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Mechanism of the Millon Reaction. II.[1] The Crystal Structure of Pigment 1

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The crystal structure of the colored substance in the Millon reaction of *p*-cresol, a complex consisting of 2-mercuri-4-methylphenol and 2-nitroso-4-methylphenol, was determined by the single crystal X-ray diffraction method.

The complex purified from chloroform crystallizes in triclinic crystal system, space group $P\bar{1}$, with each two molecules of the complex, $C_{14}H_{12}O_3NHg$, and chloroform in a cell dimensions a=10.6 Å, b=15.0 Å, c=5.6 Å, $\alpha=95°30'$, $\beta=94°20'$, $\gamma=100°30'$.

As the three-dimensional refinement of the crystal structure has not been attempted, valency angles and bond lengths are not clear, but the probable structure of this complex has been discussed from the result of the final two-dimensional refinement.

It has been reported that, in the modified Millon reaction of *p*-cresol with the Hopkins-Cole reagent, three kinds of pigments (Pigment 1,2 and 3) were produced depending on coloring conditions, and Pigment 1 was a complex consisting of 2-mercuri-4-methylphenol (MMP) and 2-nitroso-4-methylphenol (NMP), and Pigment 2 was a chelate compound of NMP and mercury.[1]

In the present investigation, the crystal structure of Pigment 1 was determined by the single crystal X-ray diffraction method, and that of Pigment 2 was assumed from the determined structure of Pigment 1.

The crystals of Pigment 1 were obtained as fiberous aggregates from a chloroform solution. Only a single crystal was obtained with a dimension of about 50 μ in diameter and the *c*-axis oscillation and Weissenberg photographs were taken with CuK radiation. Because of small size of specimen, about sixty hours exposure was necessary to take the equatorial Weissenberg photographs with sufficient intensity. During the exposure, the crystal was destroyed by X-ray radiation and the diffraction spots in the first layer line were considerably smeared out. The measurement of intensity in upper layer Weissenberg photographs was, therefore, unsuccessful.

From the *c*-axis oscillation and zero and first layer Weissenberg photographs, the lattice constants were determined as follows: $a=10.6$ Å, $b=15.0$ Å, $c=5.6$ Å, $\alpha=95°\ 30'$, $\beta=94°\ 20'$, $\gamma=100°\ 30'$

The crystal belongs to the triclinic crystal system with the space group, $P\bar{1}$. The unit cell volume and the density were determined to be 867 Å^3 and 2.10 g/cm^3, respectively. The molecular weight per formula unit was, therefore, calculated to be 550, provided that the cell contains two formula units. As mentioned later, a formula unit consists of a complex molecule and a molecule of chloroform each having the molecular weight 443.9 and 119.4, respectively. The sum of their molecular weight is 563.3 which agrees well with the observed value within the error of about 2.5% inspite of some experimental impediment as mentioned above.

Refinement of the Projected Structure along the *c*-Axis

1) Part I: Z. Tamura and Y. Kido, *Chem. Pharm. Bull.* (Tokyo), **16**, 1808 (1968).
2) Location: *Bunkyo-ku, Tokyo.*

As the present investigation was attempted to explain the arrangement of atoms around mercury atom, complete three-dimensional refinement of the crystal structure was not necessarily required, and the sufficient resolution would be obtained from the projection of the structure along the *c*-axis by using only the hko intensity data obtained from the equatorial Weissenberg photographs. The intensities of 384 independent reflexions were measured visually with the aid of a standard intensity scale.

These observed values of intensity were corrected for the Lorentz and polarisation factors, and the scale factor and the average temperature factor were determined based on the Wilson's statistical method. As the result, the temperature factor, B, was estimated to be 4.5 Å^2. Then, the atomic coordinates of the mercury atom, x=0.058, y=0.153 were obtained from the two-dimensional Patterson function, $P(u,v)$ which showed the maximum values at u=0.116 and v=0.306. The signs of the structure factors were calculated by assuming that the crystal consisted of only the mercury atom, and the distribution function of the two-dimensional electron density, $\rho(x,y)$ was calculated. It was possible to find out the atomic locations of two species of the molecule forming the complex visualized on the electron density map. In this map, there were also observed three remarkable peaks, as indicated in Table I, to which the structural model of a chloroform molecule was able to be fitted.

