

tions 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 $\text{H}(\text{sol})\text{ClO}_4$ 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., $(\text{HClO}_4)_2 \cdot \text{NaClO}_4$) could presumably be explained by the same arguments, which would also

account for the more extensive mixed association found by Bruckenstein and Saito³ 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.

Acknowledgment. This work was supported by Army Research Office (Durham) and by the National Science Foundation. The assistance furnished by the Numerical Analysis Center of the University of Minnesota is also acknowledged. We are indebted to Professor Z. Z. Hugus for advice and assistance in the least-squares treatment of our cryoscopic data.

The Crystal Structure of Azulene-1,3-dipropionic Acid¹

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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 Å 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 Å. However, the mean of the peripheral bonds in the five-membered ring is 1.404 Å while that for the seven-membered ring is 1.386 Å. 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 azulene⁴ have not furnished accurate bond lengths and angles because of disorder in the crystal structure. Structural studies of the 2-amino⁵ and 2-phenyl⁶ 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 Å 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 $K\alpha$) and precession (Mo $K\alpha$) 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-

(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.

(4) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

(5) Y. Takaki, Y. Sasada, and I. Nitta, *J. Phys. Soc. Japan*, **14**, 771 (1959).

(6) B. D. Sharma and J. Donohue, *Nature*, **192**, 863 (1961); J. Donohue and B. D. Sharma, *ibid.*, **198**, 878 (1963).

(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.

tometer (General Electric quarter circle goniostat). The average difference between the observed and calculated values of 2θ was 0.0046° . The final parameters and their estimated standard deviations are reported below.

The crystal data for azulene-1,3-dipropionic acid, $C_{16}H_{18}O_4$, mol wt 272.3, are: Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$; monoclinic, $a = 13.416 \pm 0.006$, $b = 5.261 \pm 0.002$, $c = 21.002 \pm 0.007 \text{ \AA}$, $\beta = 113.08 \pm 0.02^\circ$; $Z = 4$; $d_{\text{calc}} = 1.325 \text{ g cm}^{-3}$; $V = 1364 \text{ \AA}^3$; $F(000) = 576$; absent spectra, $h0l$ for l odd and $0k0$ for k odd; space group $P2_1/c$.

Measurement of an experimental density was not attempted because of the small amount of material in hand. The calculated density, assuming four molecules per unit cell, was quite reasonable for an organic compound containing only carbon, hydrogen, and oxygen (1.175 g cm^{-3} was found for azulene).

Plans originally were made to measure all of the data required for a three-dimensional structure determination on the diffractometer using Mo $K\alpha$ radiation. Early in the data collection, however, a small split was discovered in the end of the crystal, opposite to its point of connection to the glass mounting fiber. This imperfection, quite noticeable as a shoulder on the main diffraction maximum at goniostat χ angles greater than 60° , made the 2θ scan ranges quite variable and difficult to precalculate. This was considered to be sufficiently serious to make the sample unsatisfactory for diffractometry. The small amount of available material made any attempts to cut off the offending end seem inadvisable, and the decision was subsequently made to collect the data on film. Nevertheless, 50 reflections were measured on the diffractometer for the possible purpose of level-to-level scaling of the film data.

Equiinclination Weissenberg photographs were collected for the levels $h0l$ through $h4l$ using Ni-filtered, copper radiation ($\lambda 1.5418 \text{ \AA}$). A total of 1226 reflections were visually estimated by comparison with a calibrated intensity scale. Structure factors were calculated from the film and diffractometer intensities in the customary manner.^{9,10} The $F_{\text{film}}/F_{\text{diff}}$ ratios, within each of the levels, agreed well with one another, and the 50 diffractometer data were subsequently used for the interlevel scaling of the film data.

Solution of the Structure. The relative F 's were placed on an absolute basis and converted into normalized structure factors (E 's)¹¹ with the X-Ray 63 subprogram DATFIX. The condition that $\langle E^2 \rangle = 1$ is utilized to obtain scale and over-all temperature factors.

Preliminary work on the solution of the structure was done using packing considerations. The relatively short b axis must restrict the angle of tilt of the azulene ring with respect to the ac plane to a maximum of $ca. 45^\circ$. An examination of molecular models suggested that the propionic acid substituents would probably exist in extended forms. Consideration was also given to the strong planes, formation of reasonably planar, hydrogen-bonded, carboxylic acid "dimers" between molecules, and prohibited regions around centers and screw axes. Structure factor calculations using the most promising positions gave little encouragement for continued effort on this line. The Harker section of the Patterson synthesis at $U, 1/2, W$ was not readily interpretable.

