Theoretical Approach in Explanation of Energy Donor Properties of 1,4-Dioxane and 1,4-Dioxane-Water Complexes

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The CNDO/2 CI method was used for the examination of 1,4-dioxane and 1,4-dioxane-water complexes (2:1), taking into account various conformations of the dioxane molecule. The energies of the molecules in the ground and excited states, the energies of hydrogen bond formation, the dipole moments, the transition moments, and the oscillator strengths for both the complexed and isolated 1,4-dioxane molecules were evaluated. The results of these studies are used to reveal the influence of water on the features of energy transfer from excited, by γ-radiation, 1,4-dioxane or dioxane-water complexes to the luminophor.

Introduction

The investigations of electronic spectra in neat 1,4-dioxane revealed the remarkable effect of water on its ground and excited states. This is shown in a red shift of the emission spectrum and in a strong decrease of the luminescence efficiency [1].

A decrease of luminescence efficiency was also observed upon γ-excitation of 1,4-dioxane-water systems in the presence of a luminophor [2, 3]. Careful analysis revealed two characteristic features of this phenomenon. Firstly, the efficiency of the energy transfer from 1,4-dioxane to the luminophor (PPO: 2,5-diphenyloxazol) decreases with the addition of water. Moreover, the pattern of this dependency changes sharply if the ratio of 1,4-dioxane molecules to water molecules reaches a value of two [4]. Secondly, the dependence of a luminophor radioluminescence intensity on the reprocical temperature exhibits, in both neat 1,4-dioxane and 1,4-dioxane-water mixtures, two distinct linear regions [2, 3]. For neat 1,4-dioxane the low temperature region is characterized by a constant value of the PPO radioluminescence efficiency and, thus, a constant value of the energy transfer efficiency. However, at higher temperatures a thermally activated pathway for the energy transfer becomes available whose activation barrier is ca. 0.09 eV [5]. In the case of the 1,4-dioxane-water system the two observed regions are characterized by two different values of the activation energy. This, together with other facts, clearly demonstrates that water somehow abates the energy transfer to the luminophor, presumably due to the formation of 1,4-dioxane complexes. The formation of such complexes has been suggested earlier [1–9]. To our knowledge, however, no theoretical studies regarding the structure and composition of such species have so far been undertaken.

In this work we investigate whether a complex composed of one molecule of water and two molecules of 1,4-dioxane can be formed and what its properties in the ground and excited states are, employing quantum mechanics methods. The choice for the examination of only (1,4-dioxane)$_2 \cdot H_2O$ complexes was made on the basis of chemical intuition and some experimental indications [5, 6]. We intend to verify whether our approach can explain the features of photoluminescence and radioluminescence of dioxane and dioxane-water systems.

Methods

a) Computations

The results presented here were obtained using the LCAO MO method in the CNDO/2 scheme with the original People and Segal's parametrization [10]. This method was applied to estimate the energy of the ground and excited states of the examined structures.

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We have used thirty singly excited configurations in the CI method. Although the CNDO/2 CI method gives much higher values of excitation energy compared with both the experimental values and those obtained by the CNDO/S CI method, it is generally known that the CNDO/2 CI method is more adequate for the description of σ-systems. The error, however, is the same in both cases and should not be important when the values are compared.

The hydration energy (ΔE_{H}), i.e. the difference between the energy of the complex and the free components, was calculated using the scheme of supermolecule.

It is known that both the position and the depth of potential curve minima of the optimised structures are overestimated in the CNDO/2 computations. Therefore the presented results describe the structures and structural changes qualitatively only.

