

Both the cage effect and relaxation would be more unfavorable at -196° than at 20° , with correspondingly lower yields. Also, these considerations are consistent with larger yields of electrolytic products in polar than in nonpolar media. For benzyl acetate at 20° in hydrocarbons, the plateau value of $G(\text{CO}_2)$ was ca.

2 in contrast to $G(\text{acid})$ between 3 and 4 in polar solvents. The limiting yields in hydrocarbons were only attained at concentrations of benzyl acetate five- to tenfold greater than were required in polar solvents. This suggests that k''/k''' is greater in nonpolar than in polar media, provided k' is the same for both.

Cation and Solvent Effects on the Ultraviolet Spectra of Alkali Salts of Phenols and Enols

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The long wave length maxima of the alkali metal salts of 26 phenols and enols have been measured in two aprotic solvents, 1,2-dimethoxyethane (DME) and dimethylformamide (DMF). Corresponding measurements in water and ethanol have been made or previously reported for salts of 15 of the compounds. Even at concentrations of 10^{-4} to 10^{-5} M, all of the salts in DME and many of them in DMF are associated. In the associated salts, observed bathochromic shifts are proportional to the inverse of the cationic radii, showing the absence of appreciable covalency interactions with the alkali metals. Bathochromic shifts resulting from increased polarity of the aprotic medium (DME to DMF) are produced mainly, if not entirely, by a lengthening or cleavage of the electrostatic bond of the ion pair, rather than by direct solvation of the anion. The "tightness" of ion pairs varies in an accountable manner with variation in the structure of the anion. Hypsochromic shifts observed in going from DMF to water for many of the salts are shown to be roughly proportional to the basicities of the respective anions. The only exceptions are salts of those β -dicarbonyl compounds capable of forming U-shaped anions, presumably with enhanced chelating abilities. It is concluded that most acyclic β -dicarbonyl compounds preferentially assume a U-shape on salt formation, and remain in some form of association with their counterions, even in aqueous solution.

Introduction

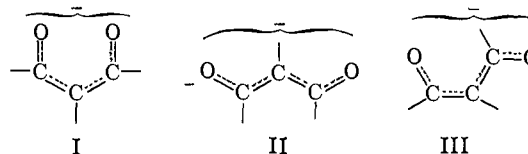
A previous report¹ described the marked acceleration by certain additives of the rate of alkylation of the sodium derivative of diethyl *n*-butylmalonate with *n*-butyl halides in benzene solution. Results indicated that this effect is produced by a specific solvation of the cation acting to dissociate the large ion-pair aggregate (mol. wt. > 10,000) of the sodio derivative known to exist in benzene solution. Extensive comparisons indicated this action to be directly related to the ability of the additive to localize electron density on both sides of a molecular plane, either by a π -orbital mechanism as in dimethylformamide (DMF) or by a lone-pair mechanism as in 1,2-dimethoxyethane (DME).

(1) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895, 2903 (1960).

Further investigation,² however, revealed a quantitative distinction between the action of DME and of DMF. Therefore, these two media were chosen in the present work for an examination of the effect of solvent change on the ultraviolet spectra of alkali salts of a number of β -dicarbonyl compounds. Hopefully, further evidence could thus be brought to bear on (a) the existence of ion association suggested by the kinetic data and (b) the detailed nature of any ion association as probed by variation in the geometry of the anion.

The well-known³ $\pi \rightarrow \pi^*$ transition energies of anions derived from β -dicarbonyl compounds are characterized by strong absorption ($\epsilon_{\text{max}} \sim 10^4$) in the ultraviolet. It has been the usual observation, however, that they are relatively insensitive to environmental influences. Nevertheless, in view of the high dilutions (10^{-4} – 10^{-5} M) experimentally accessible to this approach, detection of even slight shifts in peak positions with variation of the cation would provide conspicuous indication of a strong tendency toward ion association.

Theoretically, anions derived from acyclic β -dicarbonyl compounds can exist in any one or all of three plane-parallel molecular orbital systems which can be termed U-shaped (I), W-shaped (II), and sickle-shaped (III).⁴



Representative examples possessing the unequivocal structure III are not known. Cyclic derivatives giving U-shaped and W-shaped anions, however, are avail-

(2) Part IV in the series, "Specific Solvent Effects": H. E. Zaugg, *ibid.*, **83**, 837 (1961). The present paper is part V.

(3) (a) E. R. Blout, V. W. Eager, and D. C. Silverman, *ibid.*, **68**, 566 (1946); (b) B. Eistert and F. Geiss, *Tetrahedron*, **7**, 1 (1959); (c) M. I. Kabachnik, S. T. Ioffe, E. M. Popov, and K. V. Vatsuro, *ibid.*, **12**, 76 (1961). In these and in many references cited therein, ultraviolet spectral determinations were conducted in hydroxylic solvents.

(4) This terminology has been applied to the analogous pentadlenyl carbanion.^{5a} The need for planarity in this system has been clearly demonstrated^{5b} by the fact that bicyclo[2.2.2]octane-2,6,7-trione is neither enolic nor acidic.

(5) (a) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3031 (1963); (b) W. Theilacker and E. Wegner, *Ann.*, **664**, 125 (1963).

able. This paper reports an ultraviolet spectral comparison of various alkali salts of type I and type II compounds with the alkali salts of corresponding acyclic β -dicarbonyl compounds. β -Diketones as well as β -diesters are represented in all three groups. A series of alkali salts of phenols also is included in the comparison because the transition energies of aryl oxide anions are relatively more sensitive to environmental changes.⁶ The validity of the general approach is supported thereby. In addition, the spectral behavior of many of the salts in water and in ethanol is contrasted with that in the two selected aprotic solvents (DME and DMF).

Experimental

Materials. Cyclohexane (spectral grade), tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were stored over lithium aluminum hydride and then twice distilled (atmospheric pressure) from lithium aluminum hydride in an atmosphere of dry nitrogen just before use. Dimethylformamide (DMF) was purified and stored according to a method reported elsewhere.⁷ The concentration of basic impurity $[(\text{CH}_3)_2\text{NH}]^?$ was usually less than $10^{-5} M$.

Sodium hydride was in the form of a powdered 50% dispersion in mineral oil. Lithium hydride was in the powdered nonsuspended form. Granular cesium graphite, CsC_8 , was commercially obtained⁸ and used as such. Commercial grades of lithium, sodium, and potassium metals were cut free from surface oxides just before use.

The following commercially available compounds were purified by fractional distillation or crystallization: diethyl *n*-butylmalonate (**17**), n^{25D} 1.4210, 99.3% pure by v.p.c. analysis; diethyl 1-methylbutylmalonate (**18**), n^{25D} 1.4260, 99.0% (v.p.c.); diethyl phenylmalonate (**19**), n^{25D} 1.4877, 98.5% (v.p.c.); 2,4-pentanedione (**20**), b.p. 60° (25 mm.), 98.2% (v.p.c.); dibenzoylmethane (**22**), m.p. 74–75°; 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (**9**), m.p. 148–149°; phenol (**3**), b.p. 179–180° (atm.), m.p. 41–42°; *p*-cresol (**2**), b.p. 56° (1 mm.); *p*-chlorophenol (**4**), b.p. 67–68° (1.5 mm.); *p*-methoxyphenol (**1**), m.p. 56–57° (sublimed); *p*-nitrophenol (**5**), m.p. 114–114.5° (sublimed).

The following compounds were prepared by reported methods: 3-isopropyl-2,4-pentanedione (**23**),⁹ b.p. 180° (atm.), n^{25D} 1.4275, 99.0% (v.p.c.); isopropylidene ethylmalonate (**7**),¹⁰ m.p. 109–110°; isopropylidene phenylmalonate (**8**),¹¹ m.p. 138–139° dec.; 2,5,5-trimethyl-1,3-cyclohexanedione (**10**),¹² m.p. 159–162°; 2-allyl-5,5-dimethyl-1,3-cyclohexanedione (**12**),¹³ m.p. 147–148°; 2-*n*-propyl-5,5-dimethyl-1,3-cyclohexanedione (**11**), m.p. 163°,^{12,14} obtained by low pressure (40 p.s.i.) catalytic (Raney Ni) hydrogenation of the

(6) E. Sawicki, T. R. Hauser, and T. W. Stanley, *Anal. Chem.*, **31**, 2063 (1959).

