The Thermodynamics of Ion Association in Solution.
II. Mixed Ion Association

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Abstract: Mixed ionic aggregates, such as the triple ion ABC, are more stable than would be predicted from elementary considerations of the stability of the triplet ions ABA and CBC. A similar stabilization of the mixed ion quadrupole ABCB, as compared to ABAB and CBCB, occurs. For both mixed ion triplets and quadrupoles, entropy effects contribute R ln 2 eu toward the total stabilization. The principal stabilization, however, arises from the polarization terms in the expression describing the potential energy of the systems. Agreement is found between theory and experimental results in benzene and acetic acid.

A summary of the experimental data relating to ion association in solution has been given in part I,[1] and relationships between the association constant of an ion aggregate, the dielectric constant of the solution, and the internuclear separation of the ions have been derived from fundamental thermodynamic considerations. The ion aggregate is treated as a system of polarizable spheres in contact, held together by purely Coulombic forces, in a solvent in which the microscopic dielectric constant is the same as the macroscopic value and in which the free-energy change on solvation is approximately the same for the ion aggregate as for the free ions. The experimental data are shown to support this model, allowing reasonable internuclear separations to be calculated for aggregates up to sexapoles. The species considered were the ion pair AB, the triplet ABA (or BAB), the quadrupole $(AB)_2$, and the sexapole $(AB)_3$.

In a few cases association constants for mixed aggregates have been measured. Mixed triplets (*e.g.*, ABC) in benzene have been studied by Hughes, Ingold, Patai, and Pocker,[2] and mixed quadrupole and sexapole formation (*e.g.*, ABBC) in anhydrous acetic acid is investigated here. Extensive association in benzene has also been found by Bruckenstein and Saito[3] and Steigman and Lorenz.[4] In all cases the mixed aggregates were found to be more stable than a knowledge of the "pure" association constants (*e.g.*, constants for $(AB)_2$ and $(CB)_2$ for AB_2C) would have led one to believe indicating, to quote Hughes, *et al.*, "the mixtures are making a better than statistical use of their additional opportunities for forming triple ions and are therefore probably generating a more than statistical proportion of the mixed ions." Milne and Cubicciotti, while deriving expressions for the potential energies of alkali halide quadrupoles of the type AB_2A in the vapor, considered the formation of mixed quadrupoles of the type AB_2C and found a slight stabilization is to be expected, the stabilization increasing as the differences in size between the ions A and C increased.[5] They were able to support this finding by experiment, but the accuracy was such that quantitative treatment was not possible.

This work is concerned with the factors leading to stabilization of mixed aggregates and the comparison of theory with experimental results obtained in glacial acetic acid and in benzene.

Experimental Section

Materials. Anhydrous acetic acid was prepared by the method described elsewhere.[6] The "anhydrous" acid prepared by this slow fractionation technique was found to contain small, equal amounts of water and acetic anhydride, formed presumably by an equilibrium reaction in the vapor phase where no mineral acid was present to catalyze recombination. The equilibrium concentrations present were determined by two methods and were found to be 0.0045 M (by a spectrophotometric titration[7]). This water and acetic anhydride could be made to recombine by adding a trace of mineral acid too small to detect cryoscopically (less then 0.0001 M) and leaving for 24 hr.

Acetous perchloric and sulfuric acids were prepared from AR acids and acetic acid, the water present being reacted with a calculated quantity of acetic anhydride. Excess water was determined by Karl Fischer titration and free acetic anhydride by spectrophotometric titration.[7] The acid strength was determined by titration with acetous potassium hydrogen phthalate using crystal violet as indicator. To prevent darkening of the solutions they were stored in a refrigerator and kept out of sunlight.

Other Salts. AR grade materials were used and dried *in vacuo* at 80° for 2–4 hr before use. Purity was checked by titration.

