Isolation of Cyclopropene.—Three liters of hydrocarbon pyrolysis products, dried with magnesium perchlorate and freed of carbon dioxide with ascarite, was fractionated at atmospheric pressure (744 mm.) in a small Podbielniak column.[27] Approximately 700 ml. of gas distilled over at −36 to −35°; the residue, 3 to 4 ml. of slightly yellow somewhat viscous oil, gave no further distillate on warming to room temperature. As the original sample contained methylacetylene as well as cyclopropene, this seems to indicate that cyclopropene can combine with methylacetylene as well as with itself. The ratio of hydrogen to carbon was determined on three 10-ml. samples of pure hydrocarbon gas by burning in a semi-micro combustion furnace.

Anal. Calcd. for C_3H_4: H/C ratio, 1.33. Found: 1.332, 1.346, 1.320.

Acknowledgment.—The author wishes to acknowledge his indebtedness to Dr. E. R. Buchman for suggesting the problem and to him and to Professor H. J. Lucas for guidance during the course of the investigation. Thanks are also

due to Professor J. B. Cloke for suggestions relating to the preparation of cyclopropyl cyanide and to Mr. Alf O. Reims and to Mr. Herbert Sargent for aid with some of the preparations.

Summary

The preparation of cyclopropene by the thermal decomposition of trimethylcyclopropylammonium hydroxide on a platinum catalyst was studied in detail. The optimum temperature for cyclopropene formation was found to be 320°.

Pure cyclopropene was obtained by fractional distillation of the hydrocarbons obtained by pyrolysis of the quaternary base. It boils at −36° at 744 mm.

Cyclopropylamine was prepared from trimethylene glycol by several paths. The individual steps were investigated from a preparative point of view.

The Crystal Structure of Melamine

BY E. W. HUGHES

In an earlier paper[1] the crystal structure of dicyandiamide, the dimer of cyanamide, was reported. I have now completed a similar investigation of melamine, or cyanuric triamide, the trimer of cyanamide, with the results described below.

The earlier crystallographic investigations of melamine are recorded in Groth. The most recent investigation is that of Heydrich.[2] He found the substance to be monoclinic holohedral with axial ratios $a:b:c = 1.4121:1:0.9728$ and $\beta = 112°16'$. The birefringence is strongly negative and he placed the acute bisectrix about 6° from a in acute β. The latter observation is undoubtedly wrong but he gives refractive indices which are at least approximately in accord with the structure found below and from the method used in measuring the indices it appears possible that he has made an error only in recording the position of the bisectrix. Indeed, the true position makes with c an angle about equal to that made with c by his bisector, but in obtuse β, and such an error

might easily be made by reading a circle backward or by reversing the sign of a sine in a calculation.

The Unit Cell and Space Group

The material at first used in this investigation was from Eastman Kodak Company. Later a sample was obtained from the research laboratories of the American Cyanamid Company and a third sample was prepared by heating guanidinium carbonate according to the directions of Krall.[3] The latter claimed by this method to have prepared an isomer of melamine, the much sought "isomelamine," but in two attempts only ordinary melamine was obtained. Crystals from the different sources yielded identical diffraction patterns.

The best crystals were obtained by slow evaporation of seeded water solutions in flasks with cotton wad stoppers. The crystals stick tenaciously to surfaces on which they grow and it was necessary, in order to get good specimens, to turn the growing crystals over daily with a fine glass

(1) Hughes, THIS JOURNAL, **62**, 1258 (1940).

(2) Heydrich. Z. Krist., **48**, 278 (1910–1911).

(3) Krall. Proc. Chem. Soc., **29**, 377 (1913).

