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THE EFFECT OF A POSITIVE CHARGE ON A $\pi \rightarrow \pi^*$-TRANSITION

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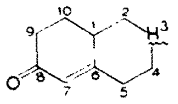
Abstract—The position of the maximum for the $\pi \rightarrow \pi^*$-transition of a bicyclic ketone containing a quaternary nitrogen atom at 3·1 Å from an α:β-unsaturated ketone system is shown to depend largely upon electrostatic (repulsion) destabilization in both ground and excited states, the latter being affected more strongly.

INTERPRETATIONS of ultraviolet absorption spectra have been of considerable value in the elucidation of structure and in the understanding of the electronic and steric effects of substituents on conjugated systems. One has only to remember the order introduced by the Woodward rules[1] into the prediction of the maxima of conjugated ketones and dienes to appreciate the value of reasonable empirical rules for such purposes. In extending the principle of the Woodward rules to other substituents, it is necessary to ensure that (1) the effects are large enough to be discussed, (2) the structural feature of concern is actually responsible for the absorption observed, and (3) the effect of the solvent can be discounted or calculated.

Georgian[2] has recently reported the interesting fact that a hetero-atom inserted at the 3-position of a bi*cyclo*[4.4.0] dec-6-en-8-one (I) causes a significant decrease in the position of the short wavelength maximum. The magnitude of the change was reportedly greater when the hetero-atom (**H**) carried a formal positive charge.



I

The values given by Georgian for 95% ethanol are listed in Table 1.

Iodide ions possess an intense absorption maximum at ca. 2195 Å in 95% ethanol.[3] The fact that iodide ion absorbs strongly in the region of the maxima given by Georgian for quaternary salts as well as the marked solvent-sensitivity of the maxima for α:β-unsaturated ketones[4] suggested that a more detailed examination of an appropriate salt[*] and of the solvent effect was necessary.

The absorption spectra of three compounds with the basic structure (I) were investigated in four different solvents. The compounds were bi*cyclo*[4.4.0] dec-5-en-4-one (II) (I, **H** = CH_2),[6,7] 3-methyl-3-azabi*cyclo*[4.4.0]dec-6-en-8-one (III) (I, **H** = $N—CH_3$)[8] and a quaternary salt derived from (III), (IV) (I, **H** = $N(CH_3)_2{}^+ClO_4{}^-$).

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[*] Methiodide salts have been used by others[5] to obtain maxima of interest in connection with this problem.

[1] R. B. Woodward, *J. Amer. Chem. Soc.* **63**, 1123 (1941); **64**, 76 (1942).

[2] V. Georgian, *Chem. & Ind.* 930 (1954); 1480 (1957).

[3] E. M. Kosower, R. L. Martin and V. W. Meloche, *J. Chem. Phys.* **26**, 1353 (1957).

[4] E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3261 (1958).

[5] C. B. Clarke and A. R. Pinder, *J. Chem. Soc.* 1967 (1958).

TABLE 1. MAXIMA FOR VARIOUS COMPOUNDS OF STRUCTURE I

H	λ_{max} (Å)
N—CH_3	2320(a)
S	2300
SO_2	2290
$SCH_3^+I^-$	2220
$N(CH_3)_2^+I^-$	2210
(CH_2)(b)	(2400)(b)

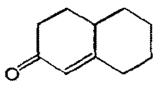
(a) Identical with the value reported.[8b] The value of 2275 Å has been given for *methanol*.[8a]

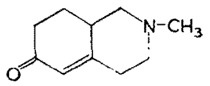
(b) The value used by Georgian,[2] and supposedly calculated by the use of the Woodward rules.[1] Use of the rules as stated gives, however, the maximum as 2440 Å. Zeiss and Martin,[7] found a maximum at 2380 Å (presumably in 95% ethanol), in agreement with the results of W. T. Tsatsos, Ph.D. Thesis, University of Wisconsin, 1954.

The solvents used were chosen to give the widest possible range of solvent polarity.[9] The results are shown in Table 2.

