The Dipole Moments and Resonance in the Tetronic Acids[1]

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The tetronic acids have abnormally high dissociation constants compared with ethyl acetoacetate, to which they are closely related structurally. Thus tetronic acid has a $pKa = 3.76$ while ethyl acetoacetate has a $pKa = 10.7$. We have proposed that there is a large amount of resonance in the tetronic acids which is responsible for their high acidity and evidence has been presented in support of this hypothesis.[2] The present study was undertaken to obtain further independent evidence on the structure of these compounds from their dipole moments.

If one or more of the resonating forms contributing to the structure of a molecule has a separation of charge, it is likely that the dipole moment of such a molecule will be abnormal. The dipole moment may be either greater or less than expected depending on whether the dipole resulting from the separation of charge is in position to support or oppose the resultant dipole in the normal form of the molecule.[3] The resultant dipole in the normal form of the molecule can be calculated from the vector addition of the group moments that the molecule contains. If there is a discrepancy between the calculated and observed dipole moment of a compound of sufficient magnitude so that induction cannot be responsible for the effect, then there is good evidence that an excited resonating form involving a separation of charge contributes appreciably to the structure of the molecule.

The dipole moments of tetronic acid, α-chlorotetronic acid, α-bromotetronic acid, methyl α-bromotetronate, α-iodotetronic acid, methyl α-iodotetronate, and l-ascorbic acid have been determined in dioxane solutions.

Results

The symbols used in the equations and table are: ω, the weight fraction of solute; d, the density of the solution; P_2, the polarization of the solute; P_{2_0}, the polarization of the solute at infinite dilution; P_{E_2}, the electronic polarization of the solute; μ, the dipole moment; T, the ab-

TABLE I

ω	d	ϵ	P_2
Tetronic Acid			
0.000000	1.02803	2.20227	
.002119	1.02866	2.26269	484
.005722	1.02976	2.36777	479
.009429	1.03092	2.47461	467
.023694	1.03533	2.95534	462
α-Chlorotetronic Acid			
.000000	1.02810	2.21042	
.001498	1.02883	2.25665	698
.002174	1.02913	2.27819	701
.003527	1.02974	2.32180	701
α-Bromotetronic Acid			
.000000	1.02803	2.20227	
.008491	1.03239	2.42294	752
.016227	1.03677	2.62259	719
.025680	1.04202	2.87741	685
Methyl α-Bromotetronate			
.000000	1.02803	2.20227	
.003162	1.02951	2.28283	825
.006424	1.02987	2.36514	817
.010184	1.03262	2.45884	784
.020860	1.03751	2.73467	746
α-Iodotetronic Acid			
.000000	1.02803	2.20227	
.006442	1.03144	2.31523	666
.010075	1.03337	2.38003	659
.019638	1.03829	2.54640	630
Methyl α-Iodotetronate			
.000000	1.02825	2.21628	
.002177	1.02931	2.26007	819
.007422	1.03222	2.36865	813
.011877	1.03454	2.45096	765
l-Ascorbic Acid			
.000000	1.02816	2.21366	
.003955	1.02996	2.25919	356
.006030	1.03070	2.28458	362
.009054	1.03218	2.32136	362

TABLE II

	P_{2_0}	P_{E_2}	μ
Tetronic acid	485	21.1	4.72
α-Chlorotetronic acid	700	26.0[4]	5.69
α-Bromotetronic acid	777	28.5	6.00
Methyl α-bromotetronate	830	32.4	6.19
α-Iodotetronic acid	689	36.9	5.59
Methyl α-iodotetronate	820	39.7	6.12
l-Ascorbic acid	360	38.2	3.93

(1) Presented before the Organic Division at the Cincinnati meeting of the American Chemical Society, April 11, 1940.

(2) Kumler, THIS JOURNAL, 60, 859 (1938).

(3) Kumler and Porter, ibid., 56, 2549 (1934).

