creased greatly. On the other hand, the carbon-deposition rate remained essentially constant during the same period on the carbided catalyst. X-Ray diffraction analysis of samples which had received essentially parallel treatment up to the point indicated on the curve are also shown in Fig. 3. The precarbided catalyst contained only Co_2C, showing that no net change in carbide content had taken place. The rate of carbon deposition on the precarbided sample was 0.0064 g. carbon/g. cobalt/hour, and the rate of decomposition of carbide in this same catalyst was calculated by means of the activation energy and rate constants previously determined[9] to be 0.0015 g. carbon/g. cobalt/hour. Thus, it is interesting to note that the rate of carbon deposition is of the same order of magnitude (though higher by a factor of 4) as the rate of carbide decomposition. The X-ray diffraction analysis of the initially uncarbided sample after twenty-two hours showed only disordered cobalt plus a small amount of Co_2C. On hydrogenation at 196°, the initially carbided sample lost carbon equal to a carbon : cobalt ratio of 0.071. On recarbiding at 196°, a nearly equal amount of carbon (0.066) was replaced.

Summary

1. Reduced cobalt–thoria–kieselguhr catalysts produced increasing amounts of free carbon and decreasing amounts of cobalt carbide on carburization with carbon monoxide at increasing temperatures in the range 243 to 298°. At the high temperatures, the maximum amount of carbide is formed within the first five hours of carburization.

2. Free carbon tends to make the catalyst inaccessible to further carbide formation.

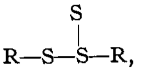
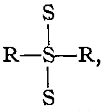
3. Carbide inhibits free-carbon deposition.

PITTSBURGH, PA. RECEIVED DECEMBER 2, 1949

[CONTRIBUTION NO. 1350 FROM THE GATES AND CRELLIN LABORATORY OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Crystal Structure of 2,2'-Diiododiethyltrisulfide

BY JERRY DONOHUE

An investigation of the crystal structure of 2,2'-diiododiethyltrisulfide (Fig. 1) was recently carried out by Dawson and Robertson[1] (hereinafter referred to as D. and R.) who found that crystals of this substance are isomorphous with the space group $D^4_4 - P4_12_1$, and that four molecules are present in the unit cell, which has a_0 = 6.01 Å. and c_0 = 29.4 Å. Since the general position of this space group is eight-fold, it follows that each molecule has point symmetry $C_2 - 2$, a fact which eliminates the possibility that this trisulfide has the thiodisulfide structure,  $R\text{—}S\text{—}\overset{S}{\overset{|}{S}}\text{—}R$, leaving only the straight-chain structure, R—S—S—S—R, and the dithiosulfone structure,  $R\text{—}\overset{S}{\underset{S}{\overset{|}{\underset{|}{S}}}}\text{—}R$, to be considered. Fourier analysis of the $(h0l)$ data led to the determination of the parameters for the sulfur and iodine atoms, and to the assignment of the straight-chain structure to molecules of 2,2'-diiododiethyltrisulfide.

This conclusion is an agreement with the previous results of Donohue and Schomaker, who assigned the straight-chain structure to the compound dimethyltrisulfide on the basis of an electron diffraction investigation.[2]

Because of the small fraction which the carbon atoms contribute to the total scattering D. and R. made no attempt to locate these atoms in their electron density plots, but merely assigned to them parameters which "were probable values only, based on the requirements of accepted single bond lengths and angles for the atoms in question." These parameters were not used to calculate the contributions the carbon atoms make to the $(h0l)$ reflections—the calculated values of F_{h0l} which were used in the final comparison with the observed values of F_{h0l} included sulfur and iodine scattering only. Nevertheless, they discussed in some detail the shape of the molecule, in particular, pointing out that the group S_1–S_2–S_1–C_2 was very nearly coplanar and *trans*, that the group S_2–S_1–C_2–C_1 was also *trans* and not quite coplanar, and that the group S_1–C_2–C_1–I had a configuration obtained by a rotation about the C_2–C_1 bond of approximately 90° from a coplanar *trans* configuration. It should be remembered, however, that this discussion is based wholly on positions of the carbon atoms for which no evidence was found by D. and R. in their electron density maps.