TABLE I

$hОl$	$F_{obsd.}$	$F_{calcd.}$	$hОl$	$F_{obsd.}$	F_{calcd}	$hОl$	$F_{obsd.}$	F_{calcd}	$hОl$	$F_{obsd.}$	F_{calcd}
001	25	+ 24	603	9	+ 8	606	4	− 3	$8,0,\bar{11}$	7	− 7
$20\bar{1}$	43	+ 46	801	8	− 8	10,0,3	<2	− 1	$12,0,\bar{10}$	11	−11
200	9	+ 9	006	13	−12	12,0,1	<2	+ 1	409	6	− 7
$20\bar{2}$	56	− 58	$10,0,\bar{3}$	5	− 3	$20\bar{9}$	2	− 2	$16,0,\bar{2}$	6	− 6
201	141	−129	$10,0,\bar{2}$	12	−11	$12,0,\bar{7}$	<2	0	$14,0,\bar{9}$	4	+ 4
002	26	− 26	$80\bar{6}$	8	− 6	208	11	+10	12,0,4	<3	0
$40\bar{1}$	30	+ 32	$40\bar{7}$	10	−10	$80\bar{9}$[a]	1	− 1	807	<3	+ 3
$40\bar{2}$	46	− 44	802	<3	0	805	7	− 6	14,0,2	<3	− 2
400	21	− 24	$10,0,\bar{4}$	<3	0	$14,0,\bar{3}$	<3	0	$16,0,\bar{7}$	<3	0
$20\bar{3}$	49	+ 48	405	<3	− 1	$14,0,\bar{4}$	3	+ 2	$10,0,\bar{11}$	11	+ 9
202	35	− 31	$10,0,\bar{1}$	<3	− 1	$14,0,\bar{5}$	<3	0	2,0,10	4	− 2
003	14	+ 15	$20\bar{7}$	4	+ 5	$14,0,\bar{2}$	<3	− 1	$2,0,\bar{11}$	<3	− 3
$40\bar{3}$	<2	+ 2	206	<3	+ 1	$12,0,\bar{8}$	6	+ 6	$16,0,\bar{1}$	<3	− 3
401	3	− 4	$60\bar{7}$	9	+ 7	$10,0,\bar{9}$	6	− 7	10,0,6	4	+ 3
$20\bar{4}$	19	+ 16	604	6	+ 6	009	<3	0	$14,0,\bar{10}$	10	−12
203	<2	− 3	$10,0,\bar{5}$	5	− 6	12,0,2	5	− 6	$16,0,\bar{8}$	4	+ 3
$60\bar{2}$	10	− 13	10,0,0	<3	+ 1	10,0,4	<3	+ 1	$12,0,\bar{11}$	5	+ 7
$60\bar{1}$	6	+ 5	007	7	− 6	$14,0,\bar{6}$	<3	− 3	16,0,0	5	+ 5
$40\bar{4}$	41	+ 39	$80\bar{7}$	19	+18	$14,0,\bar{1}$	8	− 8	0,0,11	<3	+ 2
402	8	+ 9	803	<3	0	$6,0,\bar{10}$	<3	− 2	14,0,3	<3	+ 3
004	13	− 12	$10,0,\bar{6}$	18	+18	$4,0,\bar{10}$	<3	− 1	12,0,5	<3	0
