results as quantum-mechanical calculations on the basis of perturbation theory. In addition, it allows expressions to be obtained for the transition probability in adiabatic reactions.

The authors wish to thank R. R. Dogonadze and M. A. Vorotyntsev for discussing the work.

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KINETICS OF ELECTRON TRANSFER REACTIONS BETWEEN MOLECULES OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR RADICAL ANIONS

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UDC 541.138

A comparison is made of the experimental data for electron transfer between molecules of polycyclic aromatic hydrocarbons and their radical anions [1] with the quantum theory of charge transfer in a polar medium. An expression is derived for solvent reorganization energy when electron transfer occurs between nonspherical reactants, which is described by a model based on triaxial ellipsoids.

In a recent study [1] an attempt was made to compare the experimental data for the kinetics of electron transfer between molecules of polycyclic aromatic hydrocarbons and their radical anions $R_1^- + R_2 = R_1 + R_2^-$ with the Marcus theory of electron transfer [2]. In agreement with the Marcus theory it was reckoned that in the absence of Coulombic interaction between the reactants, the rate constant for the electron transfer could be represented as

$$k = A \exp(-\Delta G^*/RT), \quad (1)$$

$$\Delta G^* = E_r/4 + \Delta G^0/2 + (\Delta G^0)^2/4E_r, \quad (2)$$

$$E_r = E_s + E_i, \quad (3)$$

$$E_s = e^2(1/\varepsilon_{op} - 1/\varepsilon_{st})\,(1/2a_1 + 1/2a_2 - 1/r). \quad (4)$$

In expressions (1)-(4) the value of the preexponential coefficient A is identified with Z, the number of collisions of the reactants in unit time, ΔG^* and ΔG^0 are the free energy of activation and the free energy of reaction, E_r is the total energy of reorganization of the system, consisting of the solvent reorganization energy E_s and the reorganization energy of the chemical bonds of the reactants E_i, a_1 and a_2 are the radii of the reactants, r is the distance between the reactant centers, ε_{op} and ε_{st} are the optical and static dielectric constants of the solvent. The further development of the quantum theory of electron transfer reactions in

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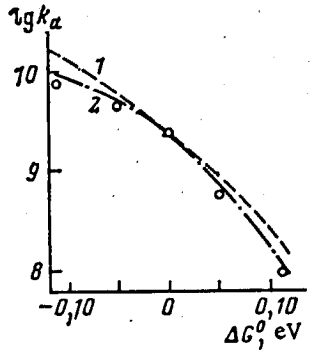


Fig. 1. Plot of log k_a against ΔG^0, corresponding to the theoretical curve of (2) with: 1) E_r = 8.8 kcal mole^{-1}; 2) E_r = 3.4 kcal mole^{-1}.

TABLE 1. Observed and Corrected Rate Constants of Electron Transfer

Reaction*	ΔG^0, eV	k, mole^{-1}·sec^{-1}	k_a, mole^{-1}·sec^{-1}
$A^-+A=A+A^-$	0	$(1,8\pm0,2)\cdot10^9$	$2,4\cdot10^9$
$A^-+B=A+B^-$	0,052	$(5,4\pm1,0)\cdot10^8$	$5,9\cdot10^8$
$A^-+P=A+P^-$	0,113	$(9,6\pm1,5)\cdot10^7$	$9,7\cdot10^7$

*A — Anthracene; B — 1,2-benzanthracene; P — pyrene.

solutions [3] has enabled Eq. (1) to be refined and in particular the limits of its applicability to become apparent. It was shown that in nonadiabatic reactions the expression for the preexponent at constant rate contains, besides a collision factor Z, also a transmission coefficient κ, which is determined by the quantum characteristics of the system and which characterizes the probability of electron transfer when the system attains the reaction configuration:

$$A=Z\cdot\varkappa. \tag{5}$$

In the case of adiabatic processes $\kappa = 1$ and $A = Z$.

