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MONOMER AND DIMER BANDS IN THE VISIBLE SPECTRUM OF ALKALI METAL DIBENZOSUBERONE KETYL

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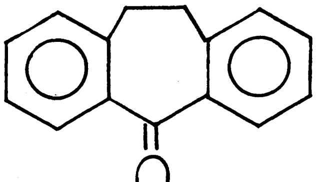
The visible spectra of the alkali metal (M^+) dibenzosuberone (D^-) ketyl were measured and assigned to the three species, the ion pair D^-M^+, its ionic dimer $(D^-M^+)_2$, and the free anion D^-. The wave numbers of the absorption maxima are linearly correlated to Z/R, where Z is a cationic charge and R Pauling's cationic radius. The coordination of dibenzo-18-crown-6 to the cation causes dissociation of $(D^-M^+)_2$ into a contact ion pair.

Some part of ion pairs of radical anions produced with alkali metal reduction in etheral solutions are known to aggregate into various forms of clusters. Among those clusters, in rigid media the presence of ionic dimers (ion quadruplet and triplet) with a definite structure was confirmed by means of epr spectroscopy.$^{1)}$ Although such dimers have been considered to exist in liquid media and affect the electronic absorption spectra, especially in visible range, of the radical anion, the available information is limited.$^{2)}$


(1)

We found that visible spectra of the alkali metal dibenzosuberone (1) ketyl exhibit two resolved bands in the range of 600--700 nm, which are assigned respectively to the ketyl ion pair D^-M^+ and its ionic dimer $(D^-M^+)_2$. For examples, Figs. 1 and 2 show the temperature and concentration dependence of the visible spectra of the lithium ketyl in tetrahydrofurane (THF). The spectrum consists of two bands at 608 nm and 656 nm in the concentration range of 10^{-3}--10^{-5} M.$^{3)}$ On dilution the intensity of the band at 656 nm relative to the one at 608 nm increases. On lowering the temperature from 25 °C to -80 °C, the band

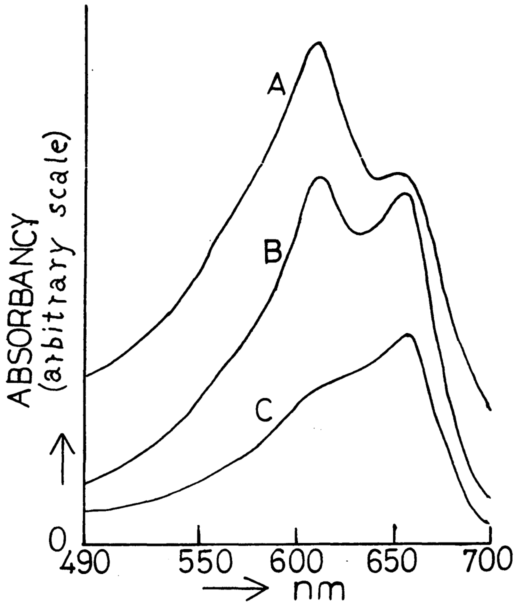


Fig. 1. Concentration dependence of the visible spectrum of the lithium dibenzosuberone ketyl in THF.
A: 1.7x10^{-3} M, B: 2.1x10^{-4} M, C: 1.4x10^{-5} M.

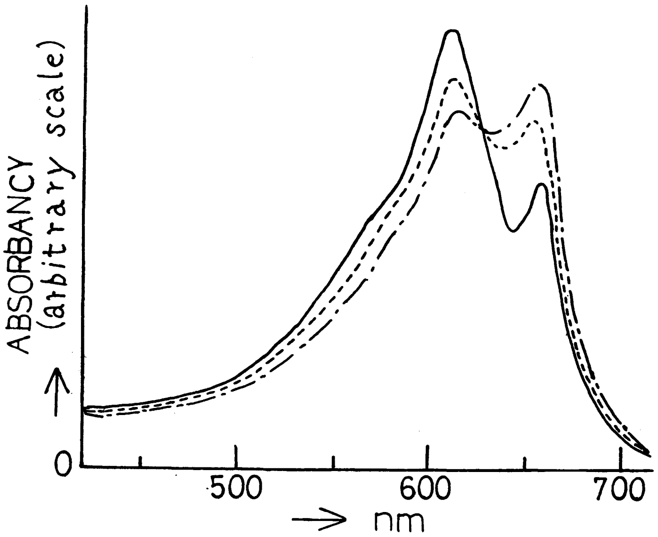


Fig. 2. Temperature dependence of the visible spectrum of the lithium dibenzosuberone ketyl in THF.
—·—·—: 25 °C, - - - - - -: -30 °C, ———: -78 °C.

at 608 nm increases its intensity at the expence of the band at 656 nm, an isosbetic point being observed at 625 nm. The concentration and temperature dependences are not affected by addition of lithium tetraphenylborone. Thus the band at 656 nm can be assigned to the non-aggregated ion pair and the one at 608 nm to its ionic dimer (ion quadruplet). The occurence of the isosbetic point almost excludes the possibility of the presence of species other than these two. Similar spectra were obtained with THF solutions of the ketyl of sodium, potassium and cesium. Both the monomer and dimer bands show bathochromic shifts with an increase in cationic radius. The absorption maxima in THF at 25 °C are listed in Table 1, together with those of the monomer in the presence of dibenzo-18-crown-6. The dimethylformamide (DMF) solution gives a single band at 724 nm, which was found to be independent of the cation species. This spectrum should belong to the free anion.4)