Table I. Distribution Function of Electron Density around the Chloroform Molecule

	x	y	Maximum values of electron density $\rho(x,y)$ (electrons/Å^2)
I	0.15	0.58	28
II	0.18	0.46	40
III	0.33	0.44	26

Table II. Atomic Coordinates and Thermal Parameters

		x	y	u(Å^2)
$C_6H_3(OH)(CH_3)(Hg)$	Hg	0.0583	0.1525	0.060
	C_1	0.220	0.147	0.055
	C_2	0.225	0.193	0.055
	C_3	0.316	0.262	0.050
	C_4	0.420	0.287	0.055
	C_5	0.429	0.225	0.055
	C_6	0.323	0.156	0.055
	O(OH)	0.127	0.073	0.045
	$C(CH_3)$	0.460	0.635	0.045
$C_6H_3O(CH_3)(NO)$	C'_1	0.080	0.775	0.030
	C'_2	0.157	0.870	0.055
	C'_3	0.255	0.920	0.065
	C'_4	0.300	0.868	0.050
	C'_5	0.230	0.782	0.050
	C'_6	0.128	0.738	0.050
	O′	0.005	0.266	0.050
	$C(CH_3')$	0.403	0.910	0.080
	N′	0.113	0.903	0.050
	O″	0.170	0.982	0.035
$CHCl_3$	Cl_1	0.174	0.460	0.060
	Cl_2	0.147	0.574	0.057
	Cl_3	0.333	0.446	0.060
	C(CH)	0.174	0.460	0.060

x and y show fractional coordinates and u shows mean square deviation of oscillation of atoms.

Namely, both of the peak locations and electron densities could be explained by arranging chlorine atoms on I and III, and chlorine and carbon atoms on II. Consequently, it was suggested that the crystal contained one molecule of chloroform per a complex molecule as a solvent of crystallization and this was also confirmed by infrared spectrum.[1)]

In order to establish definitely the location of each atom, several cycles of Fourier and difference Fourier calculations were carried out, and the atomic parameters and temperature factors of each atom were obtained as shown in Table II.

From these parameters, the reliability factor R ($R=\sum_{hk}||F_{obs}(hko)|-|F_{cal}(hko)||/\sum_{hk}|F_{obs}(hko)|$) was calculated to be 0.145 for 384 hko structure factors. Comparison of the observed and calculated structure factors is shown in Table III.