Cryoscopy. Association constants for a range of ionic solutes in anhydrous acetic acid were determined by a cryoscopic technique. The freezing points of solutions of the solute, of varying molar analytical concentrations m_s, were determined relative to that of the pure solvent and the apparent concentrations, Σm, calculated from the cryoscopic constant for acetic acid. Temperature changes in the solution were followed by following the change in resistance, ΔR, of a thermistor which was connected as one arm of a Wheatstone bridge circuit with all other resistances thermostated at 0°. The unbalance potential, P, measured across opposite arms will vary linearly with ΔR over small temperature ranges. It was found that this assumption led to an error of less than 0.001° for temperature changes of up to 0.5°. The change in potential was calibrated directly in °C with solutions of benzene and naphthalene in the concentration range of 0.01–0.15 M, assuming them to exist as monomers, using the cryoscopic constant of 3.59°/mole.[8] The thermistor was further checked against a Beckmann thermometer. From the freezing point depressions of benzene and naphthalene the cryoscopic constant was found to be 3.56 and 3.55°/mole, respectively.

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[1] L. D. Pettit and S. Bruckenstein, *J. Am. Chem. Soc.*, **88**, 4783 (1966).

[2] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).

[3] S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965).

[4] T. Steigman and P. M. Lorenz, *ibid.*, submitted for publication.

[5] T. A. Milne and D. Cubicciotti, *J. Chem. Phys.*, **29**, 846 (1958).

[6] I. M. Kolthoff and. S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

[7] S. Bruckenstein, *Anal. Chem.*, **28**, 1920 (1956).

[8] J. Kenttamaa, *Suomen Kemistilehti*, **B32**, **9**, 220 (1959).

Table I. Apparent Concentrations (M) of Some Compounds as Determined Cryoscopically in AcOH[a]

				Perchloric Acid				
m_s	0.0024	0.0065	0.0144	0.0296	0.0391	0.0485	0.0576	0.0754
Σm	0.0020	0.0060	0.0133	0.0275	0.0364	0.0420	0.0487	0.0601
m_s	0.0925	0.1090	0.1404	0.1834	0.2225	0.2578	0.5085	
Σm	0.0703	0.0811	0.0989	0.1240	0.1461	0.1653	0.2900	
				Sulfuric Acid				
m_s	0.0840	0.1226	0.1607	0.1984	0.2346	0.2888	0.3590	
Σm	0.0801	0.1186	0.1543	0.1879	0.2185	0.2608	0.3133	
				Sodium Perchlorate				
m_s	0.0208	0.0428	0.0643	0.0868				
Σm	0.0200	0.0392	0.0579	0.0762				
				Diethylanilinium Perchlorate				
m_s	0.0191	0.0413	0.0589	0.0807	0.1022			
Σm	0.0170	0.0340	0.0448	0.0562	0.0681			
				Perchloric Acid–Sodium Perchlorate				
$m_s(HClO_4)$		0.0200	0.0391	0.0576	0.0754	0.0926	0.1090	0.1250
$m_s(NaClO)_4$		0.0851	0.0835	0.0819	0.0804	0.0790	0.0776	0.0761
Σm		0.0825	0.0893	0.0950	0.1021	0.1079	0.1148	0.1222
				Perchloric Acid–Diethylanilinium Perchlorate				
$m_s(HClO_4)$		0	0.0212	0.0416	0.0613	0.0803		
$m_s(di(et)ClO_4)$[b]		0.0415	0.0406	0.0398	0.0390	0.0382		
Σm		0.0345	0.0365	0.0405	0.0462	0.0553		

[a] m_s = molar analytical concentration, $\Sigma m = \Delta T/3.59$ = apparent molar concentration as measured cryoscopically. [b] Diethylanilinium perchlorate.

The freezing points were determined in the cell described elsewhere[9] using a cold finger (a platinum wire cooled by solid CO_2) to minimize supercooling. Results reproducible to better than 0.001° were possible using a 1-mv full-scale deflection chart recorder and following the change in P with time after the bridge had been adjusted to $P \sim 0$ for the freezing pure solvent. A typical freezing curve showed supercooling of about 0.1°.