Our attention was next directed to the symbolic addition procedure.¹² The reflections were sorted into the eight parity groups¹³ by the X-Ray 63 subprogram ESORT; within each group, they were further arranged according to their E magnitudes. The 258 data with $E > 1.4$ were input to the program PHASER¹⁴ for calculation of the Σ_2 relationships and the associated probabilities.^{11,15} From

(9) All of the usual crystallographic computations were performed on an IBM 7094 computer with the X-Ray 63 system of programs. "Crystal Structure Calculations System, X-Ray 63, for the IBM 709-7090-7094," Technical Report TR-64-6 (NSG-398), Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington.

(10) The minimum and maximum structure amplitudes were 2.4 and 174.8, respectively, and the $\sin \theta/\lambda$ range of the observed data was 0.0405–0.6089.

(11) H. Hauptman and J. Karle, "Solution of the Phase Problem I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Polycrystal Book Service.

(12) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

(13) These are *ggg*, *ugg*, *gug*, *ggu*, *uug*, *ugu*, *guu*, and *uuu*; $g = \text{even}$, $u = \text{odd}$.

(14) A system of programs (PHASER) for the IBM 709-7090-7094 was used for the application of the symbolic addition procedure: H. L. Ammon, unpublished work.

(15) Many of the equations for space group $P2_1/c$, used in the application of the symbolic addition procedure are given by K. S. Dragonette and I. L. Karle, *Acta Cryst.*, **19**, 978 (1965).

a careful examination of the ESORT and PHASER lists, the reflections shown in Table I were selected to form the base for further phase development.

Table I. Phases Assigned in the Preliminary Stage of the Symbolic Addition Procedure in Their Order of Selection

Reflection	Phase	E
1 1 4	+	3.843
2 2 6	a ^a	4.069
$\bar{1}0$ 1 16	+	2.732
$\bar{1}0$ 2 2	b	3.010
2 2 7	+	2.572
3 3 14	c	3.266
$\bar{1}\bar{1}$ 2 4	d	2.587

^a The phase of 2 2 6(a) was determined as + from the Σ_1 equation¹¹ with a probability of 0.96.

It was not possible to relate any of the four unknown symbols, a–d, with one another thereby leaving the maximum number of 16 (2^4) solutions to be evaluated. The correct combination of starting phases would be expected to have a large degree of internal consistency and permit the construction of a very extensive sign pyramid. On the other hand, the pyramid derived from an incorrect starting combination would be diminished by the lack of internal consistency resulting from many sign conflicts. Therefore, the correct solution should have the fewest number of undetermined phases and almost equal numbers of + and – phases. Karle and Karle have used similar criteria in some of their structure solutions by the symbolic addition procedure.¹⁶

This information for the 16 phase pyramids, presented in Table II, predicted the best solutions to be 1, 5, and 7, and three-dimensional E maps¹⁷ were calculated using these phases. The E map for

Table II. Summary Data for the 16 Phase Pyramids

No.	a	b	c	d	—Number of phases—		
					+	–	?
1	+	+	+	+	115	112	31
2	–	+	+	+	103	93	62
3	+	–	+	+	107	109	42
4	–	–	+	+	100	82	76
5	+	+	–	+	118	126	14
6	–	+	–	+	99	89	70
7	+	–	–	+	116	114	28
8	–	–	–	+	113	78	67
9	+	+	+	–	109	97	52
10	–	+	+	–	102	114	42
11	+	–	+	–	92	112	54
12	–	–	+	–	105	96	57
13	+	+	–	–	104	97	57
14	–	+	–	–	98	114	46
15	+	–	–	–	103	92	63
16	–	–	–	–	96	106	56

the fifth solution, the best of the three, was examined first. The molecule was immediately recognizable and all 20 atoms were found in plausible positions relative to each other (Figure 1 shows the original E map).¹⁸ A structure factor calculation using data out to a $\sin \theta/\lambda$ of 0.45, the coordinates of the 20 peaks, an over-all temperature factor of 4.0 \AA^2 , and carbon atom scattering factors gave an R factor ($= \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) of 0.254. The use of oxygen scattering factors for the appropriate atoms and two cycles of least-squares refinement with individual isotopic temperature factors dropped R to 0.179.