Table III. Comparison of Observed and Calculated Structure Factors

h	k	l	F_{obs}	F_{cal}	h	k	l	F_{obs}	F_{cal}	h	k	l	F_{obs}	F_{cal}	h	k	l	F_{obs}	F_{cal}	h	k	l	F_{obs}	F_{cal}
0	1	0	16.58	18.13	-2	8	0	14.65	15.07	-4	15	0	6.90	7.24	7	9	0	0.00	0.18	-9	15	0	1.81	-0.25
0	2	0	5.84	-7.15	-2	9	0	0.00	-3.32	-4	16	0	0.00	1.37	7	10	0	7.21	6.60	10	0	0	8.56	-9.07
0	3	0	46.00	-51.74	-2	10	0	17.75	-18.18	-4	17	0	0.00	-1.21	7	11	0	6.27	5.50	10	1	0	0.00	-0.70
0	4	0	19.17	-19.85	-2	11	0	11.67	-11.37	5	0	0	6.07	-4.68	7	12	0	0.00	1.05	10	2	0	0.00	0.15
0	5	0	3.89	0.29	-2	12	0	5.85	-5.28	5	1	0	23.91	-23.45	7	13	0	5.35	-3.71	10	3	0	7.22	6.66
0	6	0	10.55	9.91	-2	13	0	5.41	5.51	5	2	0	19.27	-19.43	7	14	0	3.13	-3.03	10	4	0	0.00	2.12
0	7	0	29.06	29.01	-2	14	0	7.70	7.13	5	3	0	0.00	2.86	-7	1	0	2.31	1.96	10	5	0	2.63	1.20
0	8	0	5.29	0.91	-2	15	0	0.00	0.69	5	4	0	21.14	18.24	-7	2	0	13.03	12.94	10	6	0	3.10	-5.05
0	9	0	10.22	-5.96	-2	16	0	0.00	-1.67	5	5	0	20.25	19.64	-7	3	0	19.22	19.22	10	7	0	0.00	-2.02
0	10	0	21.19	-20.99	-2	17	0	4.40	-3.95	5	6	0	8.21	5.26	-7	4	0	2.34	0.28	10	8	0	0.00	1.42
0	11	0	0.00	-0.71	3	0	0	0.00	1.57	5	7	0	4.32	-5.05	-7	5	0	6.75	-5.17	10	9	0	2.78	3.37
0	12	0	5.28	3.92	3	1	0	9.41	-9.85	5	8	0	19.12	-17.34	-7	6	0	22.78	-24.31	-10	1	0	4.70	-3.07
0	13	0	10.87	11.03	3	2	0	42.85	-41.63	5	9	0	7.10	-3.71	-7	7	0	2.50	-2.50	-10	2	0	0.00	-2.35
0	14	0	8.14	7.24	3	3	0	15.18	-15.20	5	10	0	0.00	0.92	-7	8	0	0.00	0.78	-10	3	0	3.19	5.32
0	15	0	0.00	-1.05	3	4	0	0.00	1.45	5	11	0	9.36	7.82	-7	9	0	11.83	10.81	-10	4	0	8.50	8.85
0	16	0	6.35	-5.36	3	5	0	17.73	17.58	5	12	0	5.21	2.25	-7	10	0	5.39	5.15	-10	5	0	2.71	1.17
0	17	0	5.14	-4.71	3	6	0	17.97	16.33	5	13	0	0.00	-1.73	-7	11	0	0.00	-1.62	-10	6	0	2.69	-1.63
1	0	0	43.12	46.75	3	7	0	3.04	1.42	5	14	0	3.04	-3.00	-7	12	0	6.07	-5.03	-10	7	0	3.02	-7.85
1	1	0	9.06	9.46	3	8	0	13.07	-11.50	5	15	0	3.58	-3.43	-7	13	0	7.00	-7.66	-10	8	0	0.00	-1.13
1	2	0	11.38	-12.30	3	9	0	18.09	-15.07	5	16	0	0.00	-0.20	-7	14	0	0.00	1.37	-10	9	0	6.00	0.19
1	3	0	36.37	-35.78	3	10	0	5.80	-4.62	-5	1	0	15.69	13.91	-7	15	0	3.28	2.71	-10	10	0	6.57	6.42
1	4	0	1.95	-0.50	3	11	0	6.59	5.52	-5	2	0	25.03	25.37	-7	16	0	5.42	5.49	-10	11	0	2.36	3.57
1	5	0	7.43	7.17	3	12	0	10.56	10.40	-5	3	0	8.45	8.11	8	0	0	14.91	-14.18	-10	12	0	0.00	0.18
1	6	0	29.25	28.03	3	13	0	6.57	4.16	-5	4	0	4.64	-2.81	8	1	0	7.32	-5.56	-10	13	0	3.09	-3.80