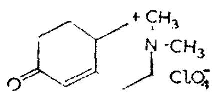
In contrast to the value of 2210 Å reported by Georgian[2] for the quaternary iodide IV (I^- replacing ClO_4^-) we have found the maximum in 95% ethanol at 2290 Å. There can be little doubt, therefore, that a positive charge at position 3 in the bicyclic molecule (I), displaces the maximum in 95% ethanol to shorter wavelengths. It is, however, clear that the use of the iodide salts leads to an erroneously exaggerated figure for this displacement.[2,5] In addition, the size of the actual displacement (from II to IV) varies with the solvent, changing from 125 Å in water to 85 Å in acetonitrile. The effect of solvent is displayed more effectively by a plot

TABLE 2. $\pi \rightarrow \pi^*$-TRANSITIONS
COMPOUND


II



III



IV

Solvent	Z(a)	II		III		IV	
		λ_{max} (Å)	ε_{max}	λ_{max} (Å)	ε_{max}	λ_{max} (Å)	ε_{max}
Water	94·6	2455	(15,100)	2390	(13,700)	2330	(15,500)
95% Ethanol	80·8	2380	(15,400)	2325	(14,100)	2290	(15,600)
Acetonitrile	71·3	2345	(15,700)	2300	(14,100)	2260	(15,500)
*cyclo*Hexane	60·1(b)	2290	(16,500)	2255	(14,200)	—(c)	

(a) Solvent polarity values.[9]

(b) Taken as equal to 2:2:4-trimethylpentane (*iso*octane).

(c) Insoluble.

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[6] E. C. Du Feu, F. J. McQuillin and R. Robinson *J. Chem. Soc.* 53 (1937).

[7] H. H. Zeiss and W. B. Martin, Jr., *J. Amer. Chem. Soc.* **75**, 5935 (1953).

[8a] A. Marchant and A. R. Pinder, *J. Chem. Soc.* 327 (1956); [b] S. M. McElvain and P. H. Parker, Jr., *J. Amer. Chem. Soc.* **78**, 5312 (1956).

[9] E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3253 (1958).

of the transition energies (i.e. the wavelength of the maximum transformed into kcal/mole by the relation $E_T = 2{\cdot}859 \times 10^{-3}\,\bar{\nu}$ (in cm^{-1})) against Z, a new standard of solvent polarity.[9] The lines for the three ketones are shown in Fig. 1.

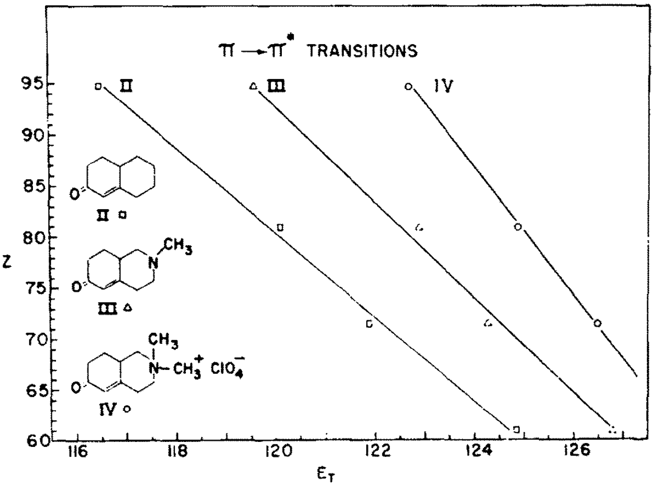
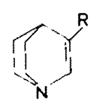
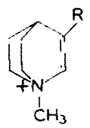


FIG. 1. A plot of the $\pi \rightarrow \pi^*$-transition energies derived from the data in Table 2 vs. the solvent polarity standard, Z.[9]

Grob *et al.*[10] have prepared a series of molecules in which the electrostatic effect of a positive charge upon an electronic transition can be observed. The structures involved were V and VI, 3-substituted-dehydroquinuclidines, and the principle utilized was to increase the electronegativity of the nitrogen by quaternization, and then to observe the longest wavelength band in a single solvent, 95% ethanol. Information concerning electron distribution in the excited state relative to the ground state was thus available by observing the direction and magnitude of the displacement



V



VI

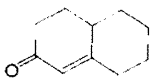
of the maximum, for the conversion V → VI. As expected, the positive charge on the nitrogen in VI destabilized excited states which produced positive charge at the adjacent carbon atom, and favored those which led to the accumulation of charge.