(4) This value was calculated from the group refractivities taken from the literature.

solute temperature. The measurements were all carried out at 25° using dioxane as a solvent. The polarizations were calculated by use of the equations

$$p_1 = \frac{\epsilon - 1}{\epsilon + 2} \frac{1}{d}$$

$$p_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{1}{d} = (1 - \omega)p_1 + \omega p_2$$

$$P_2 = M_2 \left(p_1 + \frac{p_{12} - p_1}{\omega} \right)$$

where p_1 is the specific polarization of the solvent, p_2 the specific polarization of the solute and p_{12} the specific polarization of the solution. The P_{E_2} values were calculated from the refractive indices for the D sodium line. The P_{2_0} values were obtained by plotting P_2 against ω and extrapolating the best curve to zero concentration. The dipole moments were calculated by means of the equation

$$\mu = 0.0127 \sqrt{(P_{2_0} - P_{E_2})T}$$

The dioxane was warmed to facilitate solution of the compounds but upon cooling to the working temperature of 25° no precipitation occurred.

Discussion

The tetronic acids are possible keto–enol tautomers. The moment of the keto form of tetronic acid was calculated using 110° for single–single bond angles, 125° for single–double bond angles, 2.85 for the value of the moment of the carbonyl group which takes into account the $>C^+\text{–}O^-$ resonance, and 4.12[5] for the value of the lactone moment which takes into account the $\diagdown\!\!\!\overset{+}{O}\!\!\diagup\!\!\overset{|}{C}\!\!\diagdown\!\!\overset{-}{O}$ resonance. All moments are in Debye units. The resultant moment of the lactone group was found to make an angle of 161° with the moment of the carbonyl group and the resultant moment of the molecule was found to have a value of 1.69, a value far below the observed moment of 4.72. Since there are no other resonances that can contribute to the keto structure other than the two already considered, this large difference between the calculated and observed moments effectively rules out the presence of an appreciable amount of the keto structure in dioxane solution.

The calculated moment of the enol form has a value of 2.58 if the hydroxyl group is fixed as in I, a value of 4.55 if it is fixed as in II and a value near the average moment 3.56 if the hydroxyl

(5) Marsden and Sutton, *J. Chem. Soc.*, 1383 (1936).
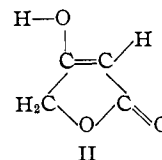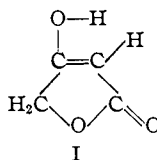
group is free to rotate. All of these moments are less than the observed moment 4.72, indicating that some resonating form with a separation of charge contributes to the structure of the molecule. Whereas no such structure was possible with the keto tautomer, with the enol tautomer a resonating form III would be expected
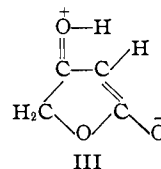
to contribute to the structure of the molecule. This form would raise the moment and it would prevent free rotation. Consequently we conclude that the hydroxyl does not rotate freely because the calculated moment for free rotation is much smaller than the observed moment and a contribution by the resonating form sufficient to raise the moment to the observed value would also certainly prevent free rotation.

Of the two ways, I and II, in which the hydroxyl group can be fixed, practically all of the evidence points to structure I. The difference between the observed moment and the calculated value for II 4.72 − 4.45 = 0.27 represents such a small amount of resonance that it would be insufficient to prevent free rotation.[6] The difference 4.72 − 2.58 = 2.14 for I represents an ample amount of resonance to restrict free rotation. The amount of resonance represented by the difference 0.27 also appears insufficient to account for the high acid strength of these compounds. With the hydroxyl groups pointing as in II the calculated

(6) In the case of esters Marsden and Sutton[5] have shown that free rotation is prevented due to resonance and that the difference between the observed and calculated moments is likewise equal to 0.27. However, the tetronic acids are much different in that the charged atoms are considerably farther apart and the angle between the resultant dipoles in the normal form and the form with a separation of charge is less than with esters. Both of these effects complement one another so that a small amount of resonance gives rise to a comparatively large difference between observed and calculated moments. Thus while with esters a difference of 0.27 between the observed and calculated value for the dipole moment represents an amount of resonance sufficient to prevent free rotation a difference of 0.27 with tetronic acid represents only about one-third or one-fourth as much resonance which is most probably insufficient to prevent rotation.

value is inconsistent with the observed moment of ascorbic acid. When they point in the opposite direction the moment of this compound is consistent with that of the other acids.

The dipole moment evidence thus indicates that tetronic acid is chiefly in the enol form in anhydrous dioxane, that a resonating form with a separation of charge contributes appreciably to the structure of the molecule, and that the hydroxyl group is fixed as in structure I.