1	7	0	9.84	8.16	3	14	0	4.40	-2.43	-5	5	0	22.73	-23.89	8	2	0	0.00	0.86	-10	14	0	3.46	-3.21
1	8	0	0.00	-0.80	3	15	0	5.16	-5.17	-5	6	0	10.32	-9.56	8	3	0	14.36	14.83	11	0	0	5.03	-4.78
1	9	0	18.52	-17.75	3	16	0	3.42	-2.76	-5	7	0	0.00	-0.01	8	4	0	2.61	5.23	11	1	0	0.00	1.25
1	10	0	7.25	-6.60	3	17	0	0.00	-0.51	-5	8	0	21.32	22.63	8	5	0	0.00	0.26	11	2	0	5.09	5.09
1	11	0	0.00	-0.09	-3	1	0	29.28	30.64	-5	9	0	10.21	10.56	8	6	0	8.60	-9.67	11	3	0	5.14	4.88
1	12	0	11.67	10.39	-3	2	0	11.70	11.16	-5	10	0	7.14	7.05	8	7	0	8.06	-7.72	11	4	0	0.00	0.20
1	13	0	9.44	9.40	-3	3	0	10.80	-9.46	-5	11	0	9.84	-6.96	8	8	0	2.60	-0.66	11	5	0	2.26	-3.24
1	14	0	6.01	1.24	-3	4	0	23.60	-21.07	-5	12	0	9.36	-9.64	8	9	0	0.00	0.85	11	6	0	5.77	-3.60
1	15	0	0.00	0.13	-3	5	0	24.78	-24.78	-5	13	0	3.85	-0.78	8	10	0	7.20	7.50	11	7	0	0.00	-1.13
1	16	0	5.66	-6.86	-3	6	0	0.00	0.08	-5	14	0	0.00	0.69	8	11	0	3.50	1.26	11	8	0	1.22	1.28
1	17	0	3.95	-0.66	-3	7	0	17.76	19.85	-5	15	0	7.22	8.68	8	12	0	1.68	1.55	-11	1	0	7.84	-6.55
-1	1	0	31.50	34.07	-3	8	0	23.17	21.09	-5	16	0	0.00	0.51	-8	1	0	4.39	-3.10	-11	2	0	2.56	-1.63
-1	2	0	0.00	-1.61	-3	9	0	0.00	1.37	-5	17	0	0.00	0.89	-8	2	0	5.05	4.80	-11	3	0	2.57	3.07
-1	3	0	30.09	-32.58	-3	10	0	11.36	-10.97	6	0	0	3.60	-2.53	-8	3	0	11.87	10.70	-11	4	0	7.69	7.75
-1	4	0	35.23	-37.43	-3	11	0	12.83	-12.56	6	1	0	31.14	-29.73	-8	4	0	8.45	8.44	-11	5	0	4.40	2.71
-1	5	0	4.38	-3.93	-3	12	0	8.75	-7.97	6	2	0	4.89	-0.18	-8	5	0	4.46	-4.77	-11	6	0	0.00	2.17
-1	6	0	4.30	3.63	-3	13	0	0.00	1.57	6	3	0	0.00	0.60	-8	6	0	11.68	-12.52	-11	7	0	6.03	-6.67
-1	7	0	33.88	37.06	-3	14	0	7.20	7.25	6	4	0	20.84	20.15	-8	7	0	11.87	-11.45	-11	8	0	3.37	-3.03
-1	8	0	8.38	7.86	-3	15	0	6.46	5.30	6	5	0	14.32	12.12	-8	8	0	0.00	-3.93	-11	9	0	0.00	-0.90
-1	9	0	8.60	-3.08	-3	16	0	0.00	0.66	6	6	0	2.55	1.07	-8	9	0	7.12	6.60	-11	10	0	4.34	4.12
-1	10	0	22.31	-22.45	-3	17	0	4.90	-5.23	6	7	0	6.46	-2.76	-8	10	0	8.17	7.38	-11	11	0	3.48	4.18
-1	11	0	10.84	-10.97	4	0	0	6.90	-8.05	6	8	0	11.47	-11.00	-8	11	0	2.70	3.65	-11	12	0	0.00	0.06
-1	12	0	0.00	2.28	4	1	0	17.12	-17.28	6	9	0	0.00	-0.52	-8	12	0	5.27	-3.29	-11	13	0	1.53	-0.48
-1	13	0	8.13	6.28	4	2	0	29.31	-31.67	6	10	0	0.00	0.92	-8	13	0	6.66	-7.48	-11	14	0	0.00	-4.19
-1	14	0	8.17	7.96	4	3	0	12.61	-11.48	6	11	0	8.19	8.60	-8	14	0	0.00	-1.39	12	0	0	0.00	0.71
-1	15	0	0.00	-0.63	4	4	0	11.16	11.83	6	12	0	0.00	0.53	-8	15	0	0.00	1.94	12	1	0	0.00	0.82
-1	16	0	0.00	-2.53	4	5	0	23.00	21.28	6	13	0	3.05	-2.34	-8	16	0	1.80	3.43	12	2	0	5.11	5.44