The coplanar *trans*- configuration suggested for the S–S–S–C group is not in agreement with the configuration found by Donohue and Schomaker[2] for dimethyltrisulfide: their data suggest a dihedral angle between the planes S–S–S and S–S–C of slightly greater than 90°.[3] Moreover,

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[1] I. M. Dawson and J. M. Robertson, *J. Chem. Soc.*, 1256 (1948).

[2] J. Donohue and V. Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).

[3] A recalculation of the dihedral angle in dimethyltrisulfide gives the value 93°. This calculation is based on the value of 4.0 Å. for the long C. . .S distance as indicated by the radial distribution function, and on the final values for the other structural parameters, which were determined by the correlation treatment. The published

Pauling recently proposed[4] that dihedral angles of 90° or slightly greater should be expected in the case of molecules containing sulfur–sulfur bonds; he used this principle to explain the stability of the S_8 molecule. It therefore seemed desirable to examine the data of D. and R. to determine whether any direct evidence for the positions of the carbon atoms could be found.

Examination of the Fourier Projection.—In the following discussion all atomic parameters are expressed in fractions of a cell edge, unless otherwise specified. The coördinates of the eight equivalent points, with the shift in the origin from that of the "International Tables for the Determination of Crystal Structures" given by D. and R., are:

(1)	x, y, z	(5)	$-y, -x, \frac{1}{4} - z$
(2)	$\frac{1}{2} - y, x, \frac{1}{2} + z$	(6)	$\frac{1}{2} + x, -y, \frac{1}{2} - z$
(3)	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$	(7)	$\frac{1}{2} + y, \frac{1}{2} + x, \frac{3}{4} - z$
(4)	$y, \frac{1}{2} - x, \frac{3}{4} + z$	(8)	$-x, \frac{1}{2} + y, -z$

The parameters of the carbon, sulfur, and iodine atoms given by D. and R., are

	x	y	z
S_1	0.674	0.301	0.067
S_2	.554	.446	.125
I	.885	.250	.948
C_1	.600	.233	.986
C_2	.617	.447	.015

The sulfur and iodine atoms of course show up very well in the published Fourier projection, but there is no indication whatever of minor maxima in the positions proposed for the carbon atoms. This is rather unexpected, since the carbon atoms contribute about as great a fraction of the total scattering as do the hydrogen atoms in various other compounds, including coronene,[5] naphthalene,[6] L-threonine,[7] and sebacic acid,[8] for which there is definite evidence of hydrogen atom peaks in Fourier syntheses. The hydrogen electrons represent 7.7, 11.8, 14.4 and 16.4% of the total number of electrons for these four respective compounds. The corresponding figure for the carbon atoms of diiododiethyltrisulfide is 12.9%.

An unequivocal identification of any of the minor peaks in the D. and R. Fourier plot as maxima corresponding to carbon atoms cannot be made at once for the reason that a rather considerable number of spurious density maxima are present. These arise from two principal causes: (1) inaccuracies in the intensity estimations due to the high absorption of the crystal (as was pointed out by D. and R.); and (2) diffraction effects from the very heavy iodine atoms, magnified by the abrupt breaking off of the Fourier series at $\sin \theta = 0.800$. As neither of these effects can be simply corrected for, possible positions for the carbon atoms must be deduced from other considerations. One possibility, which differs from that of D. and R., but has the advantage of giving a more plausible molecular configuration, immediately suggests itself. The distance between sulfur atom 1 at $x(0.674)$, $y(0.301)$, $z(0.067)$ and the iodine atom at $-x(0.115)$, $^1/_2 + y(0.750)$, $-z(0.052)$ is 4.75 Å. (These particular sulfur and iodine atoms are in adjacent molecules in the D. R. structure.) Now, the sulfur–iodine distance to be expected if the group S_1–C_2–C_1–I is planar and *trans*, and if normal bond lengths and tetrahedral bond angles are assumed, is 4.66 Å. This distance is easily increased to 4.75 Å.: for example, by expansion of the two carbon bond angles to 113°, or by lengthening each of the three bonded distances about 0.03 Å.

