energy for the solvent tetra, the *ab initio* total energy without geometry optimization, and the sum of both terms. The gauche form is more stable than the planar *cis* conformation, but the energy difference between both forms is reduced by about 1.1 kcal/mole. Due to the small changes of the molecular geometry after optimization, there are no essential consequences for the course of the solvation energy. Thus, relating the results obtained for the solvation energy to the theoretical energy difference for the optimized geometries (0.4 kcal/mole), both forms should be nearly equivalent in tetra. According to the NDDO method, this result already appears for the experimental geometry[3]. These facts show that the energy difference between both forms is very small in solution and the exact experimental determination of the structure may indeed be rather difficult.

The energy difference between the gauche and *trans* form as the most stable conformation amounts to 3.4 kcal/mole and 1.2 kcal/mole, respectively, if *ab initio* and NDDO calculations are performed using the experimental geometry. A further favouring of the *trans* form by about 0.8-1.0 kcal/mole comes from solvation in tetra dependent on the various torsion angles calculated for the gauche form in both methods. Thus, this energy difference increases in solution. Experimentally, a difference of 2.1 kcal/mole was determined in carbon disulphide. A value of 2.3 kcal/mole arises from calorimetric data [31]. In the same way an increase of the rotational barrier related to the *trans* form by about 1.7 kcal/mole is given by this continuum model. *Ab initio* values for the isolated molecule are in the range of 6.0-6.7 kcal/mole [28]. The corresponding NDDO value amounts to 3.1 kcal/mole using the experimental geometry. Unfortunately, only the value of 4.9 kcal/mole is known for the barrier arising from calorimetric studies [31].

3.3. Benzaldehyde

In benzaldehyde the two-fold barrier has been determined to be 4.7 kcal/mole in the gas phase [32] and 6.4-6.7 kcal/mole in the pure liquid [32, 33]. A calculation using the NDDO method [25] has provided a value of 3.4 kcal/mole. Fig. 4 shows the contributions of the solvation energy and the total energy based on NDDO calculations [25]. In fact, the rotational barrier is increased to about 6.5 kcal/mole in tetra. Related to the experimental gas phase value of 4.7 kcal/mole, the obtained rotational barrier of 7.8 kcal/mole is slightly overestimated by this continuum model. Due to the relatively small changes in the dipole moments of the conformations, there is only a slight influence of the electrostatic energy.

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[3] It is possible to combine the solvation energies calculated by this continuum model with the results of other *ab initio* studies [63-66]. This does not lead to essential changes of the given principal conclusions. According to Pincelli *et al.* [63] an energy difference of 0.8 kcal/mole exists between the two forms using the experimental molecular geometry. Calculations of Hehre and Pople [64] also favour the gauche form. Former calculations by Radom and Pople [65] provided a favouring of the planar *cis* form.

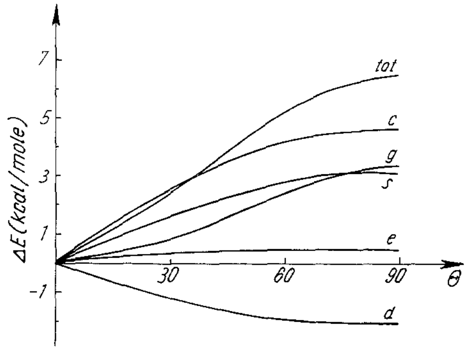

Fig. 4. Changes of the solvation energy and its contributions, the NDDO energy of the isolated molecule, and the total energy for benzaldehyde in the solvent tetra (for abbreviations cf. Fig. 2)

3.4. Propionaldehyde

Experimental examinations on propionaldehyde have shown that the structure with a *cis* arrangement of the methyl and carbonyl groups ($\theta = 0^\circ$) is the most stable form [34-39]. Using microwave spectroscopy a second minimum corresponding to a gauche form ($\theta = 131^\circ$) with an energy 0.8 kcal/mole higher is predicted [35]. The energy differences between both forms measured by NMR spectroscopy [38, 39] are 0.9-1.0 kcal/mole in solution. For the larger of the two torsional barriers ($\theta = 60^\circ$) separating the stable conformation, experimental values of 1.25 [37] and 2.28 kcal/mole [35] have been reported. Up to now, the height of the lower second barrier ($\theta = 180^\circ$) is unknown. Contrary to the results of most semiempirical MO methods [40, 41], *ab initio* calculations [42, 43] predict the correct order of stability. The NMR measurements in the solvents cyclohexane and acetonitrile yielded a negligible influence of solvation on the gauche-*cis* energy difference. This result is well accounted for by the continuum model calculations based on standard molecular geometries [44] and NDDO dipole moments [45]. Fig. 5, illustrates the course of the solvation energy and its contributions in cyclohexane. Quantitatively similar curves are estimated for acetonitrile. It is interesting to note that these curves show the same features as the potential curve for internal rotation in the gas phase (Fig. 6). The complete potential course for the solvent cyclohexane estimated by superposition of the *ab initio* [42] and solvation energies, which is shown in Fig. 6, is within the limits of the experimental curves arising from microwave and NMR spectroscopy.