Dissolved atmospheric gases were found to influence successive freezing points of the same solution. All solutions were therefore outgassed with helium before freezing. Solubilities of oxygen and nitrogen, assuming that of helium to be very small, were found to be 0.010 and 0.005 M, respectively, at 16°.

Results

The cryoscopic data obtained were used to calculate the total concentration of species in solution, Σm. It was assumed that all activity coefficients were 1, hence $\Sigma m = \Delta T/3.59$, where ΔT is the freezing point depression. Table I gives the results obtained in acetic acid solutions of perchloric acid, sulfuric acid, sodium perchlorate, and diethylaniliniun perchlorate, and two-component solutions, perchloric acid–sodium perchlorate and perchloric acid–diethylanilinium perchlorate. In addition, solutions of mercuric acetate (up to 0.064 M), silver perchlorate (up to 0.077 M), and sodium acetate (up to 0.073 M) were studied, but no detectable association beyond ion pairs could be detected. Other salts proved too insoluble for study but the following solubilities were determined: silver perchlorate, 0.019 M, and tetraethylammonium perchlorate, 0.006 M.

Apparent association constants, calculated by Kenttamaa's equation,[8] were not constant for a range of concentrations, indicating that more than one association reaction was taking place. The data for perchloric acid were, therefore, treated by an iterative method assuming both quadrupole and sexapole formation to take place. The following constants were obtained. $K_4 = (HClO_4)_2/(HClO_4)^2 = 4.77 \pm 0.27$ and $K_4K_6 = (HClO_4)_3/(HClO_4)^3 = 28.0 \pm 3.0$. The data for the other systems did not cover a sufficiently wide range of concentrations to allow reliable values for both constants to be calculated but approximate constants are as follows: sulfuric acid, $K_4K_6 = 0.90$; sodium perchlorate, $K_4 = 2.5$, $K_4K_6 = 15$ (approximate); diethylanilinium perchlorate, $K_4K_6 = 133$. Mixed constants for $HClO_4$–$NaClO_4$ were calculated by successive approximations assuming the species $HClO_4 \cdot NaClO_4$ and $(HClO_4)_2 \cdot NaClO_4$ to be present in addition to the "pure" aggregates. Values for the mixed constants were found to be

$$NaClO_4 \longrightarrow HClO_4 \cdot NaClO \quad K = 47$$

$$NaClO_4 + 2HClO_4 \longrightarrow (HClO_4)_2 \cdot NaClO_4 \quad K = 480$$

The existence of many of these mixed aggregates is also indicated by conductivity titrations.

Discussion

The equilibrium constant for an association reaction is best divided into the two components: the enthalpy change (related to the potential energy) and the entropy change accompanying the reaction. Both components are found to contribute toward the stabilization of mixed species.

Mixed Triple-Ion Formation. (a) Entropy Changes. The translational and vibrational entropy changes accompanying the formation of a mixed triplet, ABC, would expected to be approximately the mean of the changes accompanying the formation of the pure triplets, ABA and CBC. This follows from the statistical equations for the entropies. The expression for the rotational entropy, however, includes a symmetry number, σ

$$S_R = R\left[1 + \ln\left(\frac{8\pi^2IkT}{h^2\sigma}\right)\right] \tag{1}$$

which takes the value of 2 for the symmetrical triplets and 1 for the unsymmetrical species ABC. The entropy

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(9) L. D. Pettit and S. Bruckenstein, *J. Inorg. Nucl. Chem.*, 24, 1478 (1962).

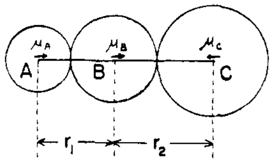

Figure 1. Mixed ion triplet.

of the symmetrical ions should therefore be R ln 2 (*i.e.*, 1.4 eu) lower than expected. If this factor is then inserted in the equation for the association constant, K

$$\Delta G = \Delta H - T\Delta S = -RT \ln K \qquad (2)$$

the value for K should be changed by a factor of 2 (*i.e.*, log K by 0.3 log unit). Hence, the entropy component should result in the mixed triplet being approximately twice as stable as the mean value for the "pure" species.