(7) H. E. Zaugg and A. D. Schaefer, *ibid.*, **36**, 2121 (1964).

(8) Callery Chemical Co., Pittsburgh 37, Pa.

(9) H. Adkins, W. Kutz, and D. D. Coffman, *J. Am. Chem. Soc.*, **52**, 3212 (1930).

(10) B. Eistert and F. Geiss, *Chem. Ber.*, **94**, 929 (1961).

(11) P. J. Scheuer and S. G. Cohen, *J. Am. Chem. Soc.*, **80**, 4933 (1958).

(12) R. D. Desai, *J. Chem. Soc.*, **135**, 1079 (1932).

(13) R. Lukeš and J. Hofman, *Chem. Listy*, **51**, 2309 (1957); *Chem. Abstr.*, **52**, 6172 (1958).

(14) W. E. Silbermann and T. Henshall, *J. Am. Chem. Soc.*, **79**, 4107 (1957).

allyl derivative; "citrylidene malonic acid" (**13**),¹⁵ m.p. 190–191° dec.; 3,5,6,7-tetrahydro-8-hydroxy-4-methyl-1(2H)-naphthalenone (**15**),¹⁶ b.p. 100–102° (0.7 mm.), n^{25D} 1.5669; 3-phenyl-2-benzofuranone (**6**),¹⁷ m.p. 114–116°; dipivaloylmethane (**21**),¹⁸ b.p. 78–80° (12 mm.), n^{25D} 1.4566, 99.9% (v.p.c.); 3-benzyl-2,4-pentanedione (**24**),¹⁹ b.p. 114° (1.8 mm.), n^{25D} 1.5260 (purity checked by elemental analysis); 4b,9a-dihydroindeno[1,2-*a*]indene-9,10-dione (**16**),²⁰ m.p. 260–261°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.75, 5.88 (purity checked by elemental analysis); 3-diphenylmethyl-2,4-pentanedione (**25**),²¹ m.p. 114–115° (identity and purity checked by infrared and n.m.r. spectra and by elemental analysis).

3-Triphenylmethyl-2,4-pentanedione (26). A solution of 13.0 g. (0.05 mole) of triphenylcarbinol, 5.0 g. (0.05 mole) of 2,4-pentanedione, and 0.4 g. of *p*-toluenesulfonic acid in 150 ml. of benzene was heated under reflux for 23 hr. in an apparatus designed to trap the water (7 ml., 77%) formed. The cooled mixture was washed with water (four 50-ml. portions) and the benzene was removed by distillation under reduced pressure. The dark residue was taken up in a minimum quantity of 95% ethanol and refrigerated with occasional scratching. The product (0.65 g., m.p. 157–161°) that crystallized was removed by filtration and recrystallized twice from 95% ethanol to give pure **26**, m.p. 166–167°, giving infrared and n.m.r. spectra consistent with the assigned diketone structure (no enol).

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_2$: C, 84.18; H, 6.48; O, 9.34. Found: C, 84.23; H, 6.50; O, 9.43.

3,4,5,6,7,10-Hexahydro-8-hydroxy-4-methyl-1(2H)-naphthalenone (14). A solution of 13.0 g. of 3,5,6,7-tetrahydro-8-hydroxy-4-methyl-1(2H)-naphthalenone (**15**) in 200 ml. of absolute ethanol was hydrogenated at room temperature and 40 p.s.i. hydrogen pressure in the presence of 1.5 g. of 5% palladium-charcoal catalyst. Uptake was complete in 0.5 hr. The catalyst was removed by filtration, the solvent was removed by distillation, and the residue was distilled under reduced pressure to give 9.1 g. (69%) of the title compound, b.p. 100–104° (0.9 mm.). Redistillation gave a center cut (7.1 g.), b.p. 101.5–102.5° (1 mm.), n^{25D} 1.5336, 99% pure (v.p.c.). The infrared spectrum of the undiluted liquid showed no absorption in the 3- μ region and none between 3.5 and 6.2 μ , indicating that this compound, like its unsaturated precursor,¹⁶ is completely enolic.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.29; H, 8.95; O, 17.76. Found: C, 73.38; H, 9.12; O, 18.04.

Preparation of Alkali Metal Salt Solutions and Ultraviolet Spectral Measurements. Method A. From 0.25 to 0.60 mmole of the compound was weighed into a 50-ml. volumetric flask filled with dry nitrogen. After dissolving it in the appropriate solvent and making up

(15) C. E. Berkoff and L. Crombie, *J. Chem. Soc.*, 3734 (1960).

(16) M. S. Newman and A. B. Mekler, *J. Am. Chem. Soc.*, **82**, 4039 (1960). The authors are indebted to Professor Newman for the gift of a generous supply of starting material.

(17) A. Bistrzycki and J. Flatau, *Ber.*, **28**, 989 (1895).

(18) G. S. Hammond, D. C. Nonhebel, and C.-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

(19) G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, 127, 797 (1925).

(20) W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, *ibid.*, 4026 (1957).

(21) R. Fosse, *Compt. rend.*, **145**, 1290 (1907).

to volume, 1 ml. of this stock solution was diluted to 100 ml., using another nitrogen-filled volumetric flask and a nitrogen-filled pipet. This sample solution was then placed in a glove box filled with nitrogen (dried by circulation through $\frac{1}{16}$ -in. pellets of Linde Type 4A Molecular Sieve) and containing an electric centrifuge, together with other necessary reagents and equipment.

The following operations were conducted in the glove box: in 10–12 ml. of the sample solution in a 15-ml. graduated conical centrifuge tube was suspended excess sodium hydride (0.04 to 0.06 g. of 50% suspension, estimated with a measuring spatula). The slurry was then centrifuged, the supernatant fluid was decanted from the sodium hydride, 8–10 ml. of fresh sample solution was added to it, and the operation was repeated. During this procedure, portions of pure solvent were submitted to the same treatment with sodium hydride in another centrifuge tube. Finally, a third 10–12-ml. portion of the sample solution was added to the washed sodium hydride and allowed to stand, with occasional stirring, for from 1 min. to 6 hr., depending on the particular compound and solvent used. In general, the weaker acids required longer times in DME, but in DMF, 15 min. usually sufficed. A sample of pure solvent was treated similarly in the second tube. A final centrifugation gave a clear supernatant sample solution, part of which (3 ml.) was transferred by pipet to a cylindrical ultraviolet cell and then discarded. Repetition with a second 3-ml. sample using the same pipet gave a filled cell which was stoppered and placed in a microdesiccator over calcium hydride. The two reference cells were filled with the sodium hydride treated solvent in the same way and likewise placed in the desiccator.

The filled and stoppered ultraviolet cells (in the desiccator) were removed from the glove box and placed in a Cary Model 11 recording spectrophotometer. The full ultraviolet spectrum (210–400 $m\mu$ for DME, THF, and cyclohexane, and 260–400 $m\mu$ for DMF) was then run off. Afterwards, peak positions were located more precisely by redetermination at the slower scanning speed of the instrument. Peak stabilities were rechecked after allowing the solution to stand for an hour. The experiment was judged satisfactory if the decrease in absorptivity did not exceed 10% in that time.

Either the stock solution or the sample solution, or an appropriate dilution of the former, was used for determining the spectrum of the substance before alkali treatment.

Molar absorptivities (ϵ) were obtained by dividing the measured absorbances by the molar concentrations. Transition energies (ΔE) in kcal./mole were calculated from the relationship, $\Delta E = 2.86 \times 10^4/\lambda_{\max}$ (in $m\mu$).

Method B. Because of its low density, lithium hydride could not be removed by centrifugation. Therefore, method A was modified by using 10–12-ml. fritted glass (porosity C or D) filter beakers as reaction vessels. The treated sample solution was then filtered by nitrogen pressure directly into the ultraviolet cell. Identical treatment was given to the reference solvent, and all operations were conducted in the glove box. When sodium hydride was employed,

it was found unnecessary to wash out the mineral oil dispersant prior to final treatment.