(16) I. L. Karle and J. Karle, *ibid.*, **17**, 1356 (1964).

(17) E maps are Fourier syntheses in which E 's are used as the Fourier coefficients. The resulting maps are much sharper than those obtained using F 's: see I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *ibid.*, **11**, 257 (1958).

(18) Of the 244 phases obtained from solution 5, only two were subsequently found to be incorrect on comparison with the phases for the fully refined structure.

Table III. Final Fractional Coordinates^a and Anisotropic Temperature Factors^b for the Carbon and Oxygen Atoms

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	0.2456 (4)	1.2879 (10)	0.8374 (3)	3.93	2.34	3.14	0.15	1.13	-0.16
C(2)	0.2053 (4)	1.1780 (10)	0.8839 (3)	3.97	2.07	3.68	-0.22	1.34	-0.26
C(3)	0.2725 (4)	0.9833 (10)	0.9224 (3)	4.07	2.34	3.28	0.09	1.23	-0.07
C(4)	0.4419 (5)	0.7905 (11)	0.9247 (3)	5.15	2.87	4.08	1.11	1.32	0.49
C(5)	0.5319 (5)	0.7563 (12)	0.9073 (3)	4.86	3.87	4.96	1.42	1.19	-0.34
C(6)	0.5587 (5)	0.8951 (13)	0.8604 (3)	4.21	5.28	4.89	0.95	1.37	-0.10
C(7)	0.5062 (5)	1.0993 (13)	0.8191 (3)	4.88	5.30	4.73	0.59	2.12	0.18
C(8)	0.4108 (5)	1.2163 (11)	0.8135 (3)	4.47	3.52	4.10	0.35	1.61	0.03
C(9)	0.3422 (4)	1.1638 (10)	0.8469 (1)	4.00	1.98	3.03	0.55	1.11	-0.14
C(10)	0.3599 (4)	0.9663 (10)	0.9011 (3)	4.27	1.94	3.29	0.06	1.09	-0.35
C(11)	0.1928 (4)	1.5008 (11)	0.7892 (3)	4.31	2.36	3.51	0.29	0.99	0.07
C(12)	0.0896 (4)	1.4162 (10)	0.7266 (3)	3.99	2.80	3.53	0.56	1.13	0.19
C(13)	0.1094 (4)	1.2301 (11)	0.6802 (3)	3.76	2.85	3.16	0.02	1.05	0.49
C(14)	0.2577 (5)	0.8175 (12)	0.9760 (3)	4.94	3.30	3.96	0.41	1.61	0.68
C(15)	0.1648 (5)	0.8891 (13)	0.9951 (3)	5.14	4.87	5.20	1.15	2.41	1.50
C(16)	0.1512 (5)	0.7173 (12)	1.0475 (3)	4.60	3.16	4.88	1.07	2.09	1.08
O(1)	0.0452 (4)	1.0530 (9)	0.6542 (2)	6.41	5.18	6.39	-2.37	3.73	-2.16
O(2)	0.1928 (3)	1.2624 (9)	0.6661 (2)	5.12	7.07	6.24	-2.63	3.14	-3.79
O(3)	0.2174 (4)	0.5515 (10)	1.0775 (3)	6.19	7.23	7.30	3.48	3.89	4.55
O(4)	0.0648 (4)	0.7474 (10)	1.0591 (3)	6.91	7.38	8.91	3.38	5.03	4.45

^a Estimated standard deviations are given in parentheses. ^b The anisotropic thermal parameters are in the form $\exp(-0.25 \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} a_i^* a_j^*)$.

Least-Squares Refinement. All refinements done in this investigation used the full matrix of the normal equations. Preliminary structure factor weights (*w*) were all unity. From the initial carbon and oxygen atom coordinates positions for 14 of the 16 hydrogen atoms (two hydrogens on oxygen were omitted) were calculated assuming a C-H bond length of 1.02 Å. With the hydrogens as fixed atoms and 23 reflections for which $|F_o - F_c| > 8.0$ removed, two cycles of refinement on the carbon and oxygen atoms with anisotropic temperature factors dropped *R* to 0.109. The *R* factor was lowered to 0.091 following a data check in which a total of nine card-punching and indexing errors was discovered.

atoms were located from a ΔF synthesis and introduced in the later stages of the refinement.

