ASSOCIATION OF RADICAL ANIONS WITH ALKALI METAL CATIONS; II. QUANTUM-CHEMICAL STUDY OF THE ASSOCIATES OF GLYOXAL, NITROBENZENE AND FLUORENONE WITH LITHIUM

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Some radical anions (glyoxal, fluorenone and nitrobenzene) were investigated by the modified LHP method. The calculated effects of cations (in ion pairs) and the effect of the polarity of the medium on energy ratios, conformation, hyperfine splitting constants and electronic spectra in the systems agree well with the available experimental data. It seems that the proposed modified LHP method can be useful in the study of ion-radical systems derived from larger conjugated molecules.

In the first paper of this series[1], the restricted open-shell Longuet-Higgins-Pople method in the π-approximation (PPP-like)[2] was modified so that it would enable calculation of the electronic structure of associates of the conjugated molecules with alkali metals. The method was successfully applied to calculation of the properties of ion pairs of radical anions with alkali metal cations. If the radical anion and cation are considered as supersystem, information is obtained on the interaction energy, the most stable position of a cation with respect to radical anion, the charge transfer from the alkali metal to the conjugated molecule, the spin density distribution at both the radical anion and the alkali metal cation, and the electronic transitions in the ion pair. By calculation, the enthalpy of the formation of ion pairs can be estimated. The solvent effect on these systems can also be evaluated, where solvation energy is expressed according to a simple relationship[3]

$$-E_{\text{solv}} = 1/2(1 - 1/\varepsilon) \sum_{\mu,\nu} Q_\mu Q_\nu \gamma_{\mu\nu} \,. \qquad (1)$$

In this paper are described calculations on the systems of glyoxal, fluorenone and nitrobenzene with lithium. The systems are chosen for two reasons: *i*) they represent structurally different types of molecules; *ii*) they were also studied experimentally in some detail.

CALCULATIONS

The restricted LHP method in the π-approximation (PPP-like) was employed[2]. Details about modifications and parametrization were given[1] in Part I. The geometry shown in Fig. 1 was considered for the systems studied. In the search for the most stable configuration of an alkali metal cation, we did not calculate the overall hypersurface, but the most probable directions of cation approximation were chosen intuitively (Fig. 1). For each position of the alkali metal, spin densities of the entire system were also calculated. Details concerning calculation of spin densities and conversion to hyperfine splitting constants have been described elsewhere[1]. Hyperfine splitting constants, a_N, for nitrogen in the nitro group were expressed as follows

$$a_N = Q_N \varrho_N + 2Q_{NO} \varrho_O , \qquad (2)$$

where the values for the parameters[4] are. $Q_N = 9.9$ mT and $Q_{NO} = -3$ mT. For calculation of the hyperfine splitting constants, $a_{^{13}C}$, the Karplus–Fraenkel relation[5] was used. Electronic transitions were computed by the limited CI method[6], where the monoexcited configurations formed from the 5 highest doubly occupied MO's, a singly occupied MO and the 4 lowest unoccupied MO's were considered.

RESULTS AND DISCUSSION

TOTAL ENERGY CALCULATIONS

Glyoxal–Li *System*

Apart from the structure of the ion pairs, the system is also interesting for its equilibrium between *cis* and *trans* isomers. Calculation of the glyoxal radical anion with-

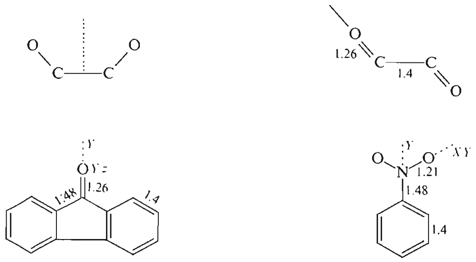

FIG. 1

Structures of the Systems Studied

Dashed lines represents directions of approaching of the cation.

out considering the effect of the cation shows that the *trans*-conformation is 0·6 eV (58 kJ mol^{-1}) more stable and the solvation energy calculated according to relation (*1*) is practically the same for both conformers. The effect of the ion pair formation on these conformations is interesting. *cis*-Glyoxal was also used for establishing α_{OLi} parameters (Part I) so that the minimum of the total energy lies between 0·2 and 0·3 nm (the distance of the Li atom is always given from the oxygen atom). For $\alpha_{OLi} = 1{\cdot}0 \cdot 10^{10}\ m^{-1}$ we obtained a minimum at 0·23 nm (Fig. 2*a*). This parameter was used also in further calculations.