The $\pi \rightarrow \pi^*$-transition of an α,β-unsaturated ketone leads to an excited state with a greater contribution from the dipolar resonance form, $\overset{+}{\mathrm{C}}\text{—}\mathrm{C}{=}\mathrm{C}\text{—}\mathrm{O}^-$ than present in the ground state. The positive charge on nitrogen at position 3 in IV would (a) decrease the contribution of the dipolar resonance form to the ground state and (b) oppose to an even greater extent the formation of an excited state with increased charge separation. Introduction of the positive charge should lead to a displacement of the maximum to shorter wavelengths. In addition, the smaller dipoles of the ground and excited states would lead to a decreased sensitivity to solvent. *Both effects* can be seen in Fig. 1.

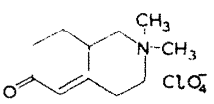
[10] C. A. Grob, A. Kaiser and E. Renk, *Chem. & Ind.* 598 (1957).

In order to examine the displacement of the maximum in a more quantitative fashion, certain facts are required about the ground states of the ketones which can be derived from measurements of the solvent sensitivities of the long wavelength $n \rightarrow \pi^*$-transitions. The long wavelength, low intensity maxima for ketones (II) and (IV) are listed in Table 3. Unfortunately, the maxima for the aminoketone (III) in most solvents were "buried" in the much more intense $\pi \rightarrow \pi^*$-transition, precluding a precise treatment of the maxima for this molecule.

TABLE 3. $n \rightarrow \pi^*$-TRANSITIONS
COMPOUND



II



IV

Solvent	λ_{max} (Å)	ε_{max}	λ_{max} (Å)	ε_{max}
Water	—		3080	(52)
95% Ethanol	3085	(66)	3185	(37)
Acetonitrile	3240	(46)	3305	(31)
*cyclo*Hexane[a]	3370	(37)	—	—

[a] In *iso*octane, the $n \rightarrow \pi^*$-transition for the aminoketone, (III), had a λ_{max} 3370 (ε 41). It is interesting to note from Fig. 2 that the quaternary salt might be expected to have a $n \rightarrow \pi^*$-transition at 3390 Å.

The transition energies derived from the maxima reported in Table 3 are plotted against **Z** in Fig. 2, and are reasonably linear in this parameter. A number of other $n \rightarrow \pi^*$-transitions have previously been found to be linear in **Z**, including that of the $\alpha{:}\beta$-unsaturated ketone, mesityl oxide.[4] The long wavelength transition for the

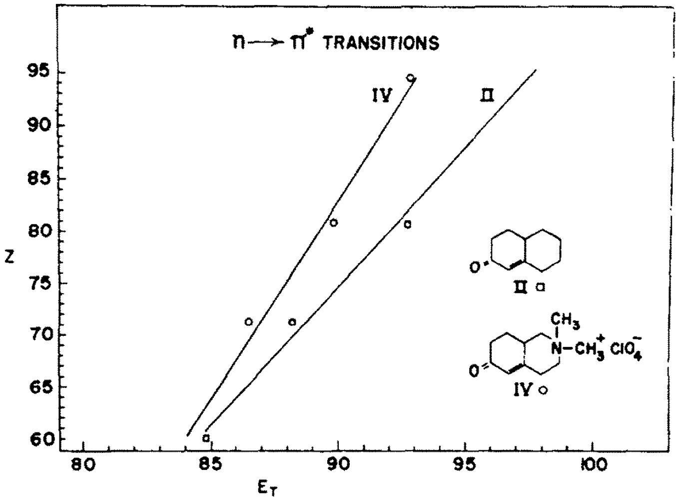
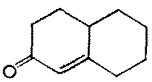


FIG. 2. A plot of the $n \rightarrow \pi^*$-transition energies for the carbocyclic ketone, II, and the quaternary ion, IV, derived from the data in Table 3 vs. the solvent polarity standard, **Z**.