The scattering factors used were the following: C and O, Berghius, *et al.*;²¹ H, Stewart, Davidson, and Simpson.²² Final coordinates and temperature factors are shown in Tables III and IV. A table containing the observed and calculated structure factors has been deposited with the American Documentation Institute.²³

Table IV. Final Fractional Coordinates and Isotropic Temperature Factors for the Hydrogen Atoms

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²
H(2)	0.137	1.230	0.889	2.5
H(4)	0.441	0.627	0.963	5.9
H(5)	0.580	0.606	0.932	4.1
H(6)	0.626	0.815	0.855	4.5
H(7)	0.551	1.191	0.797	4.8
H(8)	0.385	1.378	0.779	5.3
H(11a)	0.250	1.583	0.777	4.7
H(11b)	0.168	1.633	0.817	4.2
H(12a)	0.056	1.574	0.697	2.6
H(12b)	0.032	1.305	0.743	4.7
H(14a)	0.328	0.775	1.013	16.2
H(14b)	0.250	0.646	0.957	5.0
H(15a)	0.101	0.900	0.963	7.4
H(15b)	0.178	1.066	1.017	7.0
H(O2)	0.205	1.134	0.633	13.5
H(O4)	0.070	0.596	1.111	16.5
Average σ	0.005	0.012	0.003	

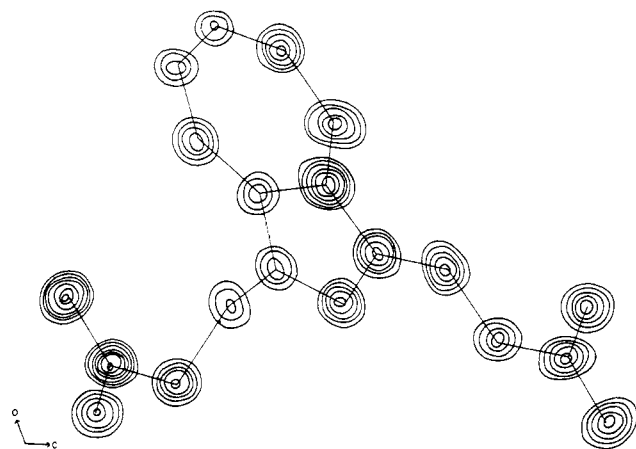


Figure 1. The original *E* map calculated with 244 phases, viewed normal to the *ac* plane. Contours are drawn at arbitrary levels. The outline of the refined structure is also shown.

The introduction of a weighting scheme (for $F_o < 14.0$, $w = 1.0$; for $F_o > 14.0$, $w = 14/F_o$) patterned after that suggested by Hughes¹⁹ followed by two cycles of anisotropic refinement on the carbons and oxygens with the hydrogens fixed gave an *R* of 0.086. Several more cycles on the hydrogens with isotropic temperature factors and the carbons and oxygens with anisotropic temperature factors gave a final *R* of 0.081. During these final cycles, $w = 0$ if $|F_o - F_c| > 5.0$ (19 with zero weight in last cycle).²⁰ The two carboxyl hydrogen

(19) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(20) The average and maximum shifts in the carbon and oxygen atomic coordinates in the last anisotropic cycle were 0.17 and 0.7 σ , respectively.

Discussion

The bond lengths and angles involving the carbon and oxygen atoms are given in Tables V and VI, and in

(21) J. Berghius, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(22) R. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(23) The structure factor table has been deposited as document No. 8918 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photo-prints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

Table V. Covalent Bond Lengths between Carbon and Oxygen Atoms and a Comparison^a with the Appropriate Values for the Azulene Ring in the Azulene-*sym*-Trinitrobenzene Complex⁷

Bond	Length, Å ^b	
	Azulene-1,3-dipropionic acid	Azulene- <i>sym</i> -trinitrobenzene complex
C(1)–C(2)	1.412 (9)	1.398 (4)
C(2)–C(3)	1.395 (7)	1.387 (4)
C(1)–C(9)	1.394 (8)	1.404 (4)
C(3)–C(10)	1.413 (9)	1.395 (4)
C(8)–C(9)	1.386 (10)	1.390 (4)
C(4)–C(10)	1.373 (8)	1.382 (4)
C(7)–C(8)	1.384 (10)	1.393 (4)
C(4)–C(5)	1.402 (11)	1.402 (4)
C(6)–C(7)	1.387 (9)	1.391 (4)
C(5)–C(6)	1.382 (11)	1.397 (4)
C(9)–C(10)	1.490 (8)	1.498 (5)
C(1)–C(11)	1.490 (7)	
C(3)–C(14)	1.497 (9)	
C(11)–C(12)	1.555 (7)	
C(14)–C(15)	1.499 (11)	
C(12)–C(13)	1.477 (9)	
C(15)–C(16)	1.490 (10)	
C(13)–O(1)	1.241 (7)	
C(16)–O(3)	1.228 (8)	
C(13)–O(2)	1.276 (8)	
C(16)–O(4)	1.285 (10)	