This suggestion was tested by considering linear triatomic molecules, the entropies of which have been measured and could be calculated accurately. The molecules CO_2, CS_4, and COS were selected since, although the bonding is very different from that expected for an ion triplet in solution, the geometry is the same. Calculated and measured entropies at 25° are as given in Table II.[10] These figures confirm the above assumptions. In general, S_T, S_V, and S_R (neglecting σ) values are such that the average values for CO_2 and CS_2 are the same as those found for COS. Inclusion of the symmetry number gives a difference of 1.0 eu in the total entropy (1.3 eu in the S_R values) which is approximately the R ln 2 units expected.

Table II. Calculated *vs.* Measured Entropies (eu)

	CO_2	CS_2	COS	$(CO_2 + CS_2)/2$
S_T	37.27	39.26	38.20	38.26
S_V	0.73	2.62	1.51	1.67
S_R	13.07	15.72	15.66	14.40
S (total)	51.07	57.60	55.37	54.33
S (measd total)	51.16	57.48	55.27	54.32

(b) Potential Energy Changes. Mixed association constants can be corrected for the influence of symmetry on the entropy changes by dividing the constants for the mixed species by two. If these adjustments are made, a stabilization of the mixed aggregate is still found. This must be due to potential energy changes in the species concerned.

The potential energy (U_3) of a mixed ion triplet, ABC, shown in Figure 1 with induced dipoles assumed in the directions indicated, may be expressed in the way outlined in part I.[1] Ion-pair formation constants may be defined as follows

$$K_{AB} = \frac{(AB)}{(A)(B)}$$

$$K_{AC} = \frac{(CB)}{(C)(B)}$$

after corrections for entropy changes have been made. Mixed triple-ion formation can take place by two paths.

$$\text{(a) CB} + \text{A} = \text{ABC}$$

$$K^{A}{}_{ABC} = \frac{(ABC)}{(CB)(A)}$$

$$\text{(b) AB} + \text{C} = \text{ABC}$$

$$K^{C}{}_{ABC} = \frac{(ABC)}{(AB)(C)}$$

If the triple-ion formation constants for the pure triplets, ABA and CBC, are K_{CBC} and K_{ABA}, respectively, the apparent stabilization of the mixed species formed by, for example, path a will be

$$S = (K^{A}{}_{ABC})^2/K_{ABA}K_{CBC} \qquad (3)$$

If S is greater than 1, apparent stabilization is found. Clearly the constants for paths a and b will be different depending on the ion-pair formation constants, K_{AB} and K_{CB}.

Of more fundamental importance is the stabilization found if the over-all constant for formation of the mixed species is greater than the mean values for the pure aggregates, *i.e.* if

$$\beta_{ABC}{}^2 > \beta_{ABA}\beta_{CBC} \qquad (4)$$

i.e., if

$$-\Delta U_3 = -2U_{ABC} + U_{ABA} + U_{CBC} > 0 \qquad (5)$$

The relationship 5 is very difficult to evaluate precisely since ΔU_3 will be the difference between two large quantities and therefore dependent on the inclusion of all the polarization terms in the original potential energy expression.