For the *trans*-glyoxal–Li ion pair, the minimum of the total energy lies at $r_{Li} = 0{\cdot}175$ nm (Fig. 2*a*). The energy of this system is, however, 1·46 eV (141 kJ mol^{-1}) higher than the energy of the ion pair with *cis* conformation. The solvation energy

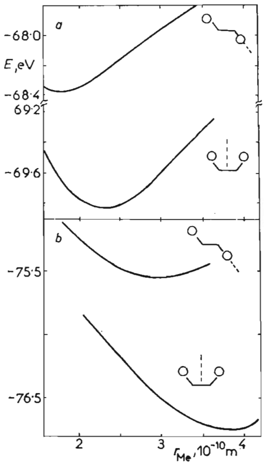

FIG. 2

Dependence of the Energies of the *trans*- and *cis*-Glyoxal Systems on the r_{Li} Distance

a Without considering solvation, *b* considering solvation.

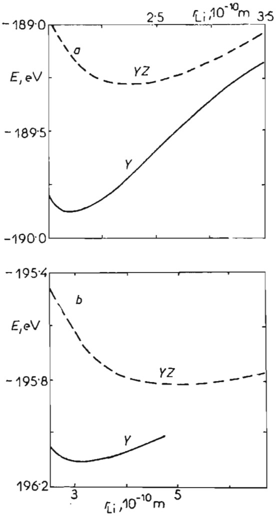

FIG. 3

Dependence of the Total Energy on the r_{Li} Distance for the Fluorenone–Li System in Directions *Y* and *YZ*

YZ is perpendicular to molecular plane in the place of oxygen. *a* Without considering solvation, *b* considering solvation.

(Fig. 2*b*) shifts the minimum in *cis* and *trans* conformations by approximately 0·13 nm to greater distances (because of the increasing solvation energy, as shown in detail in Part I) and lowers the difference between the *cis* and *trans* energies to 1·2 eV (116 kJ mol^{-1}). This result indicates that, in the dissociation of ion pairs to free ions, the conformation of the greater part of the glyoxal radical anions will probably be changed from *cis* to *trans*. This agrees qualitatively with the experimental findings[7] available for diacetyl CH_3—CO—CO—CH_3. Here it was found that the *trans* conformation for radical anions is more stable by at least 0·087 eV (8·4 kJ mol^{-1}), while for the ion pair with Li, the *cis* conformation is more stable by more than 0·13 eV (12·6 kJ mol^{-1}). If we also take into account the non-bonding interaction of the two CH_3 groups (in diacetyl) in terms of empirical 6 – 12 potentials[8], it will be found out that it stabilizes the *trans* conformation by 0·46 eV (44·3 kJ mol^{-1}); however, does not influence the qualitative trend of the above results.

Fluorenone–Li *System*

This system is among those most frequently studied experimentally[9,10]. In the present calculations, the Li cation approached in two directions: in the direction of the C=O bond (*Y* direction) and in the direction perpendicular to the plane of a molecule above the oxygen atom of the carbonyl groups (*YZ* direction). In both directions the total energy has a minimum (Fig. 3*a*). The solvent effect leads to stabilization and to a marked shift of the energy minimum in both directions (Fig. 3*b*). Fig. 4 shows the solvent effect on the energy minimum position in the *Y* direction. It could be deduced form these dependences that, under the experimental conditions, the cation–radical anion distance and thus also their interaction is different in various solvents. This was confirmed by measuring different shifts of the absorption bands in the UV spectrum and different hyperfine splitting constants in the ESR spectra for fluorenone in various solvents[10].

Although the solvation energy in the *YZ* direction is larger than in the *Y* direction, the minimum in the *Y* direction is 0·305 eV (29·2 kJ mol^{-1}) lower. This is in contradiction with the HMO calculation including electrostatic perturbation by Me (ref.[11]). Here the most stable position of Me is above the C=O bond (*YZ* direction). In contrast to calculations in[11,12] our results agree with the conclusions of experimental studies, where, on the basis of the temperature dependences for hyperfine splitting constants, it was found that the minimum in the *Y* direction for small cations, such as Li^+, Na^+, is more than 0·113 eV (10·9 kJ mol^{-1}) lower. Similar results were obtained by *ab initio* calculations on the formaldehyde radical anion–Li^+ system[13], where the minimum in the *Y* direction is by 82 kJ mol^{-1} more stable.

Comparison of the energy (including the solvation energy) of ion pairs and free ions indicates that the system of ion pairs is more stable than that of free ions, *viz.* 0·387 eV (37·4 kJ mol^{-1}) for Li in the *Y* direction and 0·085 eV (8·2 kJ mol^{-1}) for the ion pair with Li in the *YZ* direction.

Nitrobenzene–Li *System*

In seeking the most stable localization of the Li cation with respect to the nitrobenzene radical anion we considered two directions for the approach of the cation (Fig. 1). The total energy has minima in both directions (Fig. 5), the energy minimum in the Y direction being 0·219 eV (21·2 kJ mol^{-1}) more stable than in the XY direction. This is not contradictory to the experimental findings, as in the ESR spectrum[14] hyperfine splittings from the two pairs of equivalent protons (in the *ortho* and *meta* positions) were measured. The solvation energy shifts the minima to greater distances (in the Y direction to 0·29 nm, in the XY direction to 0·26 nm).