Method C. In this method the alkali metals, lithium, sodium, and potassium, and cesium graphite were used to form the corresponding salts. A 12–15-ml. glass-stoppered weighing bottle was employed as the reaction vessel and the clear solution was transferred by pipet directly to the ultraviolet cell. Usually, at intervals, the lumps of alkali metal, while still submerged in the sample solution (or pure solvent), were squeezed into small sheets using a stainless steel dissecting forceps. This increased the surface area available for reaction and substantially reduced the necessary contact time. Again, all operations were conducted in the glove box. Because the alkali metals, unlike the hydrides, react with DMF, this procedure generally was restricted to the preparation of solutions in DME. However, cesium graphite, like the hydrides, is inert to DMF. Its high density and granular character, furthermore, made method C the most convenient for preparing cesium salts in either solvent. In most instances the observed spectra were largely unaffected by prolonged contact with the alkali metal. However, in a few cases (compounds **15**, **16**, **20**, and **23**) where secondary reactions appeared to take place, relatively short contact times of 1 to 3 min. were necessary when method C was employed.

When salt formation failed by one method it sometimes succeeded by another. Thus, with the lithium salts of phenol and of compound **12** in DME, method B failed but method C produced at least a measurable concentration of salt; with the sodium salt of *p*-chlorophenol in DME, method C failed but method B succeeded; the lithium salt of dimedone was precipitated from solution in DME by method B but not by method C; formation of the lithium and sodium salts of dipivaloylmethane (**21**) in DME was incomplete by method B but complete by method C; and the sodium salt of compound **23** formed in DME using methods A and B, but reaction was incomplete using method C.

It is noteworthy that whenever either THF or DME, which had been dried over sodium metal, was inadvertently employed as solvent, sample solutions gave spectra characteristic of the respective sodium salts. Thus, the solubility of sodium metal in these ethers is clearly sufficient to effect complete conversion to salt at the low concentrations of acid used in the sample solutions.²²

Independent Checks of the Validity of the Methods. A number of spectra were determined using more than one of the foregoing methods. Thus, the sodium salts of the following compounds (identified by number) were formed in the solvent and by the methods indicated in parentheses; **3** (DME, A and C); **12** (DMF, A and B); **14** (DME, A and C); **15** (DME, A and C; DMF, A and B); and **23** (DMF, A and B; DMF, A and B). Concordant results were obtained in all cases. Furthermore, over the 3-yr. span of this work, standardization was maintained by repeated determination of the peak position of sodio-2,4-pentanedione (usually in DMF). Three operators and two different Cary spectrophotometers were

(22) Compare J. L. Down, J. Lewis, B. Moore, and G. Wilkinson; *J. Chem. Soc.*, 3767 (1959).

involved at different times, but reproducibility was always within $\pm 0.5 \mu\text{m}$. Two other validations of the method also were conducted. One involved the preparation of a solution of sodio-2,4-pentanedione in DMF sufficiently concentrated to be titrated. This was then diluted for the ultraviolet determination which checked the results of method A. The other method entailed isolating the sodium and potassium salts of *p*-nitrophenol and establishing that their solution spectra checked those obtained by methods A and C.

A stirred 0.1020 *M* solution of 2,4-pentanedione in DMF was cooled to 5–10° and treated with 0.40 g. (excess) of a 50% mineral oil dispersion of sodium hydride in an atmosphere of nitrogen. During a period of 1 hr., the stirred solution was allowed to come to room temperature, then excess hydride was allowed to settle, and the supernatant liquid was drawn into a nitrogen-filled vessel through a plug of glass wool. Two 5-ml. aliquots of this solution were each added to 25 ml. of distilled water and titrated to a bromthymol blue end point with 0.1000 *N* hydrochloric acid. The base concentrations were thus determined to be 0.0990 *M*, showing that 97% of the diketone had been converted to its sodium derivative. One milliliter of this DMF solution was then diluted to a concentration of 10.12×10^{-5} *M* with pure DMF. The spectrum of this solution was $\lambda_{\text{max}} 294 \mu\text{m}$ ($\epsilon_{\text{max}} 1.77 \times 10^4$) compared to $\lambda_{\text{max}} 294 \mu\text{m}$ ($\epsilon_{\text{max}} 1.80 \times 10^4$) found by method A.

Sodium and Potassium p-Nitrophenoxides. A cooled, filtered solution of 8 g. of *p*-nitrophenol in 50 ml. of ethanol was treated with an excess of a filtered 25% aqueous solution of sodium hydroxide. The yellow precipitate was collected at the filter, washed with ethanol, and dried *in vacuo* at 110° overnight. The dried salt became orange-red in color.

Anal. Calcd. for $\text{C}_6\text{H}_4\text{NO}_3\text{Na}$: C, 44.76; H, 2.50. Found: C, 44.18; H, 3.10.

$\lambda_{\text{max}}^{\text{DME}} 410 \pm 1 \mu\text{m}$ ($\epsilon_{\text{max}} 2.40 \times 10^4$); $\lambda_{\text{max}}^{\text{DMF}} 435 \pm 1 \mu\text{m}$ ($\epsilon_{\text{max}} 3.32 \times 10^4$) (see Table I, compound no. 5 for comparison with methods A (DMF) and C (DME); Parker and Brody²³ also reported $\lambda_{\text{max}}^{\text{DMF}} 435 \mu\text{m}$ for sodium *p*-nitrophenoxide).

Substituting potassium hydroxide for sodium hydroxide in the foregoing procedure gave potassium *p*-nitrophenoxide, $\lambda_{\text{max}}^{\text{DME}} 415 \pm 1 \mu\text{m}$ ($\epsilon_{\text{max}} 2.08 \times 10^4$), $\lambda_{\text{max}}^{\text{DMF}} 435 \pm 1 \mu\text{m}$ ($\epsilon_{\text{max}} 3.92 \times 10^4$).

Beer's Law Behavior. No significant variation in molar absorptivities were observed for the lithium salt of 2,4-pentanedione (20) in the concentration range 3.84 to 15.2×10^{-5} *M* in DME, for the sodium salt of 2,4-pentanedione (20) in the range 1.63 to 6.52×10^{-5} *M* in DMF, or for the sodium salt of dimedone (9) in the range 2.40 to 8.60×10^{-5} *M* in DMF.

Effect of Oxidation on the Ultraviolet Spectrum of the Sodium Salt of Dibenzoylmethane (22). Preliminary investigations soon revealed the difficulty of obtaining stable spectra of these sodium enolates, especially in DME and THF solutions. To determine whether hydrolysis or oxidation was responsible for this instability, a number of experiments were conducted using sodiodibenzoylmethane in DME. An appropriate solution prepared according to method A gave a

(23) A. J. Parker and D. Brody, *J. Chem. Soc.*, 4061 (1963).

spectrum ($\epsilon_{238\text{m}\mu} 15,500$, $\epsilon_{360\text{m}\mu} 19,200$) that remained essentially unchanged for over 3 hr. Then 0.01 ml. of distilled water was added to the 3 ml. of solution in the sample cell. The spectrum remained unchanged for a further period of 18 hr. Then another 0.01 ml. of water was added. Still no significant change in the spectrum was observable over a 30-min. period, so the experiment was terminated.

In a second experiment, a solution which gave a stable spectrum ($\epsilon_{238} 15,900$, $\epsilon_{360} 19,800$) was treated in the cell with 0.01 ml. of *t*-butyl peroxide. No significant change in the spectrum occurred during a subsequent 3-hr. period.

In a third experiment, however, addition of only 0.005 ml. of a 30% hydrogen peroxide solution produced, in a period of 3 hr., a change in a stable spectrum of $\epsilon_{238} 15,400$, $\epsilon_{360} 19,700$ to $\epsilon_{238} 13,300$, $\epsilon_{356} 16,900$. After 18 hr. it became $\epsilon_{230} 9200$, $\epsilon_{352} 11,300$. Thus, both the peak positions and their absorptivities were radically altered.

Molecular oxygen exerted a curious effect. Gassing a solution ($\epsilon_{238} 16,000$, $\epsilon_{360} 19,600$) with oxygen for only 2 min. completely and immediately eradicated the 238-m μ peak but left the 360-m μ peak essentially unaltered ($\epsilon_{360} 19,400$ after 3 hr.). However, similar oxygenation of a stable solution of the sodium derivative of dimedone ($\epsilon_{276} 21,500$ for 3 hr.) resulted in a significant change in absorptivity of the main peak ($\epsilon_{276} 17,800$, 1 hr. after oxygenation).