To estimate changes in the geometry under excitation of the dioxane molecule, we used Wiberg's well known formula

$$W_{\mathrm{AB}} = \Big(\sum_{l\in \mathrm{A}} \sum_{j\in \mathrm{B}} P_{lj}^2\Big)^{1/2}, \tag{1}$$

where W_{AB} is the Wiberg's index, A and B are the atoms forming a bond, l and j are the valence orbitals in atoms A and B, respectively, and P_{lj} is a matrix element of the charge-bond order matrix (Table 1).

b) Geometry of 1,4-dioxane Molecule

The values of the molecular parameters for the chair conformation of 1,4-dioxane were taken from the work of Davis and Hassel [11]. It can be shown that with both the valence angles and the length of bonds fixed, the 1,4-dioxane molecule has zero degrees of freedom. On the basis of simple geometric considerations the value of the dihedral angle $OC_2C_4C_3$ (Fig. 1) is found to be 126.27°.

It was assumed that the geometric parameters of the 1,4-dioxane molecule in the boat conformation are the same as in the chair conformation, but the dihedral angle $OC_2C_4C_3$ (Fig. 1) in this case is opposite to that for the chair conformation.

A comparison of C–C Widberg's indexes for the molecules in the ground and excited states (Table 1) indicates that the lengths of the C–O and C–C bonds change. Thus it seems reasonable to assume that the 1,4-dioxane molecule in a transient state is planar.

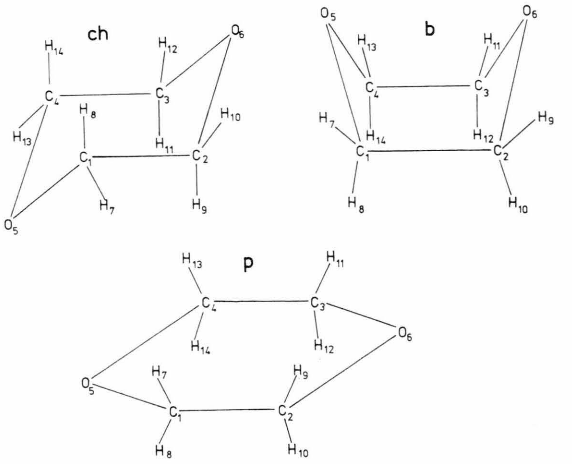

Fig. 1. A 1,4-dioxane molecule in chair (ch), boat (b) and planar (p) conformation.

Table 1. The charge densities in the ground (S_0) and excited states together with Wiberg's indices of C–C and C–O bonds for 1,4-dioxane molecule in the chair conformation (for details see Figure 1).

Atom number	S_0	S_1	S_2	S_3	S_4
1	0.13503	0.15624	0.10177	0.11912	0.10813
2	0.13503	0.15624	0.10177	0.11912	0.10813
3	0.13503	0.15624	0.10173	0.11927	0.10798
4	0.13503	0.15292	0.10173	0.11927	0.10798
5	−0.22295	0.04757	−0.00573	0.05202	0.04754
6	−0.22295	0.04757	−0.00573	0.05202	0.04754
7	−0.00911	−0.03885	−0.10132	−0.00368	0.00488
8	−0.01444	−0.09212	0.00244	−0.12291	−0.13622
9	−0.01444	−0.09197	0.00244	−0.12291	−0.13622
10	−0.00911	−0.03886	−0.10132	−0.00368	0.00488
11	−0.01444	−0.01045	0.00244	−0.12274	−0.13679
12	−0.00911	−0.04211	−0.10134	−0.03680	0.00488
13	−0.00911	−0.04211	−0.10134	−0.03680	0.00488
14	−0.01444	−0.01053	0.00244	−0.12274	−0.13679
Wiberg's indices					
C–C	1.0374	0.9367	0.9396	0.9309	0.9138
C–O	0.9829	1.0012	0.9736	1.0194	1.0170

c) Geometry of 1,4-dioxane Complexes

In this work we examined $(1,4\text{-dioxane})_2 \cdot H_2O$ complexes. The calculations were carried out for 6 possible structures of these species, namely: ch-w-ch (chair-water-chair), ch-w-b (chair-water-boat), b-w-b (boat-water-boat), ch-w-p (chair-water-plain), b-w-p (boat-water-plain) and p-w-p (plain-water-plain). In Fig. 2, as an example, the complex in the chair conformation is shown.