In comparing the experimental data with the Marcus theory in [1] a correction was made to the observed rate constants k, by taking into account the diffusion resistance

$$\frac{1}{k_a}=\frac{1}{k}-\frac{1}{k_d}, \tag{6}$$

for which k_d was evaluated from the formula [4]

$$k_d=4RT/3\eta. \tag{7}$$

The value obtained in this way of $k_d = 7.2\cdot10^9$ mole^{-1}·sec^{-1} in 1,2-dimethoxyethane at 25°C is comparable with the rate constant for electron transfer between anthracene and its radical anion, $1.8\cdot10^9$ mole^{-1}·sec^{-1}. The observed and corrected rate constants for three reactions which have been studied are given in Table 1. The calculated values of E_r for the electron exchange reaction in anthracene using the corrected value of the rate constant $k_a = 2.4\cdot10^9$ mole^{-1}·sec^{-1} are 8.8 and 3.4 kcal·mole^{-1}, if for A = Z the values 10^{11} and 10^{10} mole^{-1}·sec^{-1} are taken respectively. The corresponding plots of log k_a against ΔG^0 are shown in Fig. 1. Since the authors of [1] reckoned that the value of $Z = 10^{10}$ mole^{-1}·sec^{-1} is improbably low, they used in the subsequent treatment the value E_r = 8.8 kcal·mole^{-1}, although the corresponding plot of ln k_a against ΔG^0 differs considerably from the experimental data. Supplementary studies of the dependence of the rate constants for electron transfer on the dielectric constant of the medium [1] also pointed to a much lower value of the reorganization energy E_r. This was also indicated by the small difference between the experimental values of the activation energies of the process in the two studied solvents with different dielectric constants [1].

Below an analysis is made of the experimental data for the kinetics of electron transfer between polycyclic aromatic molecules and their radical anions, in which no assumption is made regarding the adiabaticity of the process, and evaluation of the diffusion constant k_d from formula (7) is not used, the deduction of which is based on a definite theoretical model

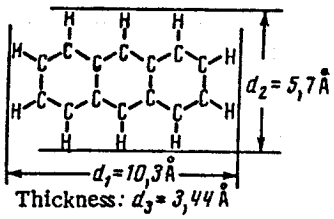


Fig. 2

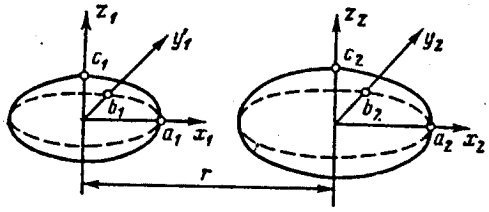


Fig. 3

and correspondence of the predictions of which with experimental values of k_d requires independent verification.

The experimental rate constants given in [1] for the three reactions (Table 1) k_1, k_2, k_3 permit us, by using known values of ΔG_1° and ΔG_2° and the formulas (1), (2), and (5), to set down three equations which contain the unknown parameters A, E_r and k_d:

$$(k_1^{-1}-k_d^{-1})^{-1}=A\exp(-E_r/4RT), \tag{8}$$

$$(k_2^{-1}-k_d^{-1})^{-1}=A\exp[-(E_r/4+\Delta G_1^\circ/2+(\Delta G_1^\circ)^2/4E_r)/RT], \tag{9}$$

$$(k_3^{-1}-k_d^{-1})^{-1}=A\exp[-(E_r/4+\Delta G_2^\circ/2+(\Delta G_2^\circ)^2/4E_r)/RT]. \tag{10}$$

Reorganizing equations (8)-(10) it is possible to reduce them to a single equation containing one unknown value E_r:

$$\frac{k_2^{-1}\exp[-(\Delta G_1^\circ/2+(\Delta G_1^\circ)^2/4E_r)/RT]-k_1^{-1}}{\exp[-(\Delta G_1^\circ/2+(\Delta G_1^\circ)^2/4E_r)/RT]-1}=\frac{k_3^{-1}\exp[-(\Delta G_2^\circ/2+(\Delta G_2^\circ)^2/4E_r]-k_1^{-1}}{\exp[-(\Delta G_2^\circ/2+(\Delta G_2^\circ)^2/4E_r)/RT]-1}. \tag{11}$$