^a The appropriate likelihood ratio test was used to evaluate the bond-length similarities in the azulene rings of the two structures. Under the null hypothesis (*i.e.*, no difference) the statistic T ($T = 1/(\sigma_1^2 + \sigma_2^2) \sum_{i=1}^p d_i^2$; σ_1^2 and σ_2^2 are the variances of the bond length estimates of the two structures and d_i is the difference between the i th bond lengths) has a χ^2 distribution with p degrees of freedom. $T = 12.68$ for the 11 common bond lengths and a χ^2 table gives a value of 0.32 for this T . Therefore, a test at a probability level of 0.05 accepts the hypothesis that bond lengths in the two azulene rings are the same. We are grateful to Dr. M. Sylvan for advice on this statistical test. ^b Estimated standard deviations are given in parentheses.

Figure 2. For comparison, Hanson's values for the azulene ring in azulene-*sym*-trinitrobenzene complex⁷ are also tabulated.

The length (1.498 Å) measured by Hanson for the C(9)–C(10) bond and the 1.490-Å value obtained in this work manifest that the transannular C–C bond in azulene is a single bond. These values are slightly longer than the central bond in 1,3-butadiene,²⁴ 1.483 Å. However, errors in all three determinations make this difference of questionable significance. The exocyclic single bonds, C(1)–C(11) = 1.490 Å and C(3)–C(14) = 1.497 Å (both presumably sp^2 – sp^3), are very similar to the C(9)–C(10) bond (presumably sp^2 – sp^2). However, it is noteworthy that the internal angles at C(1) and C(3) are not 120°, but considerably less, 107.2 and 106.9°, respectively. Apparently, this increases the s character of the exocyclic bonds. That is, the hybridization of the exocyclic orbitals on C(1) and C(3) is not pure sp^2 but between sp^2 and sp , hence the observed slight shortening in the exocyclic bonds.²⁵ An extreme case of this is seen in *sym*-triphenylcyclopropenium perchlorate,²⁶ in which the exocyclic bonds are rather short, average 1.436 Å. This is attributed to

(24) A. Almendinger, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

(25) A good discussion of bond lengths, angles, and hybridization is given in H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(26) M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

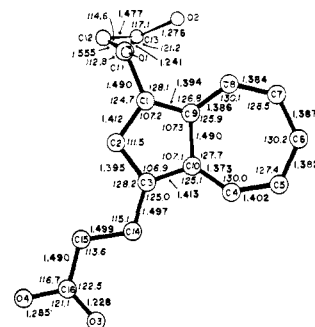


Figure 2. A drawing of azulene-1,3-dipropionic acid viewed normal to the azulene ring (plane 1, Table VII). Bond lengths (Å, darkest numbers) and angles (°) are shown for the carbon and oxygen atoms.

the fact that the internal angles in the cyclopropenium ring are all 60°. As a general rule, therefore, one might expect the exocyclic bonds to an aromatic nucleus to be shorter than “normal” if the internal ring angles associated with them contract from the trigonal value of 120°.

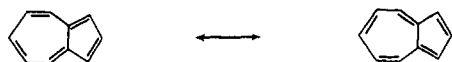
Table VI. Covalent Bond Angles for the Carbon and Oxygen Atoms and a Comparison^a with Appropriate Values for the Azulene Ring in the Azulene-*sym*-Trinitrobenzene Complex⁷