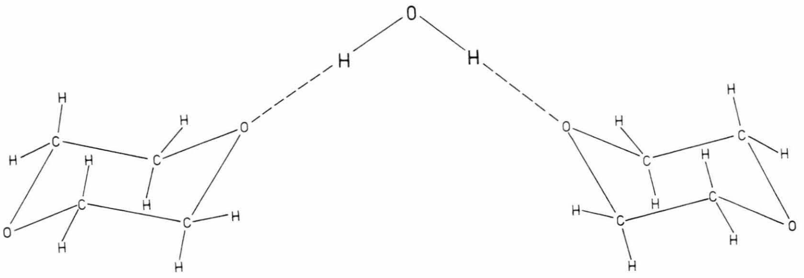

Fig. 2. Geometry of 1,4-dioxane-water complexes in chair-water-chair (ch-w-ch) conformation.

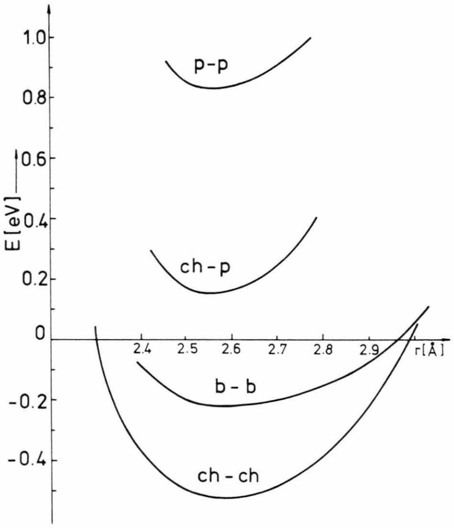

Fig. 3. The potential energy curves for several 1,4-dioxane-water complexes in the ground state: ch-ch denotes chair-water-chair conformation, ch-b indicates chair-water-boat conformation, and so on.

The minimum energy was found by optimization of the $O_d-O_w-O_d$ distances. The potential energy curves of investigated complexes are shown in Figure 3. In each case the minimum energy was obtained at the O_w-O_d distance 2.56 Å.

Table 2. The characteristic of different conformations of 1,4-dioxane molecule obtained by CNDO/2 method.

State	E_s [eV]	f	M_p	M_d [D]
chair conformation				
ground	0.000	–	–	0.0000
$S_0 \rightarrow S_1$	10.783	0.2482	0.9694	1.6982
$S_0 \rightarrow S_2$	11.860	0.0515	0.4211	0.0007
$S_0 \rightarrow S_3$	12.845	0.0000	0.0000	0.6023
$S_0 \rightarrow S_4$	13.007	0.0619	0.4409	0.0035
plain conformation				
ground	0.664	–	–	0.0066
$S_0 \rightarrow S_1$	11.115	0.0000	0.0038	0.6802
$S_0 \rightarrow S_2$	11.404	0.0113	0.2074	0.0328
$S_0 \rightarrow S_3$	12.406	0.0002	0.0078	0.0298
$S_0 \rightarrow S_4$	12.567	0.3607	1.1120	0.0662
boat conformation				
ground	0.137	–	–	2.8426
$S_0 \rightarrow S_1$	11.016	0.0231	0.2942	3.0886
$S_0 \rightarrow S_2$	12.142	0.0668	0.4767	2.2400
$S_0 \rightarrow S_3$	13.182	0.0000	0.0000	0.4968
$S_0 \rightarrow S_4$	13.225	0.0187	0.2408	2.1640

M_p – transition moment, M_d – dipole moment, f – oscillator strenght, E_s – the value of energy of different states relative to the energy of the ground state of dioxane molecule in chair conformation.