If the carbon atoms lie between the above-mentioned sulfur and iodine atoms we should expect peaks in the Fourier plot at the following places (coördinates are given in degrees for easy reference to Fig. 4 of D. and R.): C_1 at (339°, 73°) and (99°, 17°), and C_2 at (346°, 65°) and (183°, 25°). Inspection of the Fourier plot reveals that there are minor peaks at, or very near, all four of these locations. Since these peaks are quite asymmetric and in some cases overlap badly with adjacent peaks they are not suited for the location of atomic centers. If, however, we restrict the values of the carbon bond distances and carbon bond angles to those in reasonable accord with expectation, it is possible to assign coördinates to the carbon atoms which are not only in fairly good agreement with the Fourier projection, but also give sensible values for the distances and angles in the molecule. These coördinates correspond to the following parameters for the carbon atoms

	x	y	z
C_1	0.942	0.725	0.203
C_2	.960	.491	.181

Three views of the molecule with this structure are shown in Fig. 1.

Calculation of Structure Factors.—The structure factors of the 134 ($h0l$) reflections in Table III of D. and R.'s paper were calculated in order to obtain confirmatory evidence for the relocation of the carbon atoms. In all calculations the atom form factors used for iodine, sulfur, and carbon were those of James and

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value of 106° is in error. Because of the geometry of the molecule, the value for the dihedral angle changes rapidly with small changes in the other structural parameters.

(4) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 495 (1949).

(5) J. M. Robertson and J. G. White, *J. Chem. Soc.*, 607 (1945).

(6) S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.*, **2**, 238 (1949).

(7) D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, THIS JOURNAL, **72**, 2328 (1950).

(8) J. D. Morrison, W. P. Binnie and J. M. Robertson, *Nature*, **162**, 889 (1949).

Brindley or of Thomas and Fermi,[9] multiplied by a Debye–Waller temperature factor with $B = 2.3$ sq. Å. These form factors for sulfur and iodine differ somewhat from those used by D. and R.

Three sets of structure factors were calculated: set (1) includes only the contributions of sulfur and iodine atoms; set (2) includes the contributions of sulfur and iodine atoms and carbon atoms in the positions proposed by D. and R.; set (3) includes the contributions of sulfur and iodine atoms, and the carbon atoms in the revised positions noted above.

Structure factor set (1) should be nearly identical with the "F, calcd." values tabulated by D. and R. It was found, however, that the values of F_{h0l} of set (1) were on the average 83% of the corresponding values of "F, calcd." This factor of 83% may arise from the fact that D. and R. multiplied their original values of F, calcd. by the factor $744/616 = 1/0.83$, where 744 is $F(000)$ and 616 is the total number of electrons of the sulfur and iodine atoms in the cell, this factor correcting for the fact that not all of the cell contents were used in computing the values of F, calcd.[10] The procedure adopted here was to multiply the "F, meas." values of D. and R. by 0.75 for use in comparing the observed and calculated F values. The factor 0.75 differs from the factor 0.83 above because of a different averaging procedure in adjusting the scale factor.

Rather than presenting an extended table, only F values for those planes with $\sin\theta$ less than 0.52 are presented in Table I. Inspection of Table I reveals that the positions proposed by D. and R. cannot be correct—the large discrepancies in the case of (004), (101), (103), and (105) are alone sufficient to eliminate that structure. On the other hand, placement of the carbon atoms in the revised position clears up all of the major discrepancies without introducing any new ones, with the exception of (008). As this plane is by far the strongest one in this zone, its low observed value may possibly be ascribed to extinction. Other reflections for which the improved agreement with the revised carbon atom parameters is particularly striking are (104), (108), (109), (202), (208) and (403).

An over-all picture of the agreement between observed and calculated F values may be obtained from the function $\Sigma\ |F|_{\text{meas.}} - |F|_{\text{calcd.}}/\Sigma\ |F|_{\text{meas.}}$ the smallness of which is often suggested as a criterion for good agreement. Although there may be some doubt as to the validity of this function in comparing the determinations of different structures with one another, there seems to be no doubt that its decrease during the refinement of any one structure is significant. In the present work, the following values were obtained: set $F(1)$, sulfur and iodine atoms, only: 14.1%; set $F(2)$, same, with D. and R. carbon atoms: 16.4%; set $F(3)$, same, with revised carbon atoms: 11.8%. The absent reflections were not included in making these calculations. If the reflection (008), which may be subject to extinction, is also omitted, the values become 14.3, 17.0 and 11.2%, respectively.