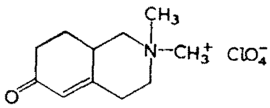
quaternary salt, (IV), is considerably less sensitive to the solvent than the corresponding transition of the carbocyclic ketone, (II). The dipole moment due to the α:β-unsaturated ketone portion of the quaternary ion, (IV), must be smaller than that of (II) on the reasonable assumption that solvent sensitivity depends upon the magnitude of the dipole moment. It is further assumed that the interaction with the solvent is roughly linear in the dipole moment for these two similarly shaped molecules.[4] The dipole moment of (II) may be taken as 4·00 D,* and the dipole moment for the α:β-unsaturated ketone system of (IV) estimated as 2·72 D. The latter value leads to an estimate of 2·5 kcal/mole for the interaction of the α:β-unsaturated ketone system portion of the molecule with water as compared with *iso*octane (or *cyclo*hexane).[4]

A method for calculating the dipole moments of the excited states of solvent sensitive electronic transitions has recently been published.[4] The information required for the calculation is (a) the difference between the transition energies in water and *iso*octane, (b) the interaction of the ground state with water, taking *iso*octane as a reference level, and (c) the Z-value difference for the pair of solvents used, in this case, *iso*octane and water.† The $\pi \rightarrow \pi^*$-transition energy for the quaternary ion is *iso*octane was estimated from the straight line shown in Fig. 1. The dipole moments thus calculated along with those estimated for the ground states are given in Table 4.

TABLE 4. DIPOLE MOMENTS



II

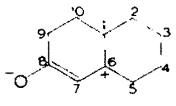


IV

	II	IV
Ground state	4·00 D[11]	2·72 D(a,b)
Excited state	9·6 D	6·4 D(b)

(a) See text. (b) Moment of α:β unsaturated ketone portion of molecule only.

The charge distributions for the model structure, (VII), can be calculated from the equation, $\mu = er$, using $r = 3{\cdot}55$ Å, and are presented for both ground and excited states in Table 5.



VII

Formula (VII) allows a clear view of the repulsion that would exist between the positive charge at position 6- and any positive charge at position 3-. Inasmuch as

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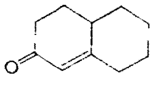
* The dipole moment of 3:5-dimethyl-2-*cyclo*hexen-1-one has been reported as 4·00 D.[11]

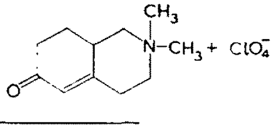
† In principle, any solvent pair would be suitable for this type of calculation, but the danger of specific interactions is clearly less for a hydrocarbon solvent-hydroxylic solvent combination. It is presumed that only negligible differences would exist between such solvents as *iso*octane and *cyclo*hexane, and the names are used interchangably in the present connection.

[11] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.* 2957 (1949).

the positive charge is increased in the excited state of the quaternary ion (IV), the increased repulsion between 6- and 3- should make excitation more difficult, i.e. require more energy. The magnitude of the increase should be directly related to the electrostatic repulsion between the charge at 3- and the *increase* in charge at the positive end of the conjugated system.

Table 5. Charge distributions[a]





Ground state	0·24	0·16
Excited state	0·56	0·38

[a] As fractions of a unit charge at one position, i.e. 6- in (VII).

Before presenting the calculation, it is necessary to point out that the charge distributions are derived directly or indirectly from experimental data, and do not at any point represent a hidden comparison between the positions of the $\pi \rightarrow \pi^*$-transitions of the ketones (II) and (IV). The assumption is also made that there is an intrinsic $\pi \rightarrow \pi^*$-transition energy for an $\alpha{:}\beta$-unsaturated ketone system of the type found in (II). A similar, much less restrictive assumption was implied in the development of the Woodward rules,[1] where the substituents are introduced directly on the conjugated system.

The electrostatic repulsive energy can be calculated with the equation 1, taking $D = 2{\cdot}0$ and r_{6-3} as 3·1 Å.* The repulsive energy should represent

$$E = q_1 q_2 / Dr \tag{1}$$

the extra energy required for the $\pi \rightarrow \pi^*$-transition of the quaternary ion (IV) over that needed for the carbocyclic ketone, (II). The repulsive energy amounts to 11·8 ± 0·8 kcal/mole and must be corrected for the attractive counteracting force between the positive charge at 3 and the O^- connected to position 8, and located at a distance of 6·5 ± 0·1 Å from the nitrogen. The attractive force is 5·6 ± 0·2 kcal/mole. The net "extra" energy required for the transition is thus calculated as 6·2 ± 1·0 kcal/mole. *It is found experimentally that the increase in transition energy for the quaternary ion in water over that for the carbocyclic ketone is* 6·2 ± 0·6 kcal/mole. The agreement between the calculated and experimental results permits the conclusion that electrostatic repulsion is responsible for most of the shift in absorption maximum when H is $N(CH_3)_2^+$ in formula I.