From these results it is clear that the instability of these spectra stems mainly from an oxidation process.²⁴

Results

Spectra in Aprotic Solvents. Table I summarizes the results of spectroscopic examination of 26 compounds and their salts in DME and DMF. The substances are grouped according to the shape of the molecule in which the anionic charge is delocalized: A, benzenoid; B, W-shaped; C, U-shaped; and D, acyclic (*i.e.*, unspecified shape). Except where no enols were detectable, long wave length absorptions of enolic and phenolic forms (cation = H^+) are listed together with those of the corresponding alkali salts.

Except where reaction was clearly incomplete, the molar absorptivities (ϵ_{max}) of various salts of a given compound do not show wide divergences and no regular trends are recognizable. With few exceptions, however, the absorptivity of a given salt is higher in DMF than in DME.²⁵

Of particular significance to the present work, however, are the observed effects of solvent and cation change on the $\pi \rightarrow \pi^*$ transition energies of the various anions. Where cation effects are sufficiently large, linear correlations ($1/r_c$ vs. ν_c) of cation radii with transition energies are possible in either solvent. These correlations are summarized in Table II.²⁷

(24) Compare E. P. Kohler and R. B. Thompson, *J. Am. Chem. Soc.*, 59, 887 (1937); G. A. Russell, A. J. Moye, and K. Nagpal, *ibid.*, 84, 4154 (1962).

(25) It is noteworthy that the absorptivities of the phenols (Table IA) are virtually identical in the two solvents. In contrast, enol absorptivities in the six cases observed (compounds 14, 15, 20, 21, 22, and 24) are invariably higher in DME than in DMF, in accord with the known²⁶ tendency of solvents of low polarity to favor the enol forms in keto-enol equilibria.

(26) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 689.

(27) Similar linear relationships have been used as evidence for ion

It will be noted that standard errors (SE) vary from 2% (compound **6**) to 36% (compound **4** in DMF) and that nearly all are less than 25%. Standard errors are generally larger in DMF than in DME because only three points, rather than four, are available for linear definition. Most of the ΔE_0 (λ_0) values listed in Table II were obtained by extrapolation to an infinite cation radius (*i.e.*, $1/r_c = 0$). They therefore represent rough estimations of the absorption maxima of the free solvated anions. For compounds **5**, **6**, **9**, and **12**, the absence of cation effects in DMF (infinite slope) despite their occurrence in DME plainly demonstrates ionization in DMF. The *observed* transition energies are therefore taken as ΔE_0 values for these anions in DMF.

Table III gives a quantitative comparison of cation effects with solvent effects for the twelve compounds of Table II. Listed in the second column are the observed reductions in transition energies (see Table I) in DME in going from lithium to cesium salts. In the third column are tabulated the same cation effects in DMF for the eight compounds where such effects were observed. In the last column are recorded the calculated reductions in transition energies (see Table II) in going from DME to DMF for the corresponding anions free of cationic influence. It will be noted that, without exception, the cation effect in either solvent is considerably greater than is the effect on the "free" anion of going from one solvent to another.

Spectra in Protic Solvents. Spectra of the alkali salts of 15 of the compounds of Table I in water and/or ethanol are listed in Table IV. All but one (compound **16**) of the twelve compounds of Tables II and III are included. Among the six compounds (**3**, **5**, **6**, **9**, **20**, **22**) for which data are available, the only hint of an appreciable cation effect is exhibited by the two acyclic derivatives **20** and **22**. The monotonous cation insensitivity of the other four is in marked contrast to their behavior in DME (and in DMF for **3**).

Especially noteworthy is the wide divergence in solvent sensitivity of these essentially cation-free anions. The last column of Table IV lists the increments in their transition energies in going from DMF to water ($\Delta E_0^{\text{H}_2\text{O}} - \Delta E_0^{\text{DMF}}$).³⁰ It will be noted, however, that, with three exceptions (**7**, **8**, and **12**), a blue shift usually results in going from the dipolar aprotic to the protic solvent.

Discussion

In the present work all demonstrations of marked environmental susceptibility to spectral change involve bathochromic shifts with increasing polarity of the

association of alkali metal ketyls in DME and DMF²⁸ as well as in dioxane and tetrahydrofuran.²⁹ These workers added an arbitrary factor of 2 Å. to the cationic radii (r_c) to allow for the anionic radii [*i.e.*, $1/(r_c + 2)$ functions were plotted *vs.* wave numbers]. In the present work, significant differences in linearity between $1/r_c$ plots and $1/(r_c + 2)$ plots generally favored the former.

(28) D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).

(29) H. V. Carter, B. J. McClelland, and E. Warhurst, *ibid.*, **56**, 455 (1960).

(30) In deriving these increments, the experimental or extrapolated ΔE_0^{DMF} values listed in Table II were used in most instances. However, for compounds **7**, **8**, and **10**, it was assumed that they, like their analogs **9** and **12**, are ionized in DMF. Hence, their $\lambda_{\text{max}}^{\text{DMF}}$ values listed in Table I were used to calculate ΔE_0^{DMF} . For compound **21**, the $\lambda_{\text{max}}^{\text{DMF}}$ for its sodium salt was arbitrarily used, as were the $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ values for the sodium salts of **20** and **22**.

aprotic solvent (DME to DMF) and with increasing cation radius (Li^+ to Cs^+). Parallel phenomena have been observed for various alkali metal ketyls^{28, 29, 31, 32} and for a series of organolithium compounds,³³ Similar solvent effects, but diametrically opposite cation effects, were found for a series of alkali salts of aromatic hydrocarbons.³⁴

One interpretation considered by these workers and favored by most of them^{28, 29, 31, 34} proposes that the perturbation of the molecular energy levels of the anion by the cationic field is the primary influence determining the observed spectral shifts in these associated anions. The role of the solvent is secondary. Solvent shifts are mainly produced indirectly by solvation of the cation, more polar aprotic solvents acting to reduce the magnitude of the cationic field relative to that in less polar aprotic solvents.^{35, 36}

The results of the present work also can best be understood by this interpretation. Indeed, the data summarized in Table III can be regarded as new evidence in support of this view. The uniformly larger cation effects as compared to solvent effects on "free" anions provide clear indication of a primary cation effect and a secondary solvent effect. Of particular significance, furthermore, are the comparisons of the four anions (**5**, **6**, **9**, **12**) that exhibit marked cation effects in DME but none in DMF. Using these *experimentally observed* ΔE_0^{DMF} values³⁹ results in negligible solvent effects compared to the corresponding cation effects in DME. Because the ΔE_0^{DMF} values for the first four compounds in Table III were derived by extrapolations of lines with relatively high standard errors (see Table II), it is probable that the insignificant solvent effects derived from the *experimental* ΔE_0^{DMF} values more accurately reflect the true magnitude of any primary solvent effect.⁴⁰

In the succeeding discussion, therefore, it will be assumed that the over-all magnitudes of the cation effects observed *in DME* for each of the four types of compounds (A, B, C, or D) and the two subgroups

(31) (a) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **86**, 412 (1964); (b) J. F. Garst, C. Hewitt, D. Walmsley, and W. Richards, *ibid.*, **83**, 5034 (1961).

(32) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964).

(33) (a) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963); (b) *J. Am. Chem. Soc.*, **85**, 1651 (1963); (c) *Chem. Ind. (London)*, 1290 (1962).

(34) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963). In this work, cation effects were investigated in only one solvent, cyclohexylamine. Since this is a hydrogen-bonding solvent, results are not strictly comparable to those observed^{28, 29, 33} in aprotic solvents.

(35) Streitwieser³⁴ interpreted the inverse cation effect he observed in cyclohexylamine as a consequence of a greater gain in solvation stabilization of the lithium ion in the excited state as compared to that of the cesium ion.

(36) Although not strictly comparable because their ionic character is less than that of most of these salts and of all of the salts of the present work, alkyllithium compounds are solvated by ethers³⁷ and by triethylamine^{37, 38} exclusively through the metal ion.

(37) (a) J. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963); (b) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

(38) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2135 (1964).