The moments of the α-halogen substituted tetronic acids are 5.69, 6.00 and 5.59 for the chloro, bromo, and iodo compounds, respectively. These moments are 2.2 to 3.0 units higher than the calculated moments for the enol forms with the hydroxyl groups pointing as in I, indicating that resonating forms with a separation of charge contribute appreciably to the structure of these molecules also. The difference 2.2 to 3.0 between the calculated and observed moments for these acids is about the same as the difference 2.14 for tetronic acid.

That the moment of the bromo compound is higher than that of the chloro or iodo compounds suggests that two or more factors are affecting the moment. To account for the high value of the bromo compound it is only necessary to have the two factors affect the moment in the reverse order as we go up or down the series Cl, Br, I.

Cases like this of a mixed order for the halogens are fairly common.[7] There is a resonance common to compounds having halogen attached to a doubly-bonded carbon atom that would con-


IV
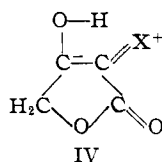
tribute to the structure of these halogen substituted acids IV. Because of the position of the charged atoms in this form, the resonance would give rise to a moment that would oppose the moment resulting from the main resonance in the compound, so that these two resonances in themselves would be two factors affecting the moment in the reverse order and hence are sufficient to account for the observed moments.
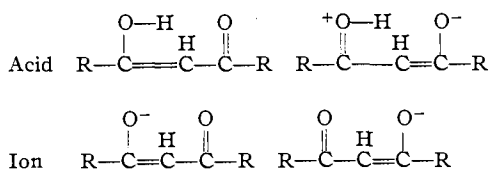
The moments of the two esters, 6.19 for methyl α-bromotetronate and 6.12 for methyl α-iodo-

tetronate, are not greatly different from the moments of the corresponding acids 6.00 and 5.59, respectively. It is known that the esters have the methyl groups attached to oxygen,[8] and hence the molecules have the enol form; consequently the fact that the moments of the acids are not far different from the moments of the esters is additional evidence that the acids are likewise in the enol form.

The observed moment of ascorbic acid 3.93 was at first surprising since it is 0.79 unit less than the moment of tetronic acid, although ascorbic acid has three more hydroxyl groups than tetronic acid. However, if we consider the β-hydroxyl group on the ring as fixed and pointing to the right, as was found to be the most probable situation in tetronic acid, then the α-hydroxyl group would have a great tendency to be fixed in the same relative position due to the repulsion of the hydrogen of the β-hydroxyl and the attraction of the negatively charged oxygen of the lactone group. With the α-hydroxyl group in this position it would greatly reduce the calculated moment of the molecule. From a study of the model it appears possible for the hydrogen on the α-hydroxyl group on the side chain to form a hydrogen bond with the oxygen of the β-hydroxyl group on the ring thus causing this third hydroxyl group to be lined up in the same way as the two hydroxyl groups on the ring. The calculated moment of the normal form of such a molecule would be sufficiently low to allow for considerable resonance and still have an observed moment of 3.93.
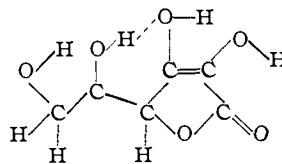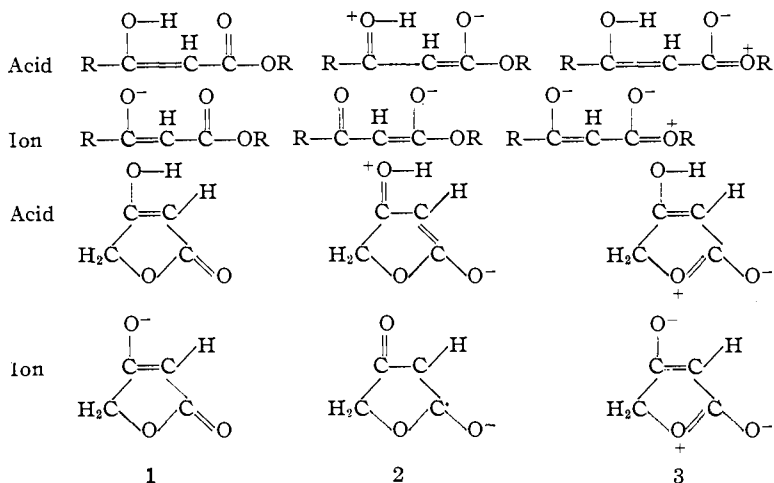

The resonating forms of unsubstituted 1,3-diketones, β-ketonic esters and β-ketonic γ-lactones may be represented as follows:

(7) Nixon and Branch, THIS JOURNAL, 58, 497 (1936).