Graphical solution of equation (11) leads to the value $E_r \approx 6.0$ RT = 3.6 kcal/mole. For this, $k_d \gg k_1, k_2, k_3$. The preexponential coefficient $A = Z\kappa$ equals $8\cdot10^9$ mole$^{-1}\cdot$sec^{-1}. Taking the value of Z as $Z = \omega_0\Delta V/2\pi \approx 10^{11}$ mole$^{-1}\cdot$sec^{-1}, where $\omega_0 = 10^{12}$ sec^{-1} is the effective frequency of the dielectric fluctuations of the solvent [3], $\Delta V = 4\pi R^2\Delta R = 400\pi$ Å^3 is the reaction volume, we reach the following conclusions: 1) The considered reactions occur nonadiabatically with $\kappa \ll 1$; 2) the reactions proceed kinetically and under the experimental conditions diffusion resistance is absent; 3) the experimental rate constants are well described by formulas (1) and (2) where E_r = 3.6 kcal/mole.

In [1] an attempt was made to compare the experimenally determined values of E_r = 3.4 kcal/mole with $Z = 10^{10}$ mole$^{-1}\cdot$sec^{-1}, and E_r = 8.8 kcal/mole (with $Z = 10^{11}$ mole$^{-1}\cdot$sec^{-1}) with the values of E_s obtained by evaluation from formula (4). For this the reasonable assumption was made for the type of reaction studied that $E_i \ll E_s \approx E_r$. According to formula (4), the reactants are depicted as spheres of radii a_1 and a_2. However the molecules of the polycyclic aromatic hydrocarbons under consideration, for example anthracene and its radical anion, have a planar structure (Fig. 2) and use of a model of conducting spheres can lead to considerable inaccuracy in the evaluation of E_s. If the radius is taken as half the largest dimension of the anthracene molecule calculated from the lengths of the C-C, C-H bonds and van der Waals radii, a = 5.15 Å, r = 2a, then in DME E_s = 12.5 kcal/mole, and if a = 2.85 Å, r = 2a, then E_s = 22.5 kcal/mole. The values of E_s obtained in this way, as noted in [1], do not agree with the experimental values.

It was of interest to calculate the reorganization energy of the solvent in reactions in which molecules of polycyclic aromatic hydrocarbons participate using a model of the reactants as conducting triaxial ellipsoids (Fig. 3).

An expression for the reorganization energy of the solvent (4) can be obtained in the quantum theory in a longwave approximation of the more general formula taking into account spatial and frequency dispersion of the permittivity of the medium [5]:

$$E_s=\frac{1}{8\pi}\left[\frac{1}{2\pi}\int_0^{kT/\hbar\alpha(1-\alpha)}\frac{d\omega\,\mathrm{Im}\,\varepsilon(\omega,k=0)}{|\varepsilon(\omega,k=0)|^2}\right]\int(\vec{D}_i-\vec{D}_f)^2\,dv=\frac{1}{8\pi}\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_{st}}\right)\int_{\infty-V_1-V_2}(\vec{D}_i-\vec{D}_f)^2dv, \tag{12}$$

where $\vec{D}_i$ and $\vec{D}_f$ are the electric induction vectors of the system in the initial and final

states, $\varepsilon(\omega, k = 0)$ is the complex dielectric constant of the medium depending on the frequency ω. The integral was calculated for the whole volume of the solvent with subtraction of the volume of the two reacting species. Formula (4) is derived from (12) on the assumption that the reacting species are conducting spheres and additionally it is assumed that $r \gg a_2$. Expression (4) is applied with an accuracy up to terms of the order $(a/r)^4$, since in its derivation the intrinsic volumes of the ions were not fully taken into account. A refined calculation leads to the expression [6]*

$$E_s = e^2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} - \frac{a_1}{4(r^2-a_1^2)} - \frac{a_2}{4(r^2-a_2^2)} - \frac{1}{8r}\ln\frac{(r-a_1)(r-a_2)}{(r+a_1)(r+a_2)}\right]. \quad (13)$$

Moreover in the case of strong polarizability of the reactants and for small distances between the reacting species a significant effect through mutual polarizability of the reactants can occur [8], which is of the order of $(a/r)^4$. However, for not too small values of r the effect of polarizability may be disregarded.