(39) The presence of a marked cation effect in DME and its absence in DMF clearly shows that a given salt is associated in the former solvent and completely ionized in the latter.²⁸

(40) The ΔE_0^{DME} and ΔE_0^{DMF} for compounds **14**, **20**, and **21** also were derived from lines with relatively high standard errors. In these cases, however, the steeper lines tend to minimize errors due to extrapolation to the x-axis. Compound **16**, admittedly, shows a significant solvent effect that cannot be rationalized out of existence in the same way that the first four were.

Table I. Long Wave Length Absorption Maxima of Phenols, Enols, and Their Salts in 1,2-Dimethoxyethane (DME) and in Dimethylformamide (DMF)

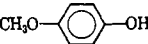
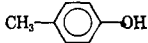
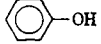


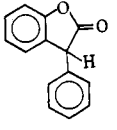
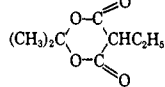
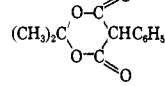
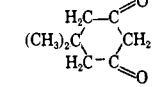
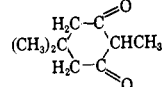
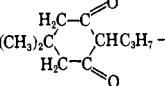
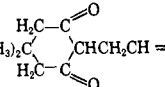
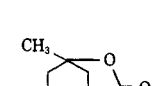
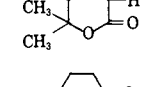
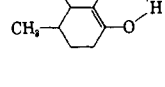
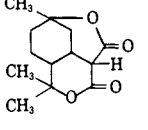
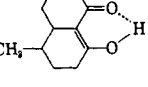
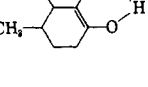
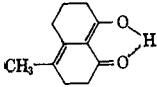
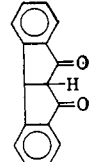
No.	Anion from	pK _a ^a	Cation ^b	DME			DMF		
				Concn., 10 ⁶ M	λ _{max} , mμ ^c	10 ⁻⁴ ε _{max}	Concn., 10 ⁶ M	λ _{max} , mμ ^c	10 ⁻⁴ ε _{max}
A. Benzenoid Charge Delocalization									
1		10.2 ^d	H ⁺	31.9	293.5	0.31	24.7	295.5	0.32
			Li ⁺				37.2	323.0	0.26
			Na ⁺	31.9	323.5	0.38	24.7	342.0	0.41
			Cs ⁺	44.7	338 ± 1	0.32	33.7	348.5	0.44
2		10.1 ^d	H ⁺	36.7	281.0	0.21	34.3	282.0	0.22
			Li ⁺	35.3	304 ± 1	0.11 ^f	32.9	315 ± 1	0.25
			Na ⁺	36.7	311.0	0.34	34.3	332.0	0.36
			K ⁺	36.7	323.0	0.37			
3		10.0 ^d	Cs ⁺	42.5	328.0	0.31	31.9	337.0	0.42
			H ⁺	35.3	274.0	0.21	33.2	275.0	0.21
			Li ⁺	33.2	296.5	0.16 ^{e,f}	42.5	309.0	0.31
			Na ⁺	38.1	302.5	0.37	33.2	323.0	0.42
4		9.4 ^d	K ⁺	39.1	314.5	0.41			
			Cs ⁺	41.0	317.5	0.35	43.9	326.0	0.49
			H ⁺	30.8	283.0	0.20	24.0	284.0	0.20
			Li ⁺	35.7	307.0	0.27	29.1	324.0	0.31
5		7.2 ^d	Na ⁺	29.4	320.0	0.32	24.0	336.0	0.38
			K ⁺	30.8	325.5	0.26			
			Cs ⁺	50.1	327 ± 1	0.24	35.4	337.5	0.41
			H ⁺	7.5	308.5	1.09	5.0	319 ± 2	1.10
6		8.1 ⁱ	Li ⁺	7.5	397 ± 1	2.42	7.7	435 ± 1	3.38
			Na ⁺	7.5	410 ± 1	2.59	4.8	435 ± 1	3.49 ^o
			K ⁺	4.7	415 ± 1	2.71		435 ± 1	3.92
			Cs ⁺	5.1	418 ± 1	2.79	5.0	434 ± 1	3.32
B. W-Shaped Charge Delocalization									
7		4.5 ⁱ	[(CH ₃) ₂ NH ₂] ^h	5.8	323 ± 1	1.74	2.1	354 ± 1	2.36
			Li ⁺	5.8	326 ± 1	1.97	6.9	354 ± 1	2.24
			Na ⁺	5.5	337 ± 2	2.28	6.1	354 ± 1	2.46
8		3.1 ⁱ	K ⁺	6.0	342.5	2.25			
			Cs ⁺	5.0	345 ± 1	2.26	5.6	354 ± 1	2.45
			Li ⁺	7.2	271.0	1.94	7.1	273.5	1.95
9		5.2 ^j	Na ⁺	7.9	272.0	1.99	7.6	274.0	1.98
			K ⁺	7.3	272.5	1.86			
			Li ⁺	9.5	244.0	1.23			
10		5.6 ^b	Li ⁺	9.0	273.5	0.96	8.6	283.5	2.00
			Na ⁺	9.9	276.0	2.15	9.9	285.0	2.52
			K ⁺	9.5	280.0	1.78			
			Cs ⁺	9.3	282.5	1.91	7.7	285.0	2.28
11			H ⁺	9.2	253.0	1.41			
			Na ⁺	9.2	289.5	2.07	8.9	295.0	2.18
12		5.4 ⁱ	H ⁺	5.0	254.0	1.14			
			Na ⁺	8.8	290.0	1.41	9.1	295.5	1.49
13			H ⁺	10.2	253.0	1.44			
			Li ⁺	8.9	285.0	2.15	9.1	291.5	2.32
			Na ⁺	10.2	287.5	2.03 ⁱ	10.2	292.5	2.39
			K ⁺	9.2	288.5	2.08			
14		11.3 ⁱ	Cs ⁺	8.5	289.5	2.07	6.7	292.0	2.32
			H ⁺	6.8	295 ± 1	0.87	10.6	298.5	0.66
			Li ⁺	10.6	312.5	1.25	10.0	313.5	1.44
			Na ⁺	11.5	315.0	1.23	10.0	315.5	1.49
14			K ⁺	12.3	316.5	1.20			
			Cs ⁺	11.8	318.5	1.15	11.1	318.5	1.30
C. U-Shaped Charge Delocalization									
13			Li ⁺	7.9	269.5	1.12	10.4	270.5	1.13
			Na ⁺	10.4	270.5	1.23	8.0	270 ± 1	1.31
			K ⁺	10.1	270 ± 1	0.74			
14			H ⁺	6.8	295 ± 1	0.87	10.6	298.5	0.66
			Li ⁺	10.6	312.5	1.25	10.0	313.5	1.44
			Na ⁺	11.5	315.0	1.23	10.0	315.5	1.49
			K ⁺	12.3	316.5	1.20			
14			Cs ⁺	11.8	318.5	1.15	11.1	318.5	1.30

Table I (Continued)