(8) Kumler, ibid., 60, 2532 (1938).

Acid   R—C=C—C—OR   R—C—C=C—OR   R—C=C—C=OR

Ion   R—C=C—C—OR   R—C—C=C—OR   R—C=C—C=OR

Acid

Ion

1   2   3

That β-ketonic esters (Ka_{enol} of ethyl acetoacetate 5×10^{-9}) are considerably weaker acids than 1,3-diketones (Ka_{enol} acetylacetone 1.3×10^{-5}) can be explained by the third resonating form 3 which is present in the former. This third form stabilizes the acid more than the ion, due to the unfavorable distribution of charge in the ion, and consequently makes the acid weaker. In β-ketonic γ-lactones such as tetronic acid, we propose that this third form is excluded in both the ion and the free acid because of the strain set up in the ring by the presence of the two double bonds. Consequently these compounds have resonating forms and acid strengths not greatly different from 1,3-diketones. The additional strength of tetronic acid Ka 1.7×10^{-4} over the enol form of acetylacetone Ka 1.3×10^{-5} can be ascribed to the negativity of the additional oxygen plus double action around the ring.

Experimental

Apparatus.—The dielectric constants were measured with an oscillating circuit containing a gold-plated fixed condenser of 114.2 $\mu\mu f$ capacity which was connected in parallel with a 1500 $\mu\mu f$ General Radio calibrated variable condenser. A commercial broadcasting station KPO operating at a frequency of 680 kilocycles was used as a source of constant frequency oscillations. The beats between the oscillating circuit and the broadcasting station were picked up on an ordinary radio and matched with a 1000-cycle tuning fork. Densities were measured with a pycnometer of approximately 10 ml. capacity. Refractive indices were taken with a Pulfrich refractometer. Temperatures were controlled to within ±0.05° by electrically regulated thermostats.

Materials

Dioxane.—Commercial 1,4-dioxane was refluxed for eight to ten hours with molten sodium and then distilled from a vacuum-jacketed adjustable-reflux column one

meter high which was packed with one-turn glass helices. The product boiled at 101.0–101.2° at 753 mm. Tetronic acid, α-chlorotetronic acid, α-bromotetronic acid, α-iodotetronic acid, methyl α-bromotetronate, methyl α-iodotetronate: These compounds were prepared as described previously,[1,9] and were of the same purity with the exception of the sample of α-chlorotetronic acid which had an equivalent weight of 138 compared with an equivalent weight of 136 for the previous preparation.

l-Ascorbic Acid.—The Merck product was used without further purification.

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Summary

The dipole moments of five tetronic acids and two esters have been determined in dioxane solution. The moments are as follows: tetronic acid 4.72, α-chlorotetronic acid 5.69, α-bromotetronic acid 6.00, methyl α-bromotetronate 6.19, α-iodotetronic acid 5.59, methyl α-iodotetronate 6.12, *l*-ascorbic acid 3.93.

As a result of a comparison of the observed with the calculated moments in tetronic acid it is concluded that: (1) the compound is chiefly in the enol form in dioxane solution; (2) a resonating form involving a separation of charge contributes to the structure of the molecule; (3) the hydroxyl group is fixed in the plane of the ring with the hydrogen of the hydroxyl oriented toward the α-carbon atom. The moments of the α-halogen substituted tetronic acids are consistent with the above interpretation.

The moments of the methyl esters are close to the moments of the acids indicating that the acids are in the enol form since the methyl groups in the esters are known to be attached to oxygen.

The resonating forms of 1,3-diketones, β-ketonic esters and β-ketonic γ-lactones are discussed. It is proposed that the reason for the high acidity of β-ketonic γ-lactones is due mainly to the exclusion of the third resonating form because of the strain in the ring resulting from the presence of the two double bonds.

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(9) Kumler, THIS JOURNAL, **60**, 855, 857 (1938).