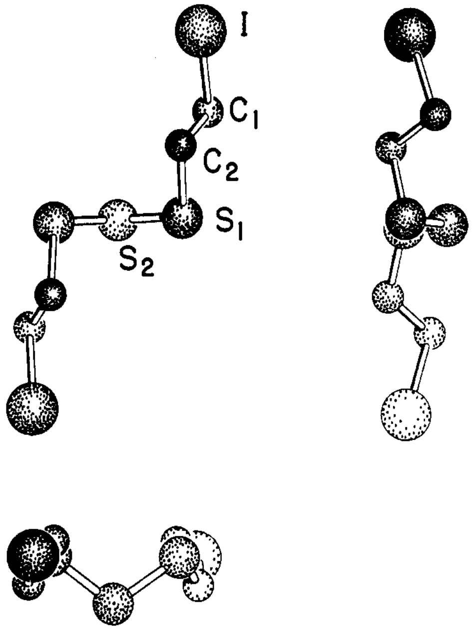

Fig. 1.—Three views of the 2,2'-diiododiethyltrisulfide molecule: above left: along the two-fold axis of the molecule; above right: perpendicular to the molecular two-fold axis and perpendicular to the c-axis of the crystal; below: perpendicular to the molecular two-fold axis and parallel to the crystal c-axis.

There is thus strong evidence for the revised positions of the carbon atoms in the comparison of observed and calculated structure factors. It is difficult to assess the limits of error to be attributed to the parameters assigned to the carbon atoms. In view of the nature of the Fourier plot, it is possible to make changes of the order of 0.1 Å. or more and not impair the agreement. It does not, moreover, seem worth while to determine what effect movements of this order of magnitude would have on the agreement between observed and calculated F values.

Discussion of the Structure

Configuration of the Molecule.—A drawing of the structure projected onto (010) appears in Fig. 2. The interatomic distances and bond angles computed with the original sulfur and iodine parameters and the revised carbon param-

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[9] "International Tables for the Determination of Crysta Structures," Gebruder Borntrager, Berlin, 1935, Vol. II, p. 571.

[10] The use of this ratio in situations of this kind is inappropriate. For, since $\overline{F^2} = \overline{\Sigma f_i^2}$, and if $f_i = Z_i f$, where f is the unitary structure factor, then $(\overline{F^2})^{1/2} = (\Sigma Z_i^2)^{1/2}(f^2)^{1/2}$; also $(F^2)^{1/2}$ is proportional to $\overline{F}$. The correct factor to use is therefore $(\Sigma 1 + \Sigma 2)^{1/2}/(\Sigma 1)^{1/2}$ where $\Sigma 1 = \Sigma Z_i^2$ for atoms included and $\Sigma 2 = \Sigma Z_i^2$ for atoms omitted. In our case, the factor is $(2Z_I^2 + 3Z_S^2 + 4Z_C^2 + 8Z_H^2)^{1/2}/(2Z_I^2 + 3Z_S^2)^{1/2} = 1.01$. The correctness of this factor is indicated by the fact that $\Sigma|F|_{\text{set}}(1) \cong \Sigma|F|_{\text{set}}(2) \cong \Sigma|F|_{\text{set}}(3)$.