No.	Anion from	pK _a ^a	Cation ^b	DME			DMF		
				Concn., 10 ⁵ M	λ _{max} , mμ ^c	10 ⁻⁴ ε _{max}	Concn., 10 ⁵ M	λ _{max} , mμ ^c	10 ⁻⁴ ε _{max}
15			H ⁺	24.6	341 ± 1	0.39	20.1	344 ± 1	0.36
			Li ⁺	24.6	347 ± 1	0.54	20.1	348 ± 1	0.60
			Na ⁺	15.8	347 ± 1	0.53 ^m	20.1	347 ± 1	0.54
			K ⁺	24.6	347 ± 1	0.41			
			Cs ⁺	17.5	348 ± 1	0.50	21.8	348 ± 1	0.59
16		≥12 ⁱ	Li ⁺	14.9	379.0	0.95	14.8	386 ± 1	0.88
			Na ⁺	14.9	387 ± 1	1.29	14.8	394 ± 1	0.94
			K ⁺	10.4	390.0	1.03			
			Cs ⁺	12.4	393 ± 1	0.89	14.0	402 ± 1	0.68
D. Acyclic Compounds									
17	<i>n</i> -C ₄ H ₉ CH(CO ₂ C ₂ H ₅) ₂	17 ⁿ	Li ⁺			... ^o			
			Na ⁺	7.6	272.0	1.69 ^p	8.6	272.0	2.35
			K ⁺	8.9	272.5	1.78			
			Cs ⁺	7.3	272 ± 1	0.23 ^q	7.2	272.0	2.04
18	CH ₃ (CH ₂) ₂ CHCH(CO ₂ C ₂ H ₅) ₂ CH ₃	18 ⁿ	Na ⁺	8.2	272.5	1.81	7.2	272.5	2.35
19	C ₆ H ₅ CH(CO ₂ C ₂ H ₅) ₂	15 ⁿ	Li ⁺			... ^o			
			Na ⁺	6.8	268.5	1.94	7.5	269 ± 1	1.93
			K ⁺	7.5	269.0	1.75			
20	CH ₂ (COCH ₃) ₂	8.9 ^j	H ⁺	9.3	272.5	0.89	10.0	273.5	0.67
			Li ⁺	9.3	291.0	1.80 ^r	10.0	292.0	1.87
			Na ⁺	9.4	293.5	1.72 ^s	9.2	294.0	1.94
			K ⁺	9.7	294.5	1.78			
			Cs ⁺	9.2	297 ± 1	1.54	9.8	297 ± 1	1.90
21	CH ₂ (COC(CH ₃) ₂) ₂	11.8 ^t	H ⁺	9.3	277.0	1.18	8.9	277.0	1.05
			Li ⁺	8.8	293.5	1.95	8.9	294.5	2.04
			Na ⁺	10.1	294.5	1.71	8.9	295.5	2.10
			K ⁺	9.3	296.0	1.72			
22	CH ₂ (COC ₆ H ₅) ₂	9.8 ^k	H ⁺	9.3	342 ± 1	2.33	9.5	348.0	2.23
			Li ⁺	9.3	357 ± 1	2.22	9.5	359 ± 1	2.18
			Na ⁺	9.0	360 ± 1	2.00 ^u	8.9	361 ± 1	2.09
			K ⁺	9.0	361.5	1.66			
			Cs ⁺	10.7	363.5	1.82	8.6	365 ± 1	1.50
23	(CH ₃) ₂ CHCH(COCH ₃) ₂	12.8 ⁿ	Li ⁺	167.0	308 ± 1	0.20 ^v	11.1	308.5	1.42
			Na ⁺	10.2	310 ± 1	0.90	9.6	309.0	1.59
			K ⁺	14.1	306 ± 1	0.88			
			Cs ⁺	20.5	307.5	1.30	9.6	309 ± 1	1.57
24	C ₆ H ₅ CH ₂ CH(COCH ₃) ₂	10.2 ⁱ	H ⁺	20.8	288.5	0.42	10.8	291 ± 2	0.31
			Li ⁺	20.8	304.5	1.10	10.8	307.0	1.16
			Na ⁺	20.8	307.5	1.11	10.8	307.0	1.32
			K ⁺	20.8	307.5	1.04			
			Cs ⁺	10.3	306 ± 1	1.43	11.3	307.0	1.43
25	(C ₆ H ₅) ₂ CHCH(COCH ₃) ₂	>12 ⁱ	Li ⁺			... ^o	11.0	307 ± 2	0.34 ^q
			Na ⁺	11.3	302 ± 2	0.37 ^q	11.0	306 ± 1	1.18
			K ⁺	18.0	305 ± 1	1.06			
			Cs ⁺	11.3	304 ± 14	0.8	11.0	306 ± 1	1.42
26	(C ₆ H ₅) ₂ CCH(COCH ₃) ₂		Li ⁺			... ^o			
			Na ⁺	16.6	304 ± 2	0.43 ^q	12.5	303 ± 1	1.34
			K ⁺	18.8	299 ± 1	1.02			
			Cs ⁺	16.6	301 ± 1	1.17	12.5	302 ± 1	1.53

^a pK_a values reported from different sources are seldom precisely comparable. However, the quoted values provide a rough comparison of aqueous acidities. ^b When the cation is H⁺, the listed wave length is that of the enol form (most of the phenol spectra show fine structure that is not listed). The absence of data for H⁺ indicates that the compound is not appreciably enolized. ^c Unless otherwise noted, experimental precision is ±0.5 mμ. ^d A. Albert and E. P. Sarjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962, p. 130. ^e Using method C, the salt precipitated from solution. ^f Salt formation was incomplete, as evidenced by absorption due to the acid form. ^g In N,N-dimethylacetamide, λ_{max} 435 mμ (ε_{max} 3.53 × 10⁴). ^h See ref. 7 for the determination of these spectra. ⁱ The authors are indebted to D. C. Wimer, J. W. Sutherland, and V. Papendick for these measurements. ^j G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940). ^k B. Eistert, E. Merkel, and W. Reiss, *Chem. Ber.*, **87**, 1513 (1954). ^l In tetrahydrofuran, salt formation (method A) was incomplete, λ_{max} 287.5 mμ (ε_{max} 0.87 × 10⁴). ^m In cyclohexane, salt formation (method A) was incomplete, λ_{max} 348 ± 1 mμ (ε_{max} 0.33 × 10⁴). ⁿ Measured spectrophotometrically in isopropyl alcohol by C. Vermesse-Jacquinet, R. Schaal, and P. Rumpf, *Bull. soc. chim. France*, 2030 (1960). ^o No detectable salt could be produced by any method. ^p In both cyclohexane and tetrahydrofuran, salt formation (method A) was incomplete, λ_{max} 272 mμ (ε_{max} 0.41 × 10⁴). ^q Salt formation was incomplete. ^r In tetrahydrofuran, λ_{max} 291.5 mμ (ε_{max} 1.73 × 10⁴). ^s In tetrahydrofuran, λ_{max} 294 mμ (ε_{max} 1.78 × 10⁴). ^t G. A. Guter and G. S. Hammond, *J. Am. Chem. Soc.*, **78**, 5166 (1956). ^u In tetrahydrofuran, λ_{max} 361 ± 1 mμ (ε_{max} 2.00 × 10⁴).

Table II. Correlation of Absorption Maxima with Cation Radii ($1/r_c$ vs. $\bar{\nu}$)^a

Compd. no. ^b	DME		DMF	
	10^{-4} (slope \pm SE) ^c	ΔE_0 , kcal. mole ⁻¹ (λ_0 , m μ) ^d	10^{-4} (slope \pm SE) ^e	ΔE_0 , kcal. mole ⁻¹ (λ_0 , m μ) ^d
A. Benzenoid				
1	3.40 \pm 0.30 ^f	79.5 (360)	4.46 \pm 0.95	77.7 (368)
2	4.16 \pm 0.84	83.5 (343)	4.81 \pm 1.16	80.7 (354)
3	4.31 \pm 0.92	86.2 (332)	5.74 \pm 1.67	84.1 (340)
4	5.20 \pm 0.39	83.8 (341)	7.51 \pm 2.70	81.8 (350)
5	8.45 \pm 0.39	66.3 (431)	∞	65.7 (435) ^g
6	6.30 \pm 0.13	80.1 (357)	∞	80.8 (354) ^g
B. W-Shaped				
9	8.68 \pm 1.95	99.5 (287)	∞	100.3 (285) ^g
12	20.17 \pm 1.04	98.0 (292)	∞	98.0 (292) ^g
C. U-Shaped				
14	18.28 \pm 2.95	89.0 (321)	21.02 \pm 4.19	89.0 (321)
16	11.68 \pm 0.57	71.4 (401)	10.44 \pm 0.73	69.6 (411)
D. Acyclic				
20	15.80 \pm 3.38	95.4 (300)	18.24 \pm 3.56	95.4 (300)
22	22.11 \pm 2.79	78.0 (367)	22.31 \pm 6.15	77.7 (368)

^a The inverse cation radii ($1/r_c$ in \AA^{-1}) are plotted on the ordinate vs. the wave numbers ($\bar{\nu}$ in \AA^{-1}) of the corresponding absorption maxima. Values for r_c employed were (in \AA): Li⁺, 0.60; Na⁺, 0.95; K⁺, 1.33; Cs⁺, 1.69. ^b See Table I for structures. ^c Except where otherwise noted, slopes and standard errors (SE) in DME were calculated statistically using data from all four alkali cations. ^d Except where otherwise noted, these values were obtained by extrapolation of $\bar{\nu}$ values to infinite cation radius (*i.e.*, $1/r_c = 0$) followed by conversion of the resulting $\bar{\nu}_0$ to its energy (ΔE_0) and wave length (λ_0) equivalents. ^e Slopes and standard errors (SE) in DMF were calculated with data from the three cations, Li⁺, Na⁺, and Cs⁺. ^f Calculated using three points: Na⁺, K⁺, and Cs⁺. ^g Observed values (see Table I).