For simplicity, the following reaction has been considered.

$$\text{ABA} + \text{CBC} = 2\text{ABC}$$

$$K_m = \frac{(ABC)^2}{(ABA)(CBC)} = \frac{(K^{A}{}_{ABC})^2 K_{BC}}{K_{ABA}K_{CBC}K_{AB}} \qquad (6)$$

i.e.

$$K_m = S\frac{K_{BC}}{K_{AB}}$$

As suggested above, the entropy change accompanying this reaction will be $2R$ ln 2 eu = 2.76 eu. Using the extended theoretical expression for the association constant derived in part I, and not correcting K_m values for symmetry effects, the following expression is obtained

$$\log K_m = \frac{-\Delta U_3}{2.30DRT} + 0.60 \qquad (7)$$

where ΔU_3 is in kilocalories. Since, from eq 6, $S = (K_{AB}/K_{CB})K_m$, the apparent stabilization, S may be expressed directly in terms of ΔU_3, which is itself dependent on the ratio of the radii of A and B and their polarizabilities. Unfortunately, no simple relationship can be given, but expected apparent stabilizations for a number of model triple ions in benzene at 25° are given in Table III.

These stabilizations may be compared with experimental values shown in Table IV. The stabilizations

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[10] E. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York, N. Y., 1957, Chapter XI.

Table III. Calculated Stabilization Energies of Some Ion Triplets

Species	r_1, A	r_2, A	U_3, kcal
a	4.0	5.0	0.86
b	4.0	5.0	5.87
c	5.0	6.0	3.57
NaKCl	2.23	2.93	5.03

[a] Model ion triplet neglecting all polarization terms. [b] Model ion triplet assuming polarizabilities (A^3) of $\alpha_A = 2.33$, $\alpha_B = 5.35$, $\alpha_C = 9.13$. [c] Model ion triplet assuming polarizabilities (A^3) of $\alpha_A = 9.13$, $\alpha_B = 5.35$, $\alpha_C = 23.29$.

found in practice are very similar in magnitude to the stabilizations found for model structures of comparable geometry, indicating that this treatment gives a reasonable explanation of the experimental observations. The figures in Table III demonstrate that the stabilizations found are largely the result of the polarization terms; there is virtually no stabilization when polarizabilities are omitted. Attempts to calculate interionic separations from the measured stabilizations failed because of the sensitivity to polarizabilities, which can only be estimated for the ions involved, and the complicated dependency of ΔU_3 on both r_1 and r_2 values.

Table IV. Experimental Values of Mixed Triplet-Ion Formation Constants in Benzene

Species	Log β_{ABC}	Log K_m	U_3, kcal
$Bu_4N \cdot Cl \cdot N_3$	21.85	0.48	−0.37
$BuN \cdot Cl \cdot NO_3$	22.35	1.32	2.23
$Bu_4N \cdot Cl \cdot ClO_4$	22.46	1.70	3.41
$Bu_4NO_3 \cdot ClO_4$	22.30	1.16	1.73

Mixed Ion-Quadrupole Formation. (a) Entropy Changes. A mixed ion quadrupole of the type AB_2C will be planar and kite-shaped (Figure 2) while the pure quadrupole, $(AB)_2$, will be a rhombus (*i.e.*, Figure 2 where $r_{AB} = r_{CB}$). The mixed quadrupole will, therefore, have C_{2v} symmetry, with a symmetry number of 2, while the pure quadrupole will have D_{2h} symmetry ($\sigma = 4$). The results of these differences in symmetry number will be identical with the mixed triplet case considered, *i.e.*, a larger entropy (by R ln 2 eu) for the mixed species as compared with the pure forms. Once the geometry of the quadrupole has been established, translational and approximate vibrational entropies may be calculated as described in part I.[1] The rotational entropy will depend on the moments of inertia about the three space axes as well as the symmetry number. These may be calculated readily for the rhombus, but for the mixed quadrupole (the kite) the position of the center of gravity must first be calculated and moments of inertia calculated about this point. If this is done, it is found that, as with ion triplets, all the entropy terms for the mixed quadrupole are the mean of those for the two corresponding pure quadrupoles apart from the R ln 2 term in the rotational entropy. No experimental data are available to test this conclusion, but calculations on the mixed alkali halides support this entirely for the translational and rotational entropy components and to within 0.3 eu for the vibrational component (where, owing to approximations in the calculation, the results are unreliable).