A plot of V_m vs Z/R,5, 6) where V_m is an abporption maxima in wave number (cm^{-1}), R a cationic radius in Å and Z a cationic charge (2 for the dimer), was found to be linear throughout the monomers and the dimers, as is shown in Fig. 3. The extrapolation of this linear plot to infinitely large radius of cation yields 13.7 kK (720 nm) for the absorption maximum of the free anion. This value agees well with the experimental one in DMF. The presence of the linear correlation in common with the

cation	D^-M^+	$(D^-M^+)_2$	C-6	R (Å)
Li	656	608	608 656	0.60
Na	676	636	689	0.96
K	691	663	696	1.33
Cs	698	671	701	1.66

Table 1. Dependence of λ_{max} on the cation for the dibenzosuberone ketyl in THF at 25 °C.

C-6: THF saturated with dibenzo-18-crown-6.

R: Pauling's cationic radius in Å.

λ_{max}: in nm.

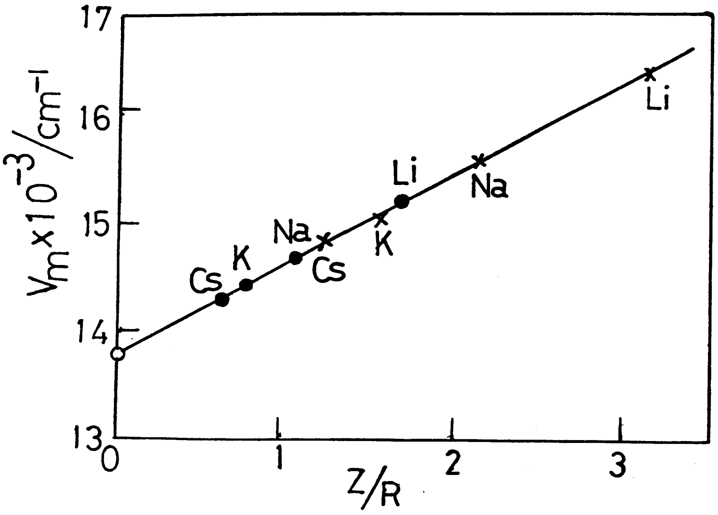


Fig. 3. Correlation between V_m and Z/R for alkali metal (M^+) dibenzosuberone (D^-).

V_m: Absorption maximum in wave number (cm^{-1}).

●: D^-M^+ and Z=1. x: $(D^-M^+)_2$ and Z=2.

○: D^- (free anion).

monomers and dimers ensures the above assignment of the bands, especially the band of shorter wave length to the ionic dimer $(D^-M^+)_2$. In addition, this leads to the following insight of the dimer. The electronic state of an anion in the dimer, being little affected by the interaction with the other anion, is considerably perturbed by the Coulombic interaction with the cations. The observed shift of the dimer is due to the latter interaction. The relative locations of two cations in the dimer will be equal to each other and not so different from the location of the cation in the monomer. As to optical spectra of ion pairs of ketyls and related anions, Warhurst and co-workers reported a linear relationship between V_m and the term of Z/(R+2).[7, 8] Application of their procedure to the present system leads to respective plots for each of the monomer and dimer series, the points for lithium ketyl considerably deviating from the linear lines. The extrapolation of the two lines to infinitely large radius gives V_m's different from each other and also different from the experimental value of the free anion.

The positions of absorption maxima of the monomer and dimer are rather insensitive to solvent, but the equilibrium between the species is sensitive. For example, in dimethoxyethane (DME) the spectrum of sodium ketyl mainly consists of the monomer band in the concentration range of 10^{-4} M, whereas in ethyl ether, p-dioxane, and 2,5-dimethyltetrahydrofurane, which are solvents of poor cation-solvating power, the spectra show the dimer band alone even at 10^{-6} M. The reported drastic and puzzling bathochromic shift of the spectra of the alkali metal benzophenone ketyl on varying the solvent from ethyl ether to DME⁹⁾ or from dioxane to THF⁷, ⁸⁾ should be explained on the basis of such a sharp solvent dependence of the monomer dimer equilibrium.

By the addition of dibenzo-18-crown-6 (C-6) to THF solutions of the sodium, potassium and cesium ketyl of (1), the dimer band disappears and the monomer band shifts in a bathochromic direction until the values listed in Table 1. Although the co-ordination of C-6 to the cation elongates the distance between the cation and the anion, the marked cation-dependence of the absorption maxima indicates that the ion pair still belongs to a contact one, in contrast to the case of carbanion ion pairs.10, 11) Addition of C-6 to the THF solution of the lithium ketyl to saturation slightly affects the locations of the maxima and the equlibrium. This will be due to an unfavorable co-ordination of C-6 to the lithium ion.12)

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