TABLE I

MEASURED AND CALCULATED STRUCTURE FACTORS

$h0l$	$F_{\text{meas.}}$	$F(1)$ S + I	$F(2)$ D and R	$F(3)$ JD
004	25	+ 34	+110	+ 43
8	319	−351	−307	−400
12	202	−228	−209	−220
16	220	+212	+215	+224
101	61	+ 71	+ 39	+ 64
2	110	−102	−104	−104
3	61	+124	+102	+ 87
4	25	+ 58	+ 63	+ 33
5	61	+ 23	− 8	+ 60
6	202	−239	−243	−246
7	80	− 93	−102	− 91
8	<25	+ 29	+ 36	+ 17
9	110	−125	−147	−117
10	31	− 18	− 23	− 23
11	55	− 87	− 86	− 75
12	31	− 32	− 26	− 25
13	43	− 27	− 41	− 44
14	171	+185	+181	+189
15	<33	− 17	− 11	− 19
16	<34	− 37	− 32	− 28
17	<34	+ 30	+ 23	+ 26
18	134	+129	+125	+134
19	86	+106	+113	+106
200	153	−172	−169	−151
1	98	−110	−115	− 96
2	147	+154	+178	+137
3	166	−179	−175	−184
4	61	− 63	− 61	− 67
5	166	−155	−160	−155
206	61	− 74	− 59	− 71
7	117	−125	−122	−114
8	165	+190	+191	+174
9	<31	− 10	− 13	− 17
10	147	−159	−148	−145
11	67	+ 69	+ 70	+ 75
12	43	+ 41	+ 42	+ 50
13	116	+130	+129	+128
14	<33	− 12	− 8	− 5
15	123	+141	+141	+137
16	<34	− 60	− 60	− 51
17	52	+ 31	+ 31	+ 31
301	43	− 43	− 36	− 50
2	31	+ 25	+ 28	+ 39
3	61	− 45	− 37	− 54
4	202	−218	−223	−222
5	<33	+ 23	+ 28	+ 35
6	<33	− 20	− 13	− 3
7	<34	− 1	+ 6	+ 2
8	117	+116	+107	+117
9	<34	+ 17	+ 20	+ 23
10	34	+ 40	+ 49	+ 37
11	92	+ 88	+ 92	+ 90
12	128	+129	+119	+132
13	55	+ 39	+ 40	+ 32
400	<35	+ 11	+ 7	+ 26
1	<35	+ 6	− 2	+ 15
2	184	−175	−192	−170
3	49	− 24	− 16	− 33

eters are presented in Table II. The values of the dihedral angles are: $S_1–S_2–S_1–C_2$ = 82°; $S_2–S_1–C_2–C_1$ = 85°; $S_1–C_2–C_1–I$ = 180°. Small variations from the normal values of those distances and angles involving the carbon atoms cannot be considered significant, and, moreover, the

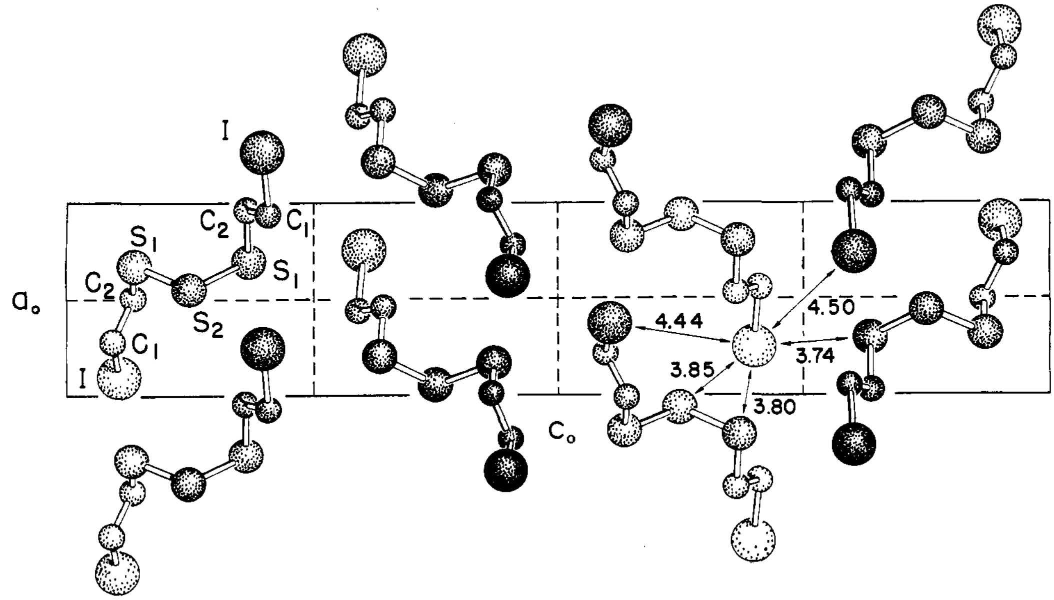

Fig. 2.—Projection of the structure of 2,2′-diiododiethyltrisulfide onto (010). Lengths of **the iodine and sulfur** van der Waals contacts are given in ångström units.

values of the dihedral angles may be in error by 10° or more, since relatively small changes in the positions of the carbon atoms correspond to large changes in these angles. The S–S–S bond angle of 113° appears to be rather larger than normal, comparing with the values of 104 ± 5° found in dimethyltrisulfide[2] and 105 ± 2° in S_8 molecules in the vapor state.[11]