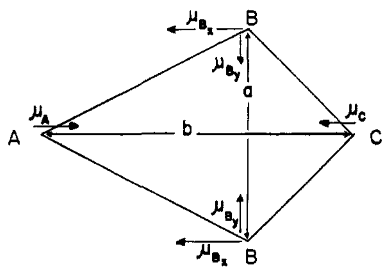

Figure 2. Mixed ion quadrupole.

(b) Potential Energy Changes. The potential energy of four ions arranged as in Figure 2 was calculated by the method outlined in part I with the aid of a Control Data 1604 computer, but, in this case, both r_{AB} and r_{CB} had to be adjusted to give a minimum energy configuration. The dipoles induced in ions A and C would act along the diagonal AC but, for convenience in calculation, the dipoles induced in the B ions were split into two components at right angles, μ_{BX} and μ_{BY}. This gives an arrangement of four ions and six dipoles. All possible interactions were considered, including repulsions of the form $B/r^{6.9}$ for each ion–ion interaction where B was calculated from the corresponding ion pair. The potential energy so calculated was minimized by first adjusting the diagonal a, keeping r values constant, and then adjusting r values assuming the angles calculated from the first iterations. Typical results are shown in Table V where the results for pure quadrupoles are included for comparison and ΔU_4 values are calculated where

$$\Delta U_4 = 2U_{4(ABCB)} - U_{4(AB)_2} - U_{4(CB)_2}$$

Values calculated by Milne and Cubicciotti[5] are also included to demonstrate the close agreement provided by the two different methods of calculation since their equation neglected all polarization terms, but instead, included a variable exponent in the repulsion term. Values for ΔU_4, which represents the small difference between two large numbers demonstrates the very good agreement between the two methods.

Table V.[a] Calculated Stabilization Energies of Some Ion Quadrupoles

Species	$2U_{4(ABBC)}$	$U_{4(ABBA)}$ + $U_{4(CBBC)}$	ΔU_4	$\Delta U_4{}^5$
NaF_2Li	857.2	853.5	3.7	2.6
CsF_2Li	799.1	785.4	13.7	14.4
$LiCl_2K$	646.9	643.3	3.6	5.2
$LiCl_2Rb$	636.0	631.3	4.7	6.8
$LiCl_2Cs$	628.3	622.0	6.3	9.2
LiI_2Na	608.0	606.4	1.6	1.2
$NaCl_2K$	577.5	576.2	1.3	
ICs_2F	534.8	530.4	4.4	
4 × 5 A[b]	315.8	313.8	2.0	

Exptl values in acetic acid at 16° for $HClO_4 \cdot NaClO_4$

2 log $\beta_{4(ABBC)}$	log $\beta_{4(ABBA)}$ + log $\beta_{4(CBBC)}$	log m	ΔU_4 (from eq 7)
24.00	21.77	2.23	13.1

[a] All U values in kcal. [b] Hypothetical kite quadrupole with stated diagonals.

The value calculated experimentally for the mixed quadrupole $NaClO_4 \cdot HClO_4$ from the cryoscopic study described is included to demonstrate that these observations can be explained in terms of the entropy and potential changes expected. However, it is difficult to visualize the shape of the solvated proton in an ion quadrupole and the fact that some changes in geometry must take place in H(solv)ClO_4 as compared with $NaClO_4$ on going from an ion pair to an ion quadrupole is demonstrated by the changes in the magnitude of K_2 and K_4 values: $HClO_4$: log K_2 = 4.87, log K_4 = 0.68; $NaClO_4$: log K_2 = 5.48; log K_4 = 0.39.

The increased stability found for the mixed sexapoles (*e.g.*, $(HClO_4)_2 \cdot NaClO_4$) could presumably be explained by the same arguments, which would also account for the more extensive mixed association found by Bruckenstein and Saito[3] in a solvent of very low dielectric constant (benzene). Equation 7 shows that the stabilization due to entropy changes is independent of dielectric constant while the enthalpy changes are inversely proportional to it.