If the mutual energy ratios between the free ions and ion pairs are studied, it will be found that, in the system for $\varepsilon = 1$, the ion pairs are 3·68 eV (356 kJ mol^{-1}) more stable. The solvation energy decreases this difference substantially, but for $\varepsilon \rightarrow \infty$ the ion pairs are still more stable than the free ions (by 0·36 eV, *i.e.* 35·8 kJ mol^{-1}). In agreement with this, the experimental value of the ΔH dissociation of ion pairs should be positive. However, for the system nitrobenzene radical anion–Na$^+$ (generated by chemical reduction) in hexamethylphosphoramide Stevenson and coworkers[14] found a negative value of ΔH ($-30{\cdot}2$ kJ mol^{-1}). A positive value ($\Delta H \approx 4-8$ kJ . mol^{-1}) was obtained[15] for electrolytically reduced nitrobenzene in dimethylformamide in the presence of $NaClO_4$ (in excess with respect to nitrobenzene). These

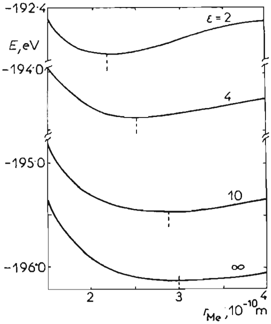

FIG. 4

Dependence of the Total Energy of the Fluorenone–Li System (in Y direction) for Various Dielectric Constants of a Solvent

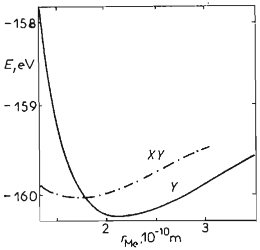

FIG. 5

Dependence of the Total Energy of the Nitrobenzene–Li System on the r_{Li} Distance for the Considered Directions of Approach Y and XY (see Fig. 1) different results are obviously influenced by several factors. In paper[14] hexamethylphosphoramide is used, one of the strongest cation solvating agents. This factor leads to the high specific stability of free ions and therefore can be the main reason for exothermic dissociation of ion pairs in this medium. When working with the excess $NaClO_4$ (ref.[15]), more complex associates can be formed. It is evident that such specific effects are not taken into account in our approximate calculations based on a simple model.

INTERPRETATION OF ESR SPECTRA OF ION PAIRS

Fluorenone–Li *System*

Fig. 6 depicts the variations in the splitting constants, a_H, with distance, r_{Li}, for both directions considered. It was found experimentally[16] for this system that, going from the free radical anion to the ion pair (with Na^+), constant a_H in position 1 will increase from 0·196 to 0·217 mT, in position 2 from 0·003 to 0·017 mT, in position 5 from 0·308 to 0·313 mT and in position 4 from 0·065 to 0·067 mT. In the presence of methanol[17], the constants will change to the values 0·242, 0·026, 0·334 and 0·073 mT, respectively. Our calculations (Fig. 6) specify these changes semiquantitatively for constants at positions 1, 3 and 4 (the constant in position 4 has the opposite sign). The value of a_H for position 2 falls to negative values (for the ion pair). However,

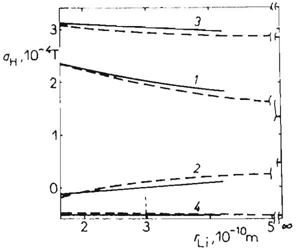

FIG. 6

Dependence of the Calculated a_H Constants of Fluorenone on r_{Li} in Directions Y (full lines) and YZ (dashed lines)

Numbers denote positions of atoms and i.p. the energy minimum position in the ion pair. $r = \infty$ corresponds to the free radical anion.

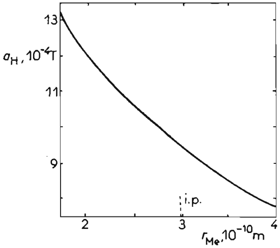

FIG. 7

Dependence of Calculated Constant a_{13C} of Fluorenone on the r_{Li} Distance it does not disagree qualitatively with the experimental value, as for smaller distances, r_{Li}, at which $a_{H_2} < 0$, the absolute value of constant a_{H_2} increases.

Fig. 7 depicts the dependence of splitting constant ^{13}C of the carbonyl group on r_{Li} in the Y direction. An increase of this constant with the approach of the cation is consistent with the experimental results[10], according to which the constant increases from a value of 0·196 mT for the free radical anion to 0·63 mT for the ion pair with Li^+.