Angle	Degrees ^b	
	Azulene-1,3-dipropionic acid	Azulene- <i>sym</i> -trinitrobenzene complex
C(2)–C(1)–C(9)	107.20 (0.46)	108.16
C(2)–C(3)–C(10)	106.86 (0.52)	109.07
C(1)–C(2)–C(3)	111.51 (0.54)	110.16
C(1)–C(9)–C(10)	107.28 (0.54)	106.44
C(3)–C(10)–C(9)	107.14 (0.45)	106.19
C(1)–C(9)–C(8)	126.77 (0.50)	126.43
C(3)–C(10)–C(4)	125.12 (0.57)	126.15
C(8)–C(9)–C(10)	125.93 (0.50)	127.15
C(4)–C(10)–C(9)	127.68 (0.62)	127.67
C(7)–C(8)–C(9)	130.12 (0.57)	129.20
C(5)–C(4)–C(10)	129.96 (0.63)	128.42
C(6)–C(7)–C(8)	128.54 (0.74)	129.02
C(4)–C(5)–C(6)	127.43 (0.57)	129.09
C(5)–C(6)–C(7)	130.22 (0.70)	129.47
C(2)–C(1)–C(11)	124.67 (0.53)	(σ) = 0.25
C(2)–C(3)–C(14)	128.16 (0.57)	
C(9)–C(1)–C(11)	128.12 (0.57)	
C(10)–C(3)–C(14)	124.97 (0.47)	
C(1)–C(11)–C(12)	112.84 (0.45)	
C(3)–C(14)–C(15)	115.10 (0.51)	
C(11)–C(12)–C(13)	114.64 (0.48)	
C(14)–C(15)–C(16)	113.60 (0.54)	
C(12)–C(13)–O(1)	120.99 (0.60)	
C(15)–C(16)–O(3)	122.47 (0.68)	
C(12)–C(13)–O(2)	117.74 (0.50)	
C(15)–C(16)–O(4)	116.47 (0.54)	
O(1)–C(13)–O(2)	121.24 (0.60)	
O(3)–C(16)–O(4)	121.04 (0.68)	

^a The statistic $T = 48.07$ (see Table V for an explanation of this test), for the 14 common bond angles in the azulene rings of the two structures, and a χ^2 table give a value of <0.01 for this T . Therefore, a test at a probability level of 0.01 rejects the hypothesis that the angles in the two rings are the same. ^b Estimated standard deviations are given in parentheses.

In a simple HMO calculation with all of the Coulomb exchange integrals assumed to be equal, a bond order of 0.4009 was obtained for the C(9)–C(10) bond, cor-

responding to a distance of 1.445 Å. A similar calculation yielded a length of 1.437 Å for the C(2)–C(3) bond in 1,3-butadiene.²⁷ The observed transannular distance for azulene, 1.490 Å, corresponds to a bond order of 0.1306. Pariser²⁸ has obtained bond orders of *ca.* 0.286, equivalent to a length of 1.47 Å, from the use of configuration interaction with either Hückel or perimeter molecular orbitals. It is interesting that the absence of transannular double-bond character is precisely what one infers from the two ground-state valence bond structures.



The average value of the peripheral bonds, 1.393 ± 0.005 Å (range 1.373–1.413 Å), and that observed by Hanson,⁷ 1.395 Å, are both in excellent agreement with the benzene C–C bond length. It is interesting to note that the benzene–azulene “aromatic” bond length is *ca.* 0.02 Å longer than that for the cyclopropenium ring, 1.373 Å.²⁶ A similar trend occurs in the saturated compounds, cyclopropane and cyclohexane, with C–C distances of 1.52 and 1.54 Å, respectively.

The average value of the peripheral bonds in the five-membered ring (1.404 ± 0.005 Å) is greater than that of the seven-membered ring (1.386 ± 0.004 Å), a feature not observed in the azulene ring of the azulene–*sym*-trinitrobenzene complex.⁷ The five-ring average appears to be about 0.01 Å longer than the benzene C–C bond while the seven-ring average is shorter by a similar amount. Although of questionable significance, the peripheral bonds of the five-membered ring appear to exhibit an alternation of long and short bonds (see Figure 2).

The average apparent carbon–hydrogen distance is 1.02 Å with a range of 0.85–1.13 Å. This value is considerably less than the standard internuclear separation of 1.09 Å. Shortening of bond lengths involving hydrogen is commonly observed in X-ray diffraction studies.

The internal angles in the five-ring at C(1), C(3), C(9), and C(10) are in good agreement with each other, average 107.1° and differ markedly from that of C(1)–C(2)–C(3), 111.5° . In Hanson's complex there were three groups of angles within the five-membered ring. The similarity of the internal angles at C(4), C(6), and C(8) in the seven-ring is striking, and their average of 130.1° differs significantly from that (127.4°) of the remaining angles. Data available for azulene itself show the C(4), C(6), and C(8) carbons to be the positions of lowest electron density and nucleophilic attack. Thus, the alternation in bond angles in the seven-membered ring is quite noticeable. Similar alternations, however, were not observed by Hanson;⁷ in fact, the internal angles at C(9) and C(10) in the seven-membered ring of the complex are nearly equal, average 127.5° , and the remaining five angles are in good agreement, with an average of 129.8° .