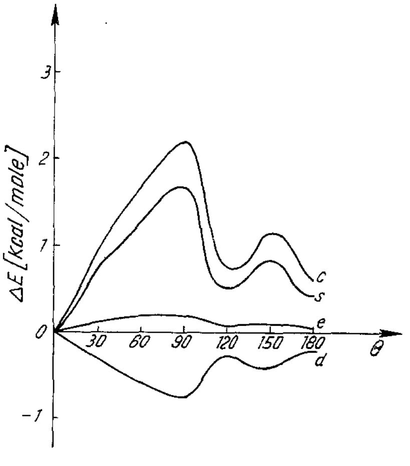

Fig. 5. Changes of the solvation energy and its contributions for propionaldehyde in the solvent cyclohexane (for abbreviations cf. Fig. 2)

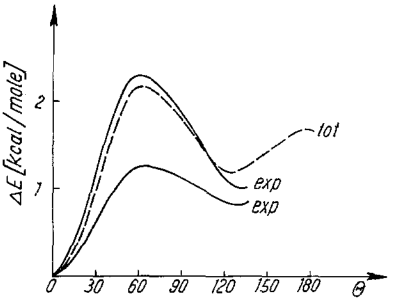

Fig. 6. Comparison of the change of the total energy composed of the *ab initio* energy and the calculated solvation energy in the solvent cyclohexane with two experimentally determined potential curves [35, 37, 39] representing upper and lower limits for propionaldehyde

3.5. Furfural

Extensive experimental examinations were performed to determine the conformational structure of furfural (for a review see Ref. [46]). In the gas phase the *cis* form (0–0 *trans*) is the most stable one. The measured values for the energy difference between this form and the planar *trans* conformation (0–0 *cis*) are 0.99 [47], 1.5 [46] and 2.03 kcal/mole [48]. The rotational barrier related to the *cis* form was determined to be 8.09 [48], 8.71 [47] and 9.16 [49] kcal/mole. In solution, this situation can change completely. The *trans* form becomes the most favoured one in solvents with a dielectric constant of $\epsilon > 5$ [46]. Consideration of the electrostatic energy term alone, assuming the same molecular volume for all conformations, can explain this behaviour satisfactorily [46]. Fig. 7 shows the course of the solvation energy and its contributions obtained by our extended continuum model for the solvent tetra. The experimentally determined dipole moments were used [47]. The NDDO energy difference [50] of 2.1 kcal/mole between the isolated planar forms is reduced to 1.7 kcal/mole. Experimentally, a value of 0.2 kcal/mole was measured in tetra [46]. The connection of the calculated solvation energy difference with the average value of 1.5 kcal/mole for this difference determined in the gas phase leads to better agreement between theory and experiment. Now, the value is 1.1 kcal/mole. The rotational barrier related to the *cis* form is increased by about 3.4 kcal/mole. For the solvent tetra the values amount to 11.5–12.6 kcal/mole dependent on the selected experimental gas phase data. Again the rotational barrier seems to be slightly overestimated by this model. Experimental values measured in the solvent dimethylether and the more polar pure liquid are 10.5 and 11.0 kcal/mole, respectively [46]. A comparison of our results with those of Abraham and Siverns [46] shows the same principal tendency of the energy change for the conformations. But the additional inclusion of cavity and dispersion term in connection with a consideration of changes in the molecular volume leads to some modification of the magnitude of the solvent effect.