-1	17	0	6.14	-6.17	4	6	0	13.94	14.39	6	14	0	5.46	-3.89	9	0	0	8.10	-8.11	12	3	0	0.00	0.84
2	0	0	10.41	9.13	4	7	0	6.14	-6.96	-6	1	0	0.00	1.14	9	1	0	2.71	-1.71	12	4	0	0.00	1.22
2	1	0	9.57	8.57	4	8	0	17.56	-14.27	-6	2	0	27.54	26.32	9	2	0	0.00	-1.22	12	5	0	2.66	-3.31
2	2	0	42.07	-44.28	4	9	0	13.43	-11.92	-6	3	0	17.38	16.46	9	3	0	8.62	8.78	-12	1	0	4.35	-4.80
2	3	0	20.50	-19.89	4	10	0	0.00	-0.28	-6	4	0	0.00	-2.29	9	4	0	4.69	3.28	-12	2	0	3.82	-3.80
2	4	0	12.31	-9.03	4	11	0	9.44	9.08	-6	5	0	16.99	-15.89	9	5	0	0.00	-0.58	-12	3	0	0.00	0.07
2	5	0	25.55	23.12	4	12	0	6.03	3.14	-6	6	0	18.82	-19.60	9	6	0	7.80	-8.27	-12	4	0	3.13	4.48
2	6	0	18.87	19.57	4	13	0	0.00	0.88	-6	7	0	3.30	5.89	9	7	0	6.10	-5.25	-12	5	0	5.37	5.78
2	7	0	0.00	0.81	4	14	0	3.37	-4.16	-6	8	0	10.32	9.29	9	8	0	0.00	0.20	-12	6	0	0.00	0.08
2	8	0	0.00	-0.71	4	15	0	5.13	-3.64	-6	9	0	14.10	16.53	9	9	0	3.01	2.77	-12	7	0	2.08	-1.64
2	9	0	21.22	-20.19	4	16	0	0.00	-1.75	-6	10	0	0.00	0.22	9	10	0	3.21	2.95	-12	8	0	3.27	-4.99
2	10	0	5.00	0.05	4	17	0	0.00	0.09	-6	11	0	0.00	-1.40	9	11	0	1.49	0.93	-12	9	0	1.86	-0.33
2	11	0	0.00	0.75	-4	1	0	27.94	28.27	-6	12	0	8.62	-7.84	-9	1	0	8.52	-8.35	-12	10	0	1.70	1.83
2	12	0	13.00	13.30	-4	2	0	9.86	11.21	-6	13	0	6.05	-6.22	-9	2	0	0.00	0.91	-12	11	0	3.89	3.50
2	13	0	6.66	5.07	-4	3	0	13.09	10.75	-6	14	0	0.00	-0.55	-9	3	0	8.91	7.71	-12	12	0	0.00	1.00
2	14	0	0.00	1.04	-4	4	0	18.24	-17.35	-6	15	0	6.03	5.95	-9	4	0	10.78	10.46	-13	0	0	1.47	1.21
2	15	0	5.49	-4.53	-4	5	0	20.13	-22.23	-6	16	0	4.97	4.69	-9	5	0	0.00	-1.16	-13	1	0	2.22	-2.17
2	16	0	4.86	-5.18	-4	6	0	5.01	-1.16	7	0	0	9.62	-7.55	-9	6	0	7.69	-7.08	-13	2	0	4.90	-5.19
2	17	0	0.00	-0.21	-4	7	0	7.00	4.94	7	1	0	18.08	-17.14	-9	7	0	2.04	-0.65	-13	3	0	0.00	-0.90
-2	1	0	20.63	22.43	-4	8	0	25.88	27.60	7	2	0	2.42	-1.07	-9	8	0	3.72	-3.72	-13	4	0	1.66	0.28
-2	2	0	5.53	6.27	-4	9	0	8.28	5.66	7	3	0	11.96	9.20	-9	9	0	3.82	3.29	-13	5	0	5.17	5.39
-2	3	0	3.91	-0.13	-4	10	0	0.00	-0.38	7	4	0	14.95	16.03	-9	10	0	6.53	6.32	-13	6	0	0.00	0.03
-2	4	0	21.89	-23.49	-4	11	0	16.83	-16.10	7	5	0	0.00	-1.01	-9	11	0	5.17	5.20	-13	7	0	0.00	-0.21
-2	5	0	25.14	-26.92	-4	12	0	8.00	-5.66	7	6	0	4.66	-3.41	-9	12	0	0.00	-3.53	-13	8	0	1.96	-2.39
-2	6	0	7.07	7.40	-4	13	0	0.00	-0.06	7	7	0	8.60	-7.86	-9	13	0	4.00	-4.71	-13	9	0	0.00	-1.27
-2	7	0	20.60	21.67	-4	14	0	7.17	6.55	7	8	0	0.00	-2.28	-9	14	0	2.09	-2.39					