The propionic acid residue on C(1) has assumed a *gauche* arrangement about the C(11)–C(12) bond, projected angle C(1)–C(11) \rightarrow C(12)–C(13) = 63.6° in contrast to the residue on C(3) which exists in the an-

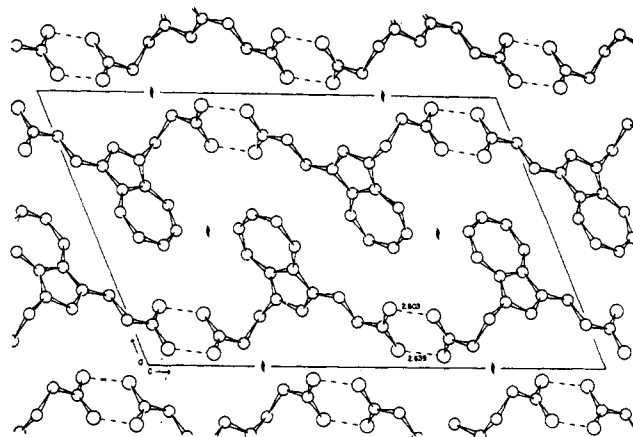


Figure 3. A view of part of the crystal structure normal to the *ac* plane. The formation of the hydrogen-bonded carboxylic acid “dimers” is shown with dashed lines.

anticipated extended configuration. Thus, the two protons on C(11) are on the same side of the azulene ring, while those on C(14) are on opposite sides. Ordinarily, a *gauche* conformation in a C–C chain would be expected to confer destabilization to a system, but crystal-packing forces and hydrogen bonding appear to have offered at least partial compensation.

The planes of the carboxyl groups are twisted about the terminal C–C bonds such that the projected angles C(11)–C(12) \rightarrow C(13)–O(2) and C(11)–C(12) \rightarrow C(13)–O(1) are 41.0 and 141.2° , respectively, and those of C(14)–C(15) \rightarrow C(16)–O(3) and C(14)–C(15) \rightarrow C(16)–O(4) are 7.6 and 166.4° , respectively. This feature appears to be a general phenomenon in fatty acids. Dumbleton and Lomer²⁹ have recently suggested that “this rotation may be a property of the fatty acid radical rather than due to an effect of the end packing of the molecules. . . .” They found that in potassium palmitate the plane of the carboxyl was rotated about the end C–C bond by 16.4° .

The least-squares planes of various groups of atoms are shown in Table VII. The substituted ring atoms, C(1) and C(3), are displaced on opposite sides of the azulene ring plane. Furthermore, C(11) and C(14), attached respectively to C(1) and C(3), are displaced similarly by approximately twice the magnitudes of the C(1) and C(3) displacements. Plane 2 is that passing through the ring atoms and the substituents C(11) and C(14), and again substantial deviations from planarity are exhibited by the atoms C(4), C(5), C(7), C(8), and C(11). From both of these planes it is seen that the zigzagging side chain is tilted toward one side of the azulene ring.

A view of the crystal lattice, normal to the *ac* plane, is shown in Figure 3. Hydrogen-bonded carboxylic acid “dimers” are formed by the interaction of the O(1)–C(13)–O(2) group of one molecule (at x, y, z) with the O'(3)–C'(16)–O'(4)³⁰ group of the *c*-glide related molecule (at $x, \frac{1}{2} - y, \frac{1}{2} + z$). The O'(1)–C'(13)–O'(2) group of the latter molecule hydrogen bonds to the O''(3)–C''(16)–O''(4) group of another molecule (at $x, y, 1 + z$) related to it by the *c* glide. This third molecule is the same as the first transformed by the unit translation parallel to *c*. The twisted con-

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(28) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).

(29) J. H. Dumbleton and T. R. Lomer, *Acta Cryst.*, **19**, 301 (1965).

(30) The primes refer to atoms in the glide related molecule.