Results and Discussion

The exposure of 1,4-dioxane to high energy radiation may cause excitation of the molecules. Our calculations revealed that only for the first four electronic transitions the oscillator strengths and transitions moments are higher than zero. Therefore we discuss these first excited states only. Table 2 shows that the energies of the excited states of all conformations are close to each other. Thus, it may be expected that upon γ-excitation, all these four states are accessible and the probability of transition depends solely on the oscillator strength.

The energy gap between the ground states of the various conformations is high enough for the compound at ambient temperature to exist virtually in the chair conformation. A rough estimation, based on the data in Table 2 and assuming Boltzman distribution of energy, demonstrates that only 4 molecules occur in the boat conformation among 1000 molecules in the chair conformation. Thus, γ-excitation of neat dioxane should be realized with the participation of the chair conformation and should be of the nature of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_4$.

Energy conversion and vibrational relaxation are usually very fast processes in higher than first excited states. Therefore, a primarily excited 1,4-dioxane molecule presumably reaches the S_1 state before any other processes occur. Two physical pathways are available for molecules in S_1 state, namely, radiative energy loss and energy transfer to other molecules present in the system, e.g. a luminophor. If direct decomposition can be neglected, 1,4-dioxane in S_1 state of chair conformation can also undergo transformation to the plain or boat structures.

Let us consider whether the results of the present calculations can explain the earlier observed rapid rise in the luminophor radioluminescence efficiency with an increase of temperature ([5] Fig. 6). It is known that the probability of non-radiative energy transfer is proportional to the square of the energy of interaction, and that the energy of interaction, ΔE, depends on the dipole moments (M_{d1}, M_{d2}) of the interacting molecules and their moments of inertia (J_1, J_2) [12]:

$$\Delta E \simeq M_{d1} \cdot M_{d2} \cdot (J_1 \cdot J_2)^{1/2}. \tag{2}$$

The energy transfer is, thus, of higher efficiency from states characterized by higher dipole moments. Analyzing the data in Table 2 one notices that the transformation from chair to boat conformation in S_1 state of a 1,4-dioxane molecule is accompanied by a remarkable increase in the dipole moment. Therefore, the experimental increase of energy transfer efficiency with temperature would result from the chair – boat transformation in the S_1 state. The shape of the experimental curve (see [5], Fig. 6) indicates the thermally activated nature of the process. Moreover, the analysis of Wiberg's indexes (Table 1) suggests plain conformation as a transition state in chair – boat transformation. If the latter process occurred in S_1 state it would have to overcome a kinetic energy barrier of about 0.33 eV (Table 2). Thus, the estimated activation energy value is much higher compared to that found experimentally (0.09 eV) [5]. Nonetheless, the agreement may be considered quite good, taking into account the semi-empirical character of the theoretical calculations.

Table 3. The characteristic of 1,4-dioxane-water complexes obtained by CNDO/2 method.