Fig. 1 shows the electron density function, $\rho(x,y)$ calculated at this stage.

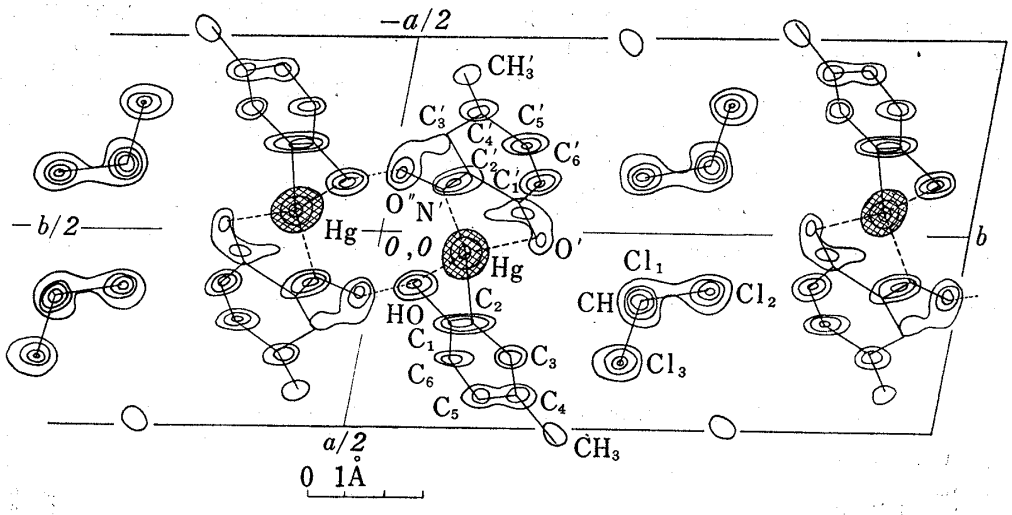

Fig. 1. The Final Two-Dimensional Electron Density Distribution, $\rho(x,y)$

From the figure it is obvious that the nitrogen atoms of NMP coordinate to the metal atom as in the cases of Ni-dimethylglyoxime[3] and Cu-salicylaldoxime.[4] In the present analysis, however, bond lengths and bond angles have not been calculated because of no information was obtained on the z-coordinates of atoms. Therefore, which resonance form in Chart 1 is dominant is left uncertain.

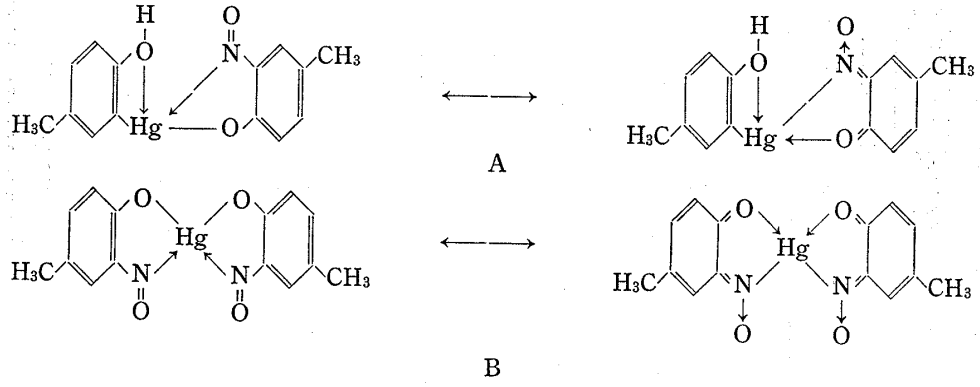

Chart 1

The spectral shape of Pigment 1 and 2 is quite similar in the visible region and their λ_{max} on the longest wave length lie near each other. Furthermore, the molar extinction coefficient of Pigment 2 is almost twice as large as that of Pigment 1.[1] Consequently, the structure of Pigment 2 is assumed to be B in Chart 1.

3) L.E. Goclycki and R.E. Rundle, *Acta Cryst.*, **6**, 487 (1953).
4) M.A. Jarski and E.C. Lingafelter, *Acta Cryst.*, **17**, 1109 (1964).