Table III. Comparison of Cation Effects with Solvent Effects

Compd. no.	$\Delta E_{Li} - \Delta E_{Cs}$, kcal. mole ⁻¹		$\Delta E_0^{DME} - \Delta E_0^{DMF}$, kcal. mole ⁻¹
	DME	DMF	
A. Benzenoid			
1	>3.8 ^a	6.5	1.8
2	6.9	6.0	2.8
3	6.4	4.8	2.1
4	5.7	3.6	2.0
5	3.6	...	0.6
6	4.9	...	-0.7
B. W-Shaped			
9	3.4	...	-0.8
12	1.6	...	0.0
C. U-Shaped			
14	1.7	1.5	0.0
16	2.7	3.0	1.8
D. Acyclic			
20	1.9	1.7	0.0
22	1.5	0.9	0.3

^a This value is for $\Delta E_{Na} - \Delta E_{Cs}$.

(diesters and β -diketones) provide *first approximations* of the relative susceptibilities of their respective electronic transitions to perturbation by an adjacent positive field. Any variation within each of the four groups and two subgroups of anions will be regarded as originating from a corresponding variation in the time-averaged proximity of the cation. This variation, in turn, may result from differences in interionic dimensions within static ion pairs or from changes in ionization constants of equilibria between ion pairs and separate ions. Because the spectral approach of the present work does not provide fine distinctions between the relative importance of these two ionic processes, the terms "tightness" or "looseness" will be used in

Table IV. Long Wave Length Absorption Maxima of Salts in Aqueous and Ethanolic Alkali

Compd. no. ^a	Cation	Water		Ethanol		$\Delta E_0^{H_2O} - \Delta E_0^{DMF}$, ^c kcal. mole ⁻¹
		λ_{max} , m μ ^b	10^{-4} ϵ_{max}	λ_{max} , m μ ^b	10^{-4} ϵ_{max}	
1	Na ⁺	306 ^d	0.32			15.7
2	Na ⁺	296 ^d	0.26			15.8
3	Li ⁺	287.0	0.25	290 \pm 1	0.31	
	Na ⁺	287 ^e	0.26	290.5	0.29	15.5
4	K ⁺	287.0	0.24	290.5	0.30	
	Na ⁺	298 ^e	0.26			14.3
5	Li ⁺	400 \pm 1	1.80	400 \pm 1	2.01	
	Na ⁺	400 \pm 1	1.72	400 \pm 1	2.10	5.8
	K ⁺	400 \pm 1	1.75	400 \pm 1	2.11	
6	Na ⁺			315 \pm 1	1.78	
	K ⁺			316 \pm 1	1.64	9.7 ^f
	Cs ⁺			316 \pm 1	1.75	
7	Na ⁺	273.5	1.87	272.0 ^g	1.85	-2.3
8	Na ⁺	270 \pm 1	1.59			-1.6
9	Li ⁺			282.0	2.78	
	Na ⁺	282.0 ^h	2.43	282.0	2.77	1.1
	K ⁺			282.0	2.75	
10	Na ⁺	294.5 ⁱ	2.43			0.2
12	Na ⁺	292.0	2.46	292.5	2.57	0
14	Na ⁺	315 \pm 1	1.40			1.7
20	Li ⁺	291.5	2.03	291.5	2.36	
	Na ⁺	293.0 ^h	2.18	293.0	2.28	2.3 ^j
	K ⁺	293.0	2.22	294.5	2.33	
21	Na ⁺	294.0 ^k	1.81			0.5 ^l
	Na ⁺	348 ^h	2.14	351 ^m	2.30	4.5 ⁿ
22	K ⁺	350 ^o	0.22			

^a See Table I for structures. ^b Unless otherwise noted, experimental precision of the results of the present work is ± 0.5 m μ . ^c See Table II for ΔE_0^{DMF} values of compounds 1-6, 9, 12, 14, 20, and 22, and Table I for compounds 7, 8, and 10. ^d L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963). ^e L. Doub and J. M. Vandenberg, *ibid.*, **69**, 2714 (1947). ^f Using $\Delta E_0^{H_2O}$ 316 m μ . ^g In methanol; ref. 3c. ^h B. Eistert, E. Merkel, and W. Reiss, *Chem. Ber.*, **87**, 1513 (1954). ⁱ Ref. 14. ^j Using $\Delta E_0^{H_2O}$ 293.0 m μ . ^k G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959). ^l Using ΔE_0^{DMF} 295.5 m μ . ^m R. A. Morton, A. Hassan, and T. C. Calloway, *J. Chem. Soc.*, **137**, 883 (1934). ⁿ Using $\Delta E_0^{H_2O}$ 348 m μ . ^o B. Eistert, F. Weygand, and E. Csendes, *Chem. Ber.*, **84**, 745 (1951).

the following discussion to include both the static and the dynamic aspects of ion-pair behavior.

The existence of a primary cation effect in which a blue shift results from an increased cationic field (*i.e.*, $\text{Cs}^+ \rightarrow \text{Li}^+$) means that excitation results in net movement of negative charge away from the center of positive charge. The cation interacts more strongly with the ground than with the excited state.^{31a} Although this phenomenon is common to all the cation-sensitive transitions of the present work, considerable quantitative variation with anion structure is evident.

Anion Structure and Cation Sensitivity. Inspection of the magnitudes of the cation effects in DME listed in Tables I and II clearly reveals that anions involving benzenoid charge delocalization are more sensitive to spectral perturbation than are any of the enolate ions. In addition, differences in spectral behavior are observable within each group.

Comparison of the five phenol salts in DME (Table II) shows that cation sensitivity increases slightly with ability of the *para* substituent to release electrons to the aromatic ring. This suggests the existence of a progressive increase (from **5** to **1**) in the tightness of corresponding ground-state ion pairs. Any cation changes in a series of tight ion pairs (*e.g.*, salts of **1**) would produce larger alterations in the effective positive field, and hence larger spectral shifts, than would the same changes in looser ones (*e.g.*, salts of **5**). This view is supported further by the uniformly diminished cation effect observed in DMF for the first four compounds, and by the fact that the weakest ion pairs (salts of **5**) in DME are the only ones of the series that ionize completely in DMF.⁴¹

Regular deviations in cation sensitivity in DME also are discernible among the three groups of enolate ions. In general, orbitals involving W-shaped delocalization (type B) appear to be more sensitive than either of the other two types (compare **9** with **14** and **15**; **9** with **20–22**; and **12** with **23–26**). But additional structural factors serve to modify this first approximation.

Thus, substitution at the 2-position of 1,3-diketones diminishes sensitivity (compare **9** vs. **12** and **20** vs. **23–26**). The fact that such substitution also leads to enhanced electron density in the anion (note the increase in *pK* from **9** to **12** and from **20** to **23**) suggests that this effect is steric rather than electronic. Any tendency toward electrostatic strengthening of the ion pair is apparently outweighed by steric repulsion. The diminished sensitivity with increased *pK* and greater bulk observed in going from **20** to **21** also supports this view. Conversely, the marked cation sensitivity of the anion derived from the U-shaped diketone **16** as contrasted with those of its cyclic analogs **14** and **15**, and its acyclic analog **22**, can be rationalized in terms of its enhanced basicity combined with an essentially flat structure, both conducive to the formation of tight ion pairs.⁴²

(41) The better cation solvent (DMF as compared to DME) would lead to larger interionic distances in the solvated ion pairs and the five-fold increase in dielectric constant would shift any ionization equilibrium away from ion association. Both influences would serve to reduce observed cation sensitivities. Although these reductions are not statistically significant for any one compound (*cf.* relative slopes in DME and DMF in Table II), the uniformity of the group trend indicates significance.

(42) The extraordinary tightness of ion pairs of **16** is indicated by the absence (Table II) of even a hint of loosening as a consequence of increased solvent polarity:

Spectra of diester anions, whether of type B, C, or D, are uniformly insensitive to cationic variation in DME (compounds **7**, **8**, **13**, **17**, and **19**). Because other evidence clearly shows⁴³ that ion pairing (or higher aggregation) does occur in solvents of low polarity, it must be concluded that this insensitivity is due to the absence of appreciable charge displacement in the excited states of these ester anions relative to the cations in the ground-state ion pairs.