$60\bar{3}$	43	− 44	10,0,1	4	+ 3	408	5	+ 4	$60\bar{9}$	5	− 5
600	3	+ 3	$40\bar{8}$	<3	0	607	<3	+ 2	$6,0,\bar{12}$	<3	+ 2
$60\bar{4}$	3	− 2	406	<3	− 1	$8,0,\bar{10}$	<3	+ 1	$8,0,\bar{12}$	<3	− 2
601	5	+ 6	$60\bar{8}$	6	− 5	806	<3	− 3	$16,0,\bar{9}$	6	+ 7
$20\bar{5}$	3	− 4	605	<3	+ 2	$2,0,\bar{10}$	<3	− 1	4,0,10	<3	− 3
204	4	+ 5	$20\bar{8}$	4	+ 6	209	5	+ 5	$4,0,\bar{12}$	<3	− 2
$40\bar{5}$	3	+ 3	207	4	+ 4	$14,0,\bar{7}$	<3	0	808	<3	− 1
403	7	− 6	$12,0,\bar{3}$	<3	+ 3	$12,0,\bar{9}$	21	−21	16,0,1	<3	− 1
005	16	− 12	$12,0,\bar{4}$	9	+ 9	14,0,0	<3	0	$18,0,\bar{4}$	<3	0
$80\bar{2}$	14	+ 15	$12,0,\bar{2}$	7	+ 6	12,0,3	4	− 3	$18,0,\bar{5}$	<3	− 2
$60\bar{5}$	4	− 6	$10,0,\bar{7}$	<3	+ 3	$10,0,\bar{10}$	17	+16	$10,0,\bar{12}$	<3	+ 1
$80\bar{3}$	10	+ 10	$80\bar{8}$	4	− 4	$14,0,\bar{8}$	10	+12	$18,0,\bar{6}$	<3	− 3
$80\bar{1}$	2	+ 3	10,0,2	6	+ 6	10,0,5	<3	− 1	$14,0,\bar{11}$	<3	+ 2
602	<2	− 2	$12,0,\bar{5}$	5	+ 6	14,0,1	<3	+ 1	$16,0,\bar{10}$	<3	0
$80\bar{4}$	6	+ 5	$12,0,\bar{1}$	5	+ 5	0,0,10	<3	− 1	$18,0,\bar{1}$	4	+ 4
800	<2	+ 3	804	3	− 3	$16,0,\bar{4}$	<3	0	0,0,12	<3	+ 3
$40\bar{6}$	<2	0	008	7	− 6	$16,0,\bar{5}$	<3	+ 2	$16,0,\bar{11}$	<3	+ 1
$20\bar{6}$	<2	− 2	$12,0,\bar{6}$	3	− 2	$16,0,\bar{3}$	<3	− 1	18,0,0	<3	+ 2
404	4	+ 3	12,0,0	2	− 1	$6,0,\bar{11}$	<3	+ 4	$16,0,\bar{12}$	<3	+ 3
205	2	− 1	$40\bar{9}$	<3	− 1	$16,0,\bar{6}$	<3	− 1	$18,0,\bar{11}$	<3	− 1
$60\bar{6}$	11	+ 11	$10,0,\bar{8}$	<3	+ 3	608	4	− 2	$16,0,\bar{13}$	4	− 5
$80\bar{5}$	6	− 6	$60\bar{9}$	3	+ 4	$4,0,\bar{11}$	<3	+ 1	$18,0,\bar{12}$	4	+ 5
			$40\bar{7}$	3	+ 3						