In the case of electron transfer between multiatom reactants the model of conducting spheres, as already noted, can lead to inaccuracies. The first attempt to describe nonspherical reactants was made in a paper by Peover and Powell [9] who suggested describing reactants with a nonuniform distribution of charge by a set of charged spheres. Hale [10] used a similar model for calculating the energy of reorganization during electrochemical reduction of substituted aromatic nitro compounds. A model of touching spheres which took into account the orientation effects of the reactants and the force picture was applied in another study [11] in order to calculate the energy of reorganization of the solvent in electron transfer reactions involving a series of substituted nitro compounds.

In an earlier paper [12] in order to describe the electron transfer in radical anions containing benzene rings a model was proposed of the reactants as conducting ellipsoids of revolution. In the case where electron transfer occurs in a direction perpendicular to the plates of the benzene rings, the expression for the solvent reorganization energy is

$$E_s = e^2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\left[\frac{\operatorname{arctg}\frac{\sqrt{a_1^2-c_1^2}}{c_1}}{2\sqrt{a_1^2-c_1^2}} + \frac{\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}}{2\sqrt{a_2^2-c_2^2}} - \frac{1}{r} + \frac{a_1^2-c_1^2}{3r^3} + \frac{a_2^2-c_2^2}{3r^3}\right]. \quad (14)$$

In the case where the reactants are so arranged that the planes of the benzene rings coincide E_S has the form

$$E_s = e^2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\left[\frac{\operatorname{arctg}\frac{\sqrt{a_1^2-c_1^2}}{c_1}}{2\sqrt{a_1^2-c_1^2}} + \frac{\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}}{2\sqrt{a_2^2-c_2^2}} - \frac{1}{r} - \frac{a_1^2-c_1^2}{6r^3} - \frac{a_2^2-c_2^2}{6r^3}\right]. \quad (15)$$

In Eqs. (14) and (15) $a_1 \geq c_1$, $a_2 \geq c_2$, a_1 and a_2 are the major semi-axes of the ellipsoids of revolution and c_1 and c_2 are the minor semi-axes. Equations (14) and (15) are derived with an accuracy up to terms of the order $(a_1/r)^4$, $(a_2/r)^4$.

We calculate E_S, assuming that the ellipsoids have the semi-axes $a_1 \geq b_1 \geq c_1$ and $a_2 \geq b_2 \geq c_2$, and that the distance between their centers is r. We consider initially the case of an arrangement of ellipsoids where their planes x_1, y_1 and x_2, y_2 coincide (Fig. 3).

The space integral appearing in (12) can be written as follows

$$\int_{\infty-V_1-V_2} (\vec{D}_i-\vec{D}_f)^2\,dv = \int_{\infty-V_1-V_2} \vec{D}_i^2\,dv + \int_{\infty-V_1-V_2} \vec{D}_f^2\,dv - 2\int_{\infty-V_1-V_2} \vec{D}_i\vec{D}_f\,dv. \quad (16)$$

The induction $\vec{D}_i$ in the initial state is established by the charge e distributed over the surface of the ellipsoid S_1. In the final state $\vec{D}_f$ is established by the charge e, distributed over the surface S_2.

*In [7] Eq. (13) has misprints.