State	E_s [eV]	f	M_p	M_d [D]	ΔE_h [eV]
chair-water-chair conformation					
ground	0.000	–	–	2.4393	−0.5283
$S_0 \rightarrow S_1$	11.908	0.00049	0.01302	2.6173	0.5101
$S_0 \rightarrow S_2$	11.918	0.17250	0.76860	2.6158	−0.4703
$S_0 \rightarrow S_3$	12.622	0.00262	0.00262	1.6906	−0.7513
$S_0 \rightarrow S_4$	12.623	0.02234	0.02234	1.6863	−0.9123
chair-water-boat conformation					
ground	0.153	–	–	5.2327	−0.5101
$S_0 \rightarrow S_1$	12.045	0.04380	0.38760	5.9281	0.5464
$S_0 \rightarrow S_2$	12.068	0.08998	0.55520	5.2941	−0.6026
$S_0 \rightarrow S_3$	12.505	0.02558	0.29070	5.0405	−1.0056
$S_0 \rightarrow S_4$	12.786	0.00333	0.10370	4.7414	−1.0646
chair-water-plain conformation					
ground	0.679	–	–	2.4474	−0.5142
$S_0 \rightarrow S_1$	12.151	0.00132	0.06870	4.0700	0.6161
$S_0 \rightarrow S_2$	12.600	0.08053	0.52500	3.3933	−0.1068
$S_0 \rightarrow S_3$	13.285	0.00019	0.02490	2.6351	−1.1939
$S_0 \rightarrow S_4$	13.431	0.15720	0.50620	2.1782	−1.3309
boat-water-plain conformation					
ground	0.832	–	–	5.2332	−0.4986
$S_0 \rightarrow S_1$	12.304	0.00916	0.18050	16.9680	0.3084
$S_0 \rightarrow S_2$	12.960	0.60770	0.60770	5.5180	−0.3992
$S_0 \rightarrow S_3$	13.325	0.00095	0.05560	30.2096	−0.1032
$S_0 \rightarrow S_4$	13.437	0.00019	0.02450	5.3569	−0.3196
boat-water-boat conformation					
ground	0.306	–	–	7.8900	−0.4969
$S_0 \rightarrow S_1$	12.298	0.04186	0.37660	8.2758	0.5068
$S_0 \rightarrow S_2$	12.298	0.11650	0.62960	8.2585	0.6668
$S_0 \rightarrow S_3$	12.654	0.00959	0.17720	7.6929	0.3498
$S_0 \rightarrow S_4$	12.657	0.00110	0.06040	7.7147	0.3348
plain-water-plain conformation					
ground	1.357	–	–	2.4474	−0.5002
$S_0 \rightarrow S_1$	12.839	0.01480	0.00061	2.6656	0.5308
$S_0 \rightarrow S_2$	12.840	0.02490	0.00017	2.6531	0.2428
$S_0 \rightarrow S_3$	13.925	0.00000	0.00000	2.5901	0.3258
$S_0 \rightarrow S_4$	13.952	0.00024	0.02789	2.5902	0.1918

ΔE_h – the value of stabilization energy through the hydrogen bond. The meaning of other symbols is the same as for Table 2.

The data computed for 1,4-dioxane-water complexes also demonstrate that only the first four transitions are actually active in radiative electronic excitation. Also the hydration energy is available from the present calculation. This quantity accounts of the stabilization of the (1,4-dioxane)$_2 \cdot H_2O$ complexes in the ground and excited states due to the formation of hydrogen bonds between water and the dioxane molecules.

The hydration energies for the ground and excited states, shown in Table 3, were determined from the difference between the sum of the total complex energy and the excitation energy in a given state of the complex, $E(S_0 \rightarrow S_i)$, and the sum of the energy of all components of the complex, $(2\,E_d + E_w)$, and the excitation energy of 1,4-dioxane molecule, $E_d(S_0 \rightarrow S_i)$:

$$\Delta E_H^{ex} = \Delta E_H^g + h \cdot c \cdot \Delta\omega\,, \quad (3)$$

where ΔE_H^{ex} and ΔE_H^g are the stabilization energies of the complex in the excited and ground state, respectively, $\Delta\omega$ represents the appropriate changes in wave number in the absorption band of the complex, *h* Planck's constant, and *c* the velocity of light.

It can be seen that the values of the hydration energy are negative in the ground state of all the complexes studied. This means that formation of dioxane-water aggregates in the ground state is thermodynamically favourable. On the other hand, the existence of 1,4-dioxane-water complexes in the first excited state, for all structures considered, is not very likely, because of the expected thermodynamic instability of these species. The water-dioxane complexes should also be stable in higher than first excited states with the exception of those containing two molecules of 1,4-dioxane in boat or plain conformation. Moreover, the stability of compleces in higher excited states increases if one dioxane molecule holds chair conformation and another changes conformation to boat or plain.

The energy difference between the ground states of various complexes, as well as the values of the hydration energy, clearly demonstrate that at ambient temperature mostly ch-w-ch complex exists. Thus, this complex is actually interacting with an incident electromagnetic radiation.