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The Crystal Structure of Azulene-1,3-dipropionic Acid[1]

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Contribution from the Department of Biological Structure, University of Washington, Seattle, Washington. *Received February 11, 1966*

Abstract: The crystal structure of azulene-1,3-dipropionic acid has been determined with visually estimated copper data. The symbolic addition procedure was used to obtain a solution starting with three origin-fixing signs and four unknown signs. The correct solution was chosen from the 16 possibilities using a computer program (PHASER). An *E* map calculated with 244 phases showed all of the atoms, and an initial structure factor calculation gave an *R* of 0.25. The refinement was carried out by full-matrix least squares with anisotropic temperature factors to a final *R* of 0.081. Hydrogen atoms were included. The propionic acid residue on C(1) is folded in contrast to the extended form on C(3). This feature is attributed to the formation of hydrogen-bonded carboxylic acid "dimers" between molecules related by the *c* glide. The transannular bond length of 1.490 ± 0.008 A is strongly suggestive of a C–C single bond (perhaps of sp^2–sp^2 hybridization). The average value of the peripheral ring bonds is 1.393 A. However, the mean of the peripheral bonds in the five-membered ring is 1.404 A while that for the seven-membered ring is 1.386 A. The internal C–C–C bond angles in the seven-membered ring at C(4), C(6), and C(8) are in good agreement with each other, and their average of 130.1° is greater than that (127.4°) of the remaining internal angles in this ring.

The molecular dimensions of azulene have long been of interest to theoretical and experimental chemists. These parameters are of special importance for the test of modern chemical ideas. X-Ray diffraction studies of azulene[4] have not furnished accurate bond lengths and angles because of disorder in the crystal structure. Structural studies of the 2-amino[5] and 2-phenyl[6] derivatives of azulene have also failed to provide a knowledge of these quantities sufficiently reliable for meaningful comparison with theoretical predictions. In a very recent study of an azulene–*sym*-trinitrobenzene complex by Hanson,[7] about 7% of the azulene molecules were discovered in an alternate orientation. It was estimated that bond-length changes no greater than 0.014 A from those reported could be caused by the disorder. The present investigation of azulene-1,3-dipropionic acid,[8] started prior to the appearance of Hanson's paper, was undertaken with the hope of providing precise molecular parameters for the azulene ring system. This compound was chosen for the reasons that (1) potential hydrogen bonding between the carboxylic acid groups would reduce any possibility of disorder and (2) the symmetrically placed aliphatic substituents would be expected to produce a minimal amount of perturbation of the aromatic nucleus.

Experimental Section

Data Collection. Azulene-1,3-dipropionic acid is deep blue in color, very similar to azulene itself. The sample contained crystals in two quite different habits, plates, and rectangular chunks. Preliminary studies showed the unit cell volume of the chunks to be approximately twice that of the plates, and, on this basis, the latter were selected for a structure determination. A crystal with dimensions *ca.* 0.15 × 0.1 mm with a thickness of 0.01 mm was mounted along the long plate axis (*b*) and used for all further measurements.

Preliminary unit cell dimensions were determined from oscillation, Weissenberg (Cu Kα) and precession (Mo Kα) photographs. These values were subsequently refined by least squares using as observational data the 2θ's (ranging from *ca.* 12–30°) for 16 general reflections, carefully measured on a Picker X-ray diffrac-

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[1] This work was presented in part at the American Crystallographic Association Annual Meeting, Austin, Texas, Feb 1966.

[2] Cowell College, University of California, Santa Cruz, Calif.

[3] Children's Cancer Research Foundation and Harvard Medical School, Boston, Mass.

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[7] A. W. Hanson, *Acta Cryst.*, **19**, 19 (1965).

[8] R. D. Breazeale, Ph.D. Thesis, Department of Chemistry, University of Washington, 1964. Dr. Breazeale kindly gave us a small amount of the material.