Changing from volume integration to surface integration we obtain

$$\int\limits_{\infty-V_1-V_2}(\vec{D}_i-\vec{D}_f)^2\,dv=\int\limits_{S_1+S_2}\varphi_i\nabla\varphi_i\,d\overleftarrow{S}_1+\int\limits_{S_1+S_2}\varphi_f\nabla\varphi_f\,d\overleftarrow{S}_2-2\int\limits_{S_2}\varphi_i\nabla\varphi_f\,d\overleftarrow{S}_2=$$
$$=4\pi e\varphi_i(S_1)+4\pi e\varphi_f(S_2)-2\int\limits_{S_2}\varphi_i\nabla\varphi_f\,d\overleftarrow{S}_2+\int\limits_{S_2}\varphi_i\nabla\varphi_i\,d\overleftarrow{S}_2+\int\limits_{S_1}\varphi_f\nabla\varphi_f\,d\overleftarrow{S}_1, \tag{17}$$

where $\vec{D}_{i,f}=-\nabla\varphi_{i,f}$, $\varphi_i(S_1)$ and $\varphi_f(S_2)$ are the potentials at the surfaces of the ellipsoids S_1 and S_2 and the arrow of $y\overleftarrow{S}$ indicates that in the calculation of the integrals the internal normal to the surface has been used. For the calculation we will disregard the effect of mutual polarizability of the reactants.

From formula (17) one can readily obtain an approximate expression for the reorganization energy for a model of conductors of arbitrary shape. Since $\varphi_i(S_1)=e/C_1$, $\varphi_f=e/C_2$, where C_1 and C_2 are the capacities of the conductors, and taking into account that for large distances between the conductors $\varphi_i(S_2)\approx\varphi_i(r)=\frac{e}{r}$, $\int\limits_{S_2}\varphi_i\nabla\varphi_i\,d\overleftarrow{S}_2\sim\frac{a^3}{r^4}$, $\int\limits_{S_1}\varphi_f\nabla\varphi_f\,d\overleftarrow{S}_1\sim\frac{a^3}{r^4}$, we find from (11)

$$E_s\approx e^2\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_{st}}\right)(1/2C_1+1/2C_2-1/r). \tag{18}$$

In order to obtain an expression for E_S with a higher accuracy, which would permit calculations to be made with not too large values of r, for example with an accuracy up to terms of the order of $(a/r)^5$, $(b/r)^5$, $(c/r)^5$, it is necessary to calculate with the indicated accuracy the integrals

$$\int\limits_{S_2}\varphi_i\nabla\varphi_f\,d\overleftarrow{S}_2,\quad\int\limits_{S_1}\varphi_f\nabla\varphi_f\,d\overleftarrow{S}_1,\quad\int\limits_{S_2}\varphi_i\nabla\varphi_i\,d\overleftarrow{S}_2.$$

For the calculation it is convenient to use the elliptic coordinates ξ, η, ζ, the relation of which with the Cartesian coordinates is determined by the expression [13]

$$\frac{x^2}{a^2+u}+\frac{y^2}{b^2+u}+\frac{z^2}{c^2+u}=1. \tag{19}$$

This equation has three roots $u_1=\xi$, $u_2=\eta$, $u_3=\zeta$, lying within the intervals $\xi\geqslant-c^2$, $-c^2\geqslant\eta\geqslant-b^2$, $-b^2\geqslant\zeta\geqslant-a^2$. The reciprocal relationship of the Cartesian coordinates with the coordinates ξ, η, ζ, is given by the equations

$$x=\pm\left[\frac{(\xi+a^2)(\eta+a^2)(\zeta+a^2)}{(b^2-a^2)(c^2-a^2)}\right]^{1/2},$$
$$y=\pm\left[\frac{(\xi+b^2)(\eta+b^2)(\zeta+b^2)}{(c^2-b^2)(a^2-b^2)}\right]^{1/2},$$
$$z=\pm\left[\frac{(\xi+c^2)(\eta+c^2)(\zeta+c^2)}{(a^2-c^2)(b^2-c^2)}\right]^{1/2}. \tag{20}$$

Distribution of potential on the outside of a charged triaxial ellipsoid has the form [13]

$$\varphi(\xi)=\frac{e}{2}\int\limits_{\xi}^{\infty}\frac{d\xi}{\sqrt{(\xi+a^2)(\xi+b^2)(\xi+c^2)}}. \tag{21}$$