The spectroscopic characteristics of the aminoketone (III) did not permit an assessment of the charge distributions present in the ground and excited states. Hall[12] found that a series of electronegative replacements, **H**, in the 4-position of the piperidine ring, (VIII), reduce the basicity. From the value for **H** = NH, and including a correction for the fact that there are 2 NH groups, it may be estimated that the electrical effect of an NH group is equivalent to 0·04 of a positive charge. The use of such an equivalent positive charge does not lead to any reasonable value

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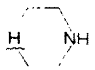
[12] H. K. Hall, Jr. *J. Amer. Chem. Soc.* **78**, 2570 (1956).

for the difference in ground and excited state charge-distributions for the aminoketone (III). However, is seems likely that the electronegativity of the nitrogen is



VIII

overcome to some extent by the opportunities for hydrogen-bonding by the protonated ion, and that the equivalent charge given is a minimum value.

CONCLUSIONS

The preceding discussion has illustrated the use of **Z**-values in calculating certain excited state dipole moments and in rationalizing in a satisfactory fashion the effect of a positive charge on the position of absorption of an $\alpha:\beta$-unsaturated ketone. Further studies on such systems, especially (I) with different **H**, offer interesting possibilities for evaluating long-range electrical effects in organic molecules. No single, simple measurement will provide accurate information;[5] it appears especially necessary to learn about the variation of both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$-transitions with solvent. The technique of solvent variation is also useful in establishing that the transitions under study are indeed related to recognizable types.[†]

EXPERIMENTAL

Spectra. All spectra were measured in Spectrograde or purified solvents with a Cary recording spectrophotometer, Model 11 at about 25°. The $n \rightarrow \pi^*$-transitions had more than one band in *cyclo*hexane; the most intense absorption band was used to obtain λ_{max} as listed in Table 3.

3-*Methyl*-3-*azabi*cyclo[4.4.0]-*dec*-6-*ene*-8-*one* (III). This aminoketone was prepared by the method of McElvain and Parker,[8] and was freshly distilled prior to spectroscopic examination. The methiodide, prepared in ether, was crystallized from ethanol.

3:3-*Dimethyl*-3-*azabi*cyclo[4.4.0]-*dec*-6-*ene*-8-*one ion perchlorate.* To a solution of 8·19 g (0·0266 mole) of the methiodide (III) in 25 ml water was added slowly a solution of 5·47 g (0·0264 mole) silver perchlorate in 10 ml water. The silver iodide formed was removed by filtration, and the clear aqueous solution was passed through 50 g amberlite IR 45 resin prepared as follows: 50 g of the resin were washed with two 250 ml portions water. After decanting the second wash, the resin was treated with 300 ml 4·5 M perchloric acid for 30 min. The column prepared from this resin was then washed with water until the eluate no longer tested acid to Congo red paper (36–40 l.).

The aqueous solution of quaternary perchlorate eluted from this column was evaporated to dryness at 40–45° under reduced pressure. The crystalline residue was readily recrystallized from either water or aqueous ethanol, m.p. 196–197°.

(Found: C, 47·44; H, 6·40; Calc. for $C_{11}H_{18}O_5NCl$: C, 47·23; H, 6·49%).

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[*] The distance between positions 6 and 3 was estimated with Catalin Molecular Models as 3·1 ± 0·1 Å. A calculation[12] indicated a slightly smaller figure, using the *cyclo*hexylidene structure as the model.

[†] The compound which has an acetyl group in place of the methyl group at the 3-position of the aminoketone (III) does not give a linear plot of transition energies against **Z**. The explanation for its special behaviour will be reported elsewhere (unpublished results).

[12] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* **77**, 2505 (1955).