Enolate Structure and Aprotic Solvent Sensitivity. The data of Table II show that the ultimate solvent effect (*i.e.*, unmistakable ion association in DME, but complete dissociation in DMF) exhibited by salts of *p*-nitrophenol (**5**) extends to salts of compound **6**, and to salts of the two W-shaped diketones, **9** and **12**, but not to salts of **14** and **16** (U-shaped) and **20** and **22** (acyclic). Indeed, the ion pairs of salts of the last four compounds are so tight that their cation sensitivities are not altered significantly by the solvent change. Qualitative results observed (Table I) for the less sensitive salts are also consistent with these findings.

In the β -diketone series, the remaining W-shaped salts of **10** and **11** show marked solvent sensitivity in contrast to U-shaped salts of **15** and acyclic salts of **21**, **23–26**, despite the fact that the behavior of most of the acyclic (**21**, **23**, **24**, **27**) salts suggests the presence of cation effects in DME. In the less sensitive diester series, discernible solvent effects are confined to W-shaped orbitals (**7**, **8**); U-shaped (**13**) and acyclic compounds (**17–19**) are quite insensitive.

The quantitative results (Table II) combined with the qualitative observations (Table I) plainly indicate that salts with W-shaped orbitals generally form ion pairs that are weaker (more ionizable?) than the corresponding salts from U-shaped or acyclic compounds. They further suggest the obvious interpretation that the U-shaped and acyclic compounds, for which a U-shape is optional, form tighter ion pairs because of their bidentate chelate geometry. The proximity of the cation, in turn, effectively neutralizes any unfavorable dipole-dipole interactions expected to be present⁴⁵ in the free U-shaped anion. Consideration of the spectral behavior of these salts in hydroxylic solvents further supports this conclusion.

Anion Structure and Spectral Sensitivity to Hydroxylic Solvents. The marked blue shift of aryl oxide ion absorption in going from aprotic to hydroxylic solvents has been reported by other workers.^{6,23} It has been ascribed by Parker and Brody²³ to a general hydrogen-bonded stabilization of the ground state by the protic solvent. Previous considerations of protic solvent effects on the rates of some displacement reactions also had led Miller and Parker⁴⁶ to conclude that non-specific solvation of anions is very strong when the positive portion of the solvent dipole is on hydrogen

(43) For example, even in DMF, an 0.15 *M* solution of the lithium salt of diethyl malonate displays an n.m.r. shift for the α -hydrogen atom 6 c.p.s. downfield from that of a corresponding solution of the sodium salt.⁴⁴ Furthermore, the ultraviolet absorption peak (272 $m\mu$) of the sodium salt of diethyl *n*-butylmalonate (**17**) is identical in the four solvents, cyclohexane, tetrahydrofuran, DME, and DMF, despite the fact that kinetic and cryoscopic studies^{1,2} have shown that its state of aggregation varies greatly over this solvent series.

(44) H. E. Zaugg and A. D. Schaefer, unpublished data.

(45) C. M. Lee and W. D. Kumler (*J. Am. Chem. Soc.*, **83**, 4586 (1961); *ibid.*, **84**, 565 (1962)) have found, for example, that acyclic imides tend to avoid the U-shaped conformation.

(46) J. Miller and A. J. Parker, *ibid.*, **83**, 117 (1961).

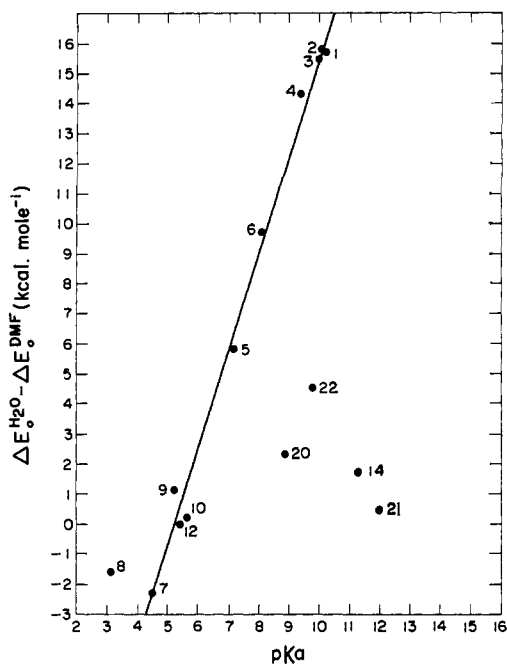


Figure 1. Correlation of anion basicity with ground-state hydration.

and relatively weak otherwise. This view gains support from the findings of Prue and Sherrington⁴⁷ who concluded, on the basis of conductance measurements on several inorganic perchlorates, that in DMF the anion is "naked," but in hydroxylic solvents both counterions move with a solvation sheath.⁴⁸

Accordingly, one might assume that the ΔE_0^{DMF} values listed in Table II represent the transition energies of approximate standard states in which the anions are relatively free of both solvent and cation. Any observed divergences in the $\Delta E_0^{\text{H}_2\text{O}} - \Delta E_0^{\text{DMF}}$ values of Table IV could then be ascribed to disparate hydrogen-bonded stabilization by water of the respective anionic ground states. These stabilizations, in turn, should be proportional to anion basicities.

In Figure 1, the $\Delta E_0^{\text{H}_2\text{O}} - \Delta E_0^{\text{DMF}}$ values of the 15 compounds listed in Table IV are plotted against their respective aqueous pK values. In accord with ex-

(47) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

(48) A concise survey of recent work on anion solvation by protic and aprotic solvents is included by R. Gompper in *Angew. Chem. Intern. Ed. Engl.*, **3**, 560 (1964), and provides a useful supplement to the earlier one by A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

pectation, the first 11 fall close to a straight line of slope 2.92 ± 0.20 .^{49,50} The last four, however, are scattered well off the line; but of the whole group, *these four are the only ones capable of forming U-shaped anions*. The direction of their divergence from expected behavior shows that their anionic ground states are not stabilized by hydrogen-bonded solvation to the extent that their basicities would indicate. Similar deviations would be expected for the more basic anions derived from compounds 16–19 and 23–26. That this divergence is restricted to those substances with structurally enhanced "chelating" ability, strongly suggests that some form of association with a cation, even in hydroxylic media, is responsible for this diminished hydrogen-bonded solvation. Of further qualitative interest is the observation that, of the six compounds for which cation effects are listed in Table IV, 20 and 22, the only potentially U-shaped ones, both display spectral suggestion of ion association even in water.

Finally, the conclusion that acyclic enolates exist as U-shaped ion pairs is in agreement with that of Brändström⁵¹ and of Murdoch and Nonhebel,⁵² arising from a consideration of the rates and products of many enolate alkylation and acylation reactions, with that of Guter and Hammond,⁵³ based on the demonstrated lithium-chelating ability of dipivaloylmethane (21), and with that of Bauld,⁵⁴ derived from the observed differential reducibility of acyclic vs. W-shaped enolate ions.

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(49) That anions 7 and 8 display a reversal of sign in their $\Delta E_0^{\text{H}_2\text{O}} - \Delta E_0^{\text{DMF}}$ values indicates that DMF does not provide a true standard state. These two anionic ground states apparently are slightly less stabilized in water than they are in DMF. Small, but observable, differentiation of anion solvation by DMF also is demonstrated by the fact⁷ that the relative acidities in water of compounds 5 and 6 are reversed in DMF.

(50) It is noteworthy that the four phenols (1–4), whose ΔE_0^{DMF} values were derived by extrapolation (Table II), correlate well with the seven compounds whose ΔE_0^{DMF} values were experimentally ascertainable.³⁰ This outcome lends support to the validity of the extrapolation method^{28,29} for estimating ΔE_0 values of cation-paired anions.

(51) A. Brändström, *Arkiv Kemi*, **6**, 155 (1953).

(52) H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.*, 2153 (1962).

(53) G. A. Guter and G. S. Hammond, *J. Am. Chem. Soc.*, **78**, 5166 (1956).

(54) N. L. Bauld, *ibid.*, **86**, 2305 (1964).