3.6. Formamide.

The experimental data for the internal rotation energy of formamide were obtained by NMR measurements in solution. The estimated parameters are the enthalpy of activation $\Delta H^{\neq}$ or the Arrhenius activation energy E_a. The barrier grows from 16 to 21 kcal/mole with increasing polarity of the solvent [51–55]. Therefore, it can be expected that solute-solvent and solute–solute interactions will have a complex effect upon the hindered rotation in this polar molecule. Kamei [52] has determined an E_a value of 21.3 ± 1.3 kcal/mole in water. For an explanation of the relatively high barrier he assumes that the

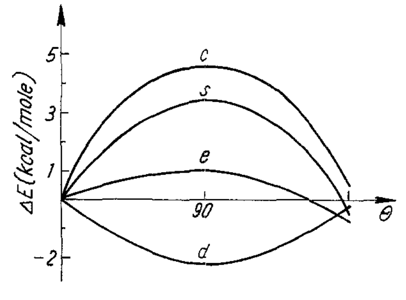

Fig. 7. Changes of the solvation energy and its contributions for furfural in the solvent tetra (for abbreviations cf. Fig. 2)

hydrogen bonds between the formamide molecules and water are stronger than those between the formamide molecules themselves. Thus, a strengthening of the C-N bond occurs. Christensen *et al.* and Pople *et al.* [42, 56] have published full *ab initio* MO studies of formamide in the ground and transition states. The theoretical barrier heights obtained are 19.9 and 24.7 kcal/mole, respectively. The values calculated by the semiempirical CNDO and PCILO methods [57-59] are in the same order of magnitude. These theoretical results are in formal accordance with the experimental data, but considered in the light of the strong influence of solvation on the barrier the calculated values seem to be clearly overestimated. The calculations with our continuum model based on the experimental geometry [60] and dipole moments from NDDO [45] show both in water and tetra that the solvation stabilization energy in the transition state ($\theta = 90°$) is decreased to 11.5 and 4.2 kcal/mole, respectively. The course of the solvation energy and its contributions is presented in Fig. 8 for the solvents water and tetra. It can be seen that the total solvation energy follows the course of the electrostatic energy. Due to the large decrease of the dipole moment in the transition state the nature of the solute-solvent interaction is predominantly electrostatic. Harding and Goddard [61] have recently published exact calculations on the basis of the general valence bond concept. These authors estimated the barrier to be 14.2 kcal/mole and concluded that the Hartree-Fock model considerably overestimated the gas phase barrier of formamide. Relating our results for the solvation energy to this value, we obtain a rotational barrier of 25.7 kcal/mole in water, which is too large by 4.4 kcal/mole in comparison with the experimentally determined value of 21.3 kcal/mole.

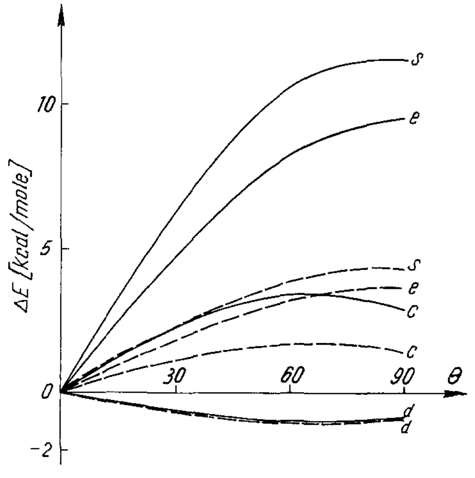

Fig. 8. Changes of the solvation energy and its contributions for formamide in the solvents water (——) and tetra (– – – –)

4. Conclusions

All results obtained by the suggested continuum model are in notably good agreement with the experimental data. The general trends of the changes in the conformational structure of the compounds examined during transition from the gas phase into the solvated state are correctly accounted for. The rotational barriers seem to be slightly overestimated. The calculations on formamide show that a comparison of the results of quantum chemical methods with data from solution experiments is questionable. Thus, an alteration of some conclusions arising from calculations on isolated molecules could be possible. Some modifications of the formalism described here, e.g. a modification of the rather rough volume model, a continuous change of the dielectric constant in the way suggested by Block and Walker [62] and the inclusion of dipole-dipole interactions, are being tested.

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Appendix

Assuming a hard-sphere-like packing and $(a/b) \gg 1$, the radius of the nth solvation layer is calculated by the recursion formula:

$$r_n = (r_{n-1}^2 - r_b^2)^{1/2} + 2(2/3)^{1/2} r_b. \tag{A1}$$

$$r_1 = (a+b)/\beta; \qquad r_b = b/\beta$$

Then the number of molecules in the nth solvation layer is given by

$$Z_n = \frac{2\pi}{\sqrt{3}} (r_n/r_b)^2. \tag{A2}$$

If a and b have comparable sizes (A1) and (A2) are expected to be approximately valid to within a small error.

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