Nitrobenzene–Li *System*

We calculated the effect of the distance of Li from nitrobenzene on the splitting constants for the Y direction. Calculations show that this direction is energetically more suitable and gives the same splitting constants for *ortho* and *meta* hydrogens, which agrees with the experimental findings[14]. Dependence of the a_H and a_N constants respectively on distance rx_i is illustrated in Fig. 8.

Experimental study[14] of the changes in the hyperfine splitting constants going from the free radical anion to the ion pair showed that a_N constant increases from 0·849 mT to 1·085 mT (for Li^+ ion pair) and constant a_H for the *para* proton decreases from 0·421 mT to 0·410 mT. In our calculations, the change of a_N and a_H respectively is relatively well specified for the *para*-hydrogen (Fig. 8).

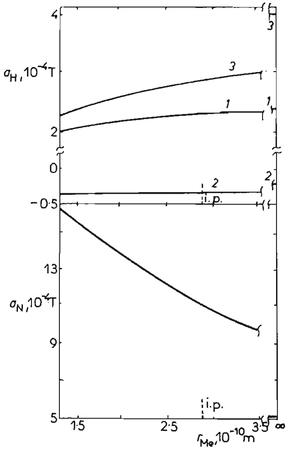

FIG. 8

Dependence of Calculated Constants a_H and a_N of Nitrobenzene

For details see caption for Fig. 6.

Constant a_{Li} calculated for the systems considered are always positive and increase with increasing distance r_{Li}. On the basis of these calculations, it can be assumed that the effect of localization of an unpaired electron on an alkali metal occurs predominantly. Contribution from spin polarization is smaller. Experimental data are known only for Na and K, where the constants a_{Me} are between 0·03 and 0·05 mT, respectively[18]. The constant a_{Li} calculated at the energy minimum of an ion pair has the value, ~0·14 mT.

CALCULATIONS OF THE ELECTRONIC SPECTRA OF ION PAIRS

Apart from the calculation of the total energy and spin densities we calculated the individual electronic transitions by the CI method for each radical anion–cation structure. Here we will describe calculations on the fluorenone radical anion–Li^+ system. Table I contains the energies and oscillator strengths of the individual electronic transitions. It can be seen that the first three transitions are shifted hypsochromically with the approach of a cation. Clearly, the cation stabilizes the ground state more than the respective excited state, as in the ground state there is a negative charge (caused mainly by an unpaired electron) localized predominantly on the carbonyl group. On the other hand, in the mentioned three states the electron charge is transferred from the C=O group to benzene rings considerably more distant from Li^+ and thus also the mutual stabilization is smaller. Similar changes were

TABLE I

Electronic Transitions Calculated for the Fluorenone Radical Anion–Li^+ System for Various Distances r_{Li}

r_{Li}, 10^{-10} m Y Direction	1st transition		2nd transition		3rd transition		transition r.a.[b] → → Li^+	
	E^a	f	E^a	f	E^a	f	E^a	f
1·55	17·12	0·014	19·08	0·075	22·55	0·010	33·35	0·027
1·70	16·81	0·013	18·95	0·082	22·55	0·006	31·60	0·017
2·30	15·81	0·012	18·35	0·098	22·57	0·001	25·39	0·011
2·60	15·43	0·012	18·10	0·100	22·54	0·001	23·15	0·009
3·00	15·00	0·011	17·80	0·110	22·48	0·006	20·68	0·005
3·50	14·60	0·011	17·50	0·110	22·37	0·013	18·22	0·003
4·00	14·30	0·010	17·29	0·110	22·25	0·020	16·28	0·001
r.a.[b]	13·06	0·009	16·10	0·104	21·37	0·015	—	—

[a] Energies are given in 10^3 cm^{-1}; [b] r.a. calculation for the free radical anion.

also found experimentally[10,16,19]. The intense absorption band of fluorenone at 18000 cm^{-1} (corresponding mainly to the second transition in Table I) is shifted hypsochromically during ion pair formation by 1000–2000 cm^{-1}. Although simultaneous formation of dimers complicates experimental study of this shift[19], agreement with the calculated changes of the electronic transitions is evident.

In addition to transitions at which an excitation within the radical anion takes place, the calculation also yields a transition at which excitation from the radical anion to a cation occurs (Table I). With the approach of Li^+, this transition (from a singly occupied MO of the radical anion) is strongly shifted hypsochromically, which is connected with increasing interaction of the radical anion with the cation. This interaction destabilizes the antibonding MO localized at the alkali metal and stabilizes a singly occupied MO localized at fluorenone. It is worth nothing that, if the band corresponding to this transition could be measured, it would be located at still higher energies, as follows from these calculations, as the solvation stabilization is much smaller in the excited state than in the ground state. Similar changes in electron transitions were also observed for the other systems investigated[20]. Here agreement with the experimental findings is evident.

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