TABLE II

INTERATOMIC DISTANCES AND ANGLES IN 2,2′-DIIODODIETHYLTRISULFIDE

Bond distances, Å.		Bond angles	
S_1–S_2	2.05	S_1–S_2–S_1	113°
S_1–C_2	1.86	S_2–S_1–C_1	98°
C_2–C_1	1.55	S_1–C_2–C_1	114°
C_1–I	2.09	C_2–C_1–I	109°

The van der Waals Radius of Sulfur.—Each iodine atom makes two close contacts with other iodine atoms, and three close contacts with sulfur atoms. These contacts, which are indicated in Fig. 2, are I...I = 4.44 Å. and 4.50 Å., and I...S = 3.74 Å., 3.80 Å. and 3.85 Å. The shortest contacts between the layers in elementary iodine[12] are 4.35, 4.40 and 4.46 Å. As in diiododiethyltrisulfide, these distances are slightly greater than 4.30 Å., the distance predicted on the basis of the van der Waals radius of 2.15 Å.[13] If we assume a slightly increased van der Waals radius of 2.20 Å. for iodine, we obtain, by subtracting this value from the three I...S distances, values of 1.54, 1.60 and 1.65 Å. for the van der Waals radius of sulfur. These values compare with the radii derived from the closest S...S contacts between S_8 molecules in rhombic sulfur,[14] namely, 1.64 Å. and 1.66 Å. All of these values, however, are significantly smaller than the ionic radius of 1.85 Å., the value taken as the van der Waals radius.[13] It thus appears that a downward revision of about 0.25 Å. should be made in the van der Waals radius of bicovalent sulfur.

Acknowledgments.—I wish to thank Dr. E. W. Hughes of this Laboratory for pointing out the derivation giving the correct scale factor for use when atoms are omitted in the calculation of structure factors. Most of the calculations were performed by Mrs. June Jenkins and Miss Lillian Casler.

Summary

The data of Dawson and Robertson on the crystal structure of 2,2′-diiododiethyltrisulfide have been examined. Reassignment of the parameters of the carbon atoms leads to a structure which is in agreement with the Fourier projection of electron density on (010), and which gives much improved agreement of observed with calculated structure factors. In this structure the dihedral angles S–S–S–C and S–S–C–C are both close to 90°, while the group S–C–C–I is coplanar and *trans*. It is also suggested that the van der Waals radius of bicovalent sulfur be revised downward 0.25 to 1.60 Å.

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[11] C. S. Lu and J. Donohue, THIS JOURNAL, **66**, 818 (1944).

[12] "Strukturbericht," Vol. II, p. 5.

[13] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 164.

[14] B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

PASADENA 4, CALIF. RECEIVED NOVEMBER 4, 1949

[CONTRIBUTION FROM THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH]

Heterogeneity of the Binding Sites of Bovine Serum Albumin[1]

BY FRED KARUSH[1a]

In a previous communication[2] it was shown that the binding by bovine serum albumin of three alkyl sulfates could not be described by the simple mass action equation based on the assumption of a single intrinsic association constant, even if correction is made for electrostatic interaction. If, on the other hand, the free energies of binding of the various sites were assumed to obey a Gaussian distribution, then a theoretical expression deduced on this basis could, with proper parameters, yield an adequate description of the binding data.[2a]

The limited range of data available in that study, particularly with regard to the average number of anions bound per protein molecule, did not, however, permit a critical evaluation of this particular heterogeneity assumption. To achieve this, the binding of the anionic azo dye *p*-(2-hydroxy-5-methylphenylazo)-benzoic acid was investigated since it was anticipated that this dye would permit more extensive data to be secured, as indeed turned out to be the case. The use of a dye was especially advantageous in that it greatly simplified the analytical problem.

In addition to serving as a test of the heterogeneity theory the binding studies reported here

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[1] Presented in part before the Division of Biological Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1949.

[1a] Investigation conducted during tenure of a Fellowship in Cancer Research of the American Cancer Society, recommended by the Committee on Growth of the National Research Council; present address: The Neurological Institute, New York 32, N. Y.

[2] F. Karush and M. Sonenberg, THIS JOURNAL, **71**, 1369 (1949).

[2a] In the present paper the term "heterogeneity" is used in the general sense of non-homogeneity. Previously[2] it was employed in the more restricted sense of referring to a Gaussian distribution.