The surfaces of the ellipsoid correspond to $\xi=0$; thus

$$\varphi_i(S_1)=\frac{e}{C_i}=\frac{e}{2}\int\limits_{0}^{\infty}\frac{d\xi}{\sqrt{(\xi+a_i^2)(\xi+b_i^2)(\xi+c_i^2)}}=\frac{e}{\sqrt{a_i^2-c_i^2}}F_i(\nu_i,q_i), \tag{22}$$

$$\varphi_i(S_2)=\frac{e}{C_2}=\frac{e}{2}\int_0^{\infty}\frac{d\xi}{\sqrt{(\xi+a_2^2)(\xi+b_2^2)(\xi+c_2^2)}}=\frac{e}{\sqrt{a_2^2-c_2^2}}F_1(\nu_2,q_2),$$

$$\nu_{1,2}=\arcsin\sqrt{\frac{a_{1,2}^2-c_{1,2}^2}{a_{1,2}^2}};\quad q_{1,2}=\sqrt{\frac{a_{1,2}^2-b_{1,2}^2}{a_{1,2}^2-c_{1,2}^2}}\quad . \tag{23}$$

where $F_1(\nu, q)$ is an elliptic integral of the first order.

In order to calculate the integral $\int_{S_2}\varphi_i\nabla\varphi_i\,d\vec{S}_2$ it is convenient to express first $\nabla\varphi_i\cdot d\vec{S}_2$:

$$\nabla\varphi_i\,d\vec{S}_2=-\left(\frac{\partial\varphi}{\partial n}\right)_{S_2}dS_2=\frac{e\,dS_2}{\sqrt{\eta_2\zeta_2}}\quad . \tag{24}$$

Bearing in mind that on the surface of the ellipsoid S_2 $\xi_1\gg c_1^2$, $\xi_1\gg b_1^2$, $\xi_1\gg a_1^2$, we calculate $\int_{S_2}\varphi_i\nabla\varphi_i\,d\vec{S}_2$ approximately, with an accuracy up to the terms $(a/r)^4$, by substituting for $\varphi_i(\xi_1)$ an expansion derived from (21):

$$\varphi_i(\xi_1)=\frac{e}{\sqrt{\xi_1}}\left[1-\frac{a_1^2+b_1^2+c_1^2}{6\xi_1}+\frac{3a_1^4+3b_1^4+2a_1^2b_1^2+2b_1^2c_1^2+2a_1^2c_1^2}{40\xi_1^2}\right]. \tag{25}$$

Now changing in (24) to the Cartesian coordinates (x_2, y_2, z_2), connected with the ellipsoid S_2:

$$\frac{\eta_2\zeta_2}{a_2^2b_2^2c_2^2}=\frac{x_2^2}{a_2^4}+\frac{y_2^2}{b_2^4}+\frac{z_2^2}{c_2^4}, \tag{26}$$

expressing ξ_1 with the aid of an approximate solution of Eq. (19) first in terms of x_1, y_1, z_1 and then in terms of $x_2 = x_1 - r$, $y_2 = y_1$, $z_2 = z_1$:

$$\xi_1=r^2+2rx_2+x_2^2+y_2^2+z_2^2-a_1^2+\frac{a_1^2(y_2^2+z_2^2)-c_1^2z_2^2-b_1^2y_2^2}{r^2} \tag{27}$$

and integrating with respect to S_2 we obtain

$$\begin{aligned}\int_{S_2}\varphi_i\nabla\varphi_i d\vec{S}_2=\frac{4\pi e^2}{r}\Bigg[1&+\frac{2a_1^2-b_1^2-c_1^2}{6r^2}+\frac{2a_2^2-b_2^2-c_2^2}{6r^2}+\\&+\frac{8a_1^4+3(b_1^4+c_1^4)+2b_1^2c_1^2-8a_1^2(b_1^2+c_1^2)}{20r^4}+\\&+\frac{8a_2^4+3(b_2^4+c_2^4)+2b_2^2c_2^2-8a_2^2(b_2^2+c_2^2)}{20r^4}+\\&+\frac{8a_1^2a_2^2+3(b_1^2b_2^2+c_1^2c_2^2)-4(a_1^2b_2^2+a_2^2b_1^2+a_1^2c_2^2+a_2^2c_1^2)+c_1^2b_2^2+c_2b_1^2}{6r^4}\Bigg].\end{aligned} \tag{28}$$