Table VII. Displacements (A) of Atoms from Their Least-Squares Planes^a

Atom	Planes						
	1 ^b	2	3	4	5	6	7
C(1)	0.035	0.019	0.022				
C(2)	0.001	-0.003	0.024				
C(3)	-0.025	-0.017	0.021				
C(4)	0.012	0.028	0.053				
C(5)	0.018	0.033	0.042				
C(6)	0.006	0.008	-0.006				
C(7)	-0.018	-0.030	-0.058				
C(8)	-0.016	-0.034	-0.056				
C(9)	0.007	-0.003	-0.003				
C(10)	-0.021	-0.015	0.006				
C(11)	0.064*	0.032	0.020				
C(12)	1.446*	1.410*	1.396*	0.003	0.168*	0.083	
C(13)	2.554*	2.518*	2.496*	-0.011	0.036*	-0.024	
C(14)	-0.042*	-0.018	0.044				
C(15)	-0.185*	-0.161*	-0.085				
C(16)	-0.172*	-0.133*	-0.033				
O(1)	3.684*	3.652*	3.638*	0.004	-0.067*	-0.082	-0.035
O(2)	2.320*	2.280*	2.242*	0.004	-0.067*	-0.011	0.035
O(3)	-0.193*	-0.143*	-0.036				
O(4)	-0.109*	-0.070*	0.044				
H(O2)				0.013*	0.001*	-0.066*	
C'(15) ^c				0.380*	0.003	0.034	
C'(16)				0.251*	-0.007	-0.001	
O'(3)				0.144*	0.003	-0.035	-0.035
O'(4)				0.287*	0.002	0.035	0.035
H'(O4)				0.059*	-0.111*	-0.107*	

^a Asterisks indicate displacements of atoms not included in the calculation of the least-squares planes. ^b The equation of the plane passing through the ten atoms of the azulene ring is $-0.2305x - 0.2244y - 0.778z + 1.0 = 0$. Equations of the other planes may be obtained from the authors on request. ^c The primed atoms are related to the reference molecule at x, y, z by the glide operation; see text.

figuration of the C(1) β -propionic acid moiety is thus necessary to accomplish this intermolecular hydrogen-bonding scheme which results in infinite "ribbons" of molecules parallel to the glide direction. With the exception of the carboxylic acid dimers, there were no intermolecular distances less than 3.4 Å.

The carboxyl atoms and their α -carbon atoms (C(12) and C(15)) are planar (planes 4 and 5) within the error of the determination. The atoms comprising the hydrogen-bonded dimer (see Figure 3), together with the α carbons, are clearly nonplanar (plane 6). In fact, there is an alternation in the displacement of the four oxygens from their least-squares plane (plane 7), such that the line O(1)···O(2) is twisted at an angle of about 6° from that of O'(3)···O'(4). In the more commonly occurring "centrosymmetric" hydrogen-bonded dimers, the carboxyl atoms are clearly nonplanar with the two planes defining the carboxyl groups parallel and separated by a distance of about 0–0.5 Å.^{31,32} Oxygen-oxygen intermolecular distances between "dimers" are shown in Figure 3 and agree with previously measured values.

The principal axes of the vibration ellipsoids were calculated and are particularly interesting for the oxygen atoms (see Table VIII). The anisotropy of these atoms is considerable, and the directions of their maxi-

(31) G. A. Jeffrey and M. Sax, *Acta Cryst.*, **16**, 430 (1963).

(32) J. H. Robertson, *ibid.*, **17**, 316 (1964).

Table VIII. Principal Axes of the Vibration Ellipsoids of the Oxygen Atoms

Atom	B_1 , Å ²	B_2 , Å ²	B_3 , Å ²	Direction cosines of B_1	Angle, ^a deg
O(1)	9.1	3.3	4.4	0.4753, -0.5653, 0.4339	21
O(2)	10.8	2.8	4.0	0.2147, -0.7321, 0.5150	19
O'(3)	12.4	2.6	4.6	0.2735, 0.6878, 0.5114	19
O'(4)	13.4	3.5	4.5	0.2825, 0.6242, 0.5594	24

^a The acute angle between the direction of B_1 and the normal to plane 6, Table VII.

imum vibrations are almost normal to the "dimer" plane (plane 6, Table VII).

The thermal ellipsoids of the azulene ring carbon atoms were considerably more isotropic than those of the oxygens. In almost all cases, the major axes of these ellipsoids deviated less than 10° from the azulene ring plane (plane 1, Table VII).

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