The question remains how the present calculations can explain the above mentioned photophysical phenomena accompanying γ-irradiation of water-dioxane mixtures [4, 5]. From an examination of the electronic transition data for neat dioxane in chair conformation (Table 2), and those corresponding to ch-w-ch complex (Table 3), it can be noted that oscillator strengths and transition moments are markedly higher in the former case. This means that the efficiency of energy absorption is higher for neat 1,4-dioxane than for dioxane-water systems. The same factors decrease the efficiency of energy transfer. Therefore, both above effects are presumably responsible for the decrease of the radioluminescence efficiency of PPO with increase of the amount of water in the system (see [4], Fig. 3). It is worth noting that the latter effect is observable until the amount of water in 1,4-dioxane attains the molecular ratio 2:1 [4]. Further increase of water concentration does not influence the efficiency of energy transfer to PPO. This fact strongly supports the existence of $(1,4\text{-dioxane})_2 \cdot H_2O$ already in the ground state. A similar approach can also account for the decrease of the luminescence intensity of 1,4-dioxane in the presence of water, observed by Hirayama et al. [1].

We also attempted to explain the temperature effect in the PPO radioluminescence efficiency observed for dioxane-water mixtures (see [5], Fig. 6). Examination of the E_s and ΔE_H values shown in Table 3 reveals that at ambient temperature, 1,4-dioxane-water mixtures of appropriate molar ratio are composed solely with $(1,4\text{-dioxane})_2 \cdot H_2O$ in the form ch-w-ch. Thus, this species actually interacts with γ-radiation. If electron-vibrational energy conversion and vibrational relaxation were very fast in higher than first electronic states, then the molecule would reach the S_1 state of ch-w-ch structure, which is thermodynamically unstable. If decomposition of the complex in S_1 state to electronically excited 1,4-dioxane and water molecule in ground state occurred instantaneously, the effect of an increase of temperature should be similar to that observed for neat dioxane. The experimental data (see [5], Fig. 6) reveal, however, a different dependence of the PPO relative radioluminescence intensity on reprocical temperature in both cases, thus indicating the different origin of the energy donor. This might mean that a ch-w-ch complex in S_1 state can exist due to the presence of some kinetic barrier to the decomposition to more stable components. The slight increase of the radioluminescence intensity in the low temperature region may result from the increase of the energy interaction (2) due to the increase of the moment of inertia of $(1,4\text{-dioxane})_2 \cdot H_2O$ with temperature. The latter effect is not very pronounced in neat 1,4-dioxane. Another factor influencing the energy transfer process would be the transformation to a more polar structure, e.g. ch-w-b. If the transition state for such a transformation were ch-w-p structure, then the activation barrier should be ca. 0.24 eV (from data in Table 3). This value markedly exceeds the experimental value of the Arrhenius activation energy $(E_{a(exp)})$, equal to 0.02 eV, characteristic for the low temperature region [5]. The theoretically estimated value $(E_{a(theor)})$ correlates much better with the experimental activation energy for the high temperature region, equal to 0.06 eV [5]. Thus, it seems reasonable to assume that the ch-w-ch → ch-w-b transition in S_1 state proceeds as a thermally activated process which takes place in the high temperature region. The correlation between theoretically estimated (0.24 eV) and experimental (0.06 eV) values is rather poor, similar to what was noted above in the case of neat 1,4-dioxane. It is worth noting, however, that the ratios of $E_{\mathrm{a(theor)}}/E_{\mathrm{a(exp)}}$ for the high temperature region are nearly the same for neat 1,4-dioxane and dioxane-water system.

The explanation presented above of the effect of temperature on the radioluminescence efficiency of PPO seems more likely than that proposed by one of us earlier [5], which admitted the formation of PPO excimers.

Undoubtedly, the presented calculations are oversimplified and do not explain all the experimental facts. Noneless, the proposed approach forms an useful framework for considering photophysical features of dioxane and dioxane-water systems.

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