Using (25) and (27) it is possible to make an approximate calculation of $\int_{S_1}\varphi_i\nabla\varphi_i\,d\vec{S}_1$ and $\int_{S_1}\varphi_i\nabla\varphi_i\,d\vec{S}_1$:

$$\int_{S_2}\varphi_i\nabla\varphi_i\,d\vec{S}_2=-\frac{4\pi e^2}{r}\left(\frac{a_2b_2c_2}{r^3}+O\left(\frac{a^5}{r^5}\right)\right), \tag{29}$$

$$\int_{S_1}\varphi_i\nabla\varphi_i\,d\vec{S}_1=-\frac{4\pi e^2}{r}\left(\frac{a_1b_1c_1}{r^3}+O\left(\frac{a^5}{r^5}\right)\right). \tag{30}$$

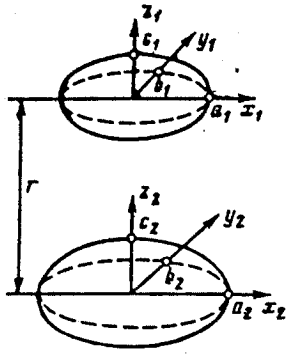


Fig. 4

Substituting expressions (28)-(30) in (17) and (12) and taking into account that in the case which interests us $a_1 = a_2$, $b_1 = b_2$, $c_1 = c_2$, we obtain

$$E_s = e^2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\left\{\frac{F_1(\nu, q)}{\sqrt{a^2-c^2}} - \frac{1}{r}\left[1 + \frac{2a^2-b^2-c^2}{3r^2} + \frac{abc}{3r^3} + \frac{4[8a^4+3(b^4+c^4)-8(b^2+c^2)+2b^2c^2}{15r^4} + O\left(\frac{a^5}{r^5}\right)\right]\right\}. \quad (31)$$

In the deduction of Eq. (31) we assumed that the ellipsoids were arranged so that their axes coincide along the semi-axes a_1 and a_2 (Fig. 3). In the case of an arrangement of the ellipsoids such that the planes of the benzene rings are parallel, the corresponding expression for E_S is derived from (31) by replacement in the square parentheses for $1/r$ $a \leftrightarrows c$ [see Eq. (32)].

The expression $F_1(\nu, q)/\sqrt{a^2 - c^2}$ is the effective reciprocal radius of the reactants. In the case where a = 5.15 Å, b = 2.85 Å, c = 1.72 Å the effective radius is 3.14 Å and for small distances between the reactants, for example in the case of the orientation of the molecules shown in Fig. 4, E_r can be assumed to have low values close to the experimental values. Thus for the indicated orientation from the formula

$$E_s = e^2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\left(\frac{F(\nu, q)}{\sqrt{a^2-c^2}} - \frac{1}{r}\left[1 + \frac{2c^2-a^2-b^2}{3r^2} + \frac{abc}{r^3} + \frac{4[8c^4+3(a^4+b^4)-8c^2(a^2+b^2)+2a^2c^2]}{15r^4}\right]\right) \quad (32)$$

with r = 4.96 Å we obtain E_S = 3.55 kcal/mole which is in good agreement with the experimental value of E_S = 3.6 kcal/mole. Of course the accuracy of Eqs. (31) and (32) is higher, the greater the distance between the reactants; however, for small distances they permit evaluation of the reorganization energy in which the closer is the shape of the molecule to being spherical (least difference between a, b, and c) the greater is the accuracy guaranteed by Eqs. (31) and (32).

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