[a] The limit of copper radiation.

rod. Samples of all sizes up to nearly 2 mm. long and 1 mm. thick were obtained. The forms observed are {001}, {110} and {011} with occasionally other minute faces not identified. Complete sets of 20° oscillation photographs were made with CuKα radiation about the a, b and c axes of Heydrich, using rather large crystals.[4] From these the unit cell edges were found to be $a = 10.54$ Å., $b = 7.45$ Å. and $c = 7.25$ Å. (all ±0.5%, CuKα

$\lambda = 1.539$ Å.). These values are in good agreement with those of Shanker, Baljekar and Prasad,[5] $a = 10.52$ Å., $b = 7.44$ Å. and $c = 7.33$ Å. Since there was a considerable discrepancy between Heydrich's value of β, 112°16′ and that of Groth, 111°47′, and the crystal form does not permit a direct goniometric determination, β was evaluated from X-ray spacing measurements on a number of reflections in the back-reflection region of the camera. These values all fall well within the

(5) Shanker, Baljekar and Prasad. J. Ind. Chem. Soc., 16, 671 (1939).

TABLE II

$0kl$	$F_{obsd.}$	$F_{calcd.}$	$0kl$	$F_{obsd.}$	$F_{calcd.}$	$0kl$	$F_{obsd.}$	$F_{calcd.}$	$0kl$	$F_{obsd.}$	$F_{calcd.}$
001	25	+24	053	4	− 3	047	5	+5	095	3	−4
011	50	+46	061	8	+ 7	008	7	−6	068	4	−5
020	5	+ 4	035	4	− 4	018	7	−7	049	<3	−1
002	26	+26	062	4	− 4	075	2	+2	0,10,4	<3	+2
021	17	−18	006	13	−12	066	<2	−2	0,11,1	4	+5
012	10	+12	054	3	− 3	091	<2	−1	078	3	−2
022	38	−35	016	<3	0	028	6	−5	087	3	+2
031	2	+ 1	045	<3	− 1	084	2	−3	059	3	−3
003	14	+15	063	4	+ 4	057	<2	+1	096	<3	−1
013	12	−11	026	14	+13	092	5	−4	0,11,2	<3	+3
032	9	− 7	071	18	+19	038	2	+2	0,10,5	<3	+2
023	2	− 1	036	<3	− 1	093^a	6	−7	0,11,3	3	−3
040	4	− 5	072	4	− 3	076	4	−2	0,11,4	<3	+1
041	3	+ 2	064	6	− 7	085	4	+4	097	6	+4
004	13	−12	055	8	+ 8	048	<3	+1	088	7	−7
033	15	−14	007	7	− 6	067	6	−6	0,12,0	3	+2
014	17	+16	046	10	+11	009	<3	0	0,10,6	<3	+4
042	31	−31	073	<2	− 2	0,10,0	<3	−2	0,12,1	<3	+2
024	10	+10	017	5	− 6	019	<3	+3	0,12,2	<3	0
051	5	+ 6	027	9	+ 8	094	4	+5	0,11,5	3	+3
043	7	− 7	080	2	+ 3	0,10,1	<3	+1	0,12,3	<3	0
034	7	− 6	081	5	− 4	058	6	+6	0,10,7	<3	+1
052	5	− 3	065	5	− 4	029	4	−4	0,12,4	3	−3
005	16	−12	074	5	+ 6	0,10,2	5	−7	0,11,6	<3	−2
015	4	− 5	037	4	+ 3	086	5	+5	0,13,1	4	+4
025	<2	+ 3	056	4	− 5	039	<3	+1	0,12,5	<3	0
044	8	+ 9	082	2	+ 2	077	<3	−3	0,12,6	3	+4
060	41	+42	083	<2	− 1	0,10,3	6	−6			

^{a} The limit of copper radiation.

TABLE III

$hk0$	$F_{obsd.}$	$F_{calcd.}$	$hk0$	$F_{obsd.}$	$F_{calcd.}$	$hk0$	$F_{obsd.}$	$F_{calcd.}$	$hk0$	$F_{obsd.}$	$F_{calcd.}$
110	16	−18	530	17	+16	650	12	−13	380	<2	−1
200	9	+ 9	620	22	+22	830	2	+ 2	670	<2	+1
210	47	+52	440	<2	+ 1	910	4	+ 4	11,1,0	2	+3
020	5	+ 4	150	8	+ 7	170	21	−21	950	2	+4
120	14	−16	250	5	− 5	560	8	+ 9	860	3	−3
310	68	+69	710	5	+ 5	270	19	+18	480	4	−3
220	<1	0	630	7	+ 8	920	5	+ 5	10,4,0	3	+4
400	21	−24	350	8	+ 9	840	<2	+ 1	11,2,0	5	+6
320	31	+32	540	7	+ 9	750	<2	0	770	2	+1
130	12	+10	720	11	−10	370	14	+16	580	<2	−2
410	11	+12	450	3	+ 2	930	<2	+ 1	11,3,0	<2	−1
230	10	−11	060	41	+42	660	<2	0	190	3	−2
420	9	+ 9	160	5	+ 6	10,0,0	<2	+ 1	960	1	−2
330	16	+16	640	7	+10	470	5	+ 6	10,5,0	5	+6
510	4	+ 4	800	<3	+ 3	10,1,0	3	− 3	290	2	−3
040	4	− 5	730	3	− 3	10,2,0	5	+ 5	12,0,0	2	−1
140	<2	0	810	2	− 3	850	<2	+ 3	12,1,0	3	−3
240	6	+ 8	260	3	− 4	940	<2	− 1	680	5	+6
430	8	− 7	550	8	− 7	080	2	+ 3	390	3	+2
520	13	−14	360	2	+ 2	570	<2	+ 1	870	<1	0
600	3	+ 3	820	6	+ 6	180	11	−12	11,4,0	2	−3
340	16	−17	740	10	+ 9	760	5	+ 4	12,2,0	<1	+2
610	17	+16	460	6	− 8	280	9	−10	490	6	−6
						10,3,0	<2	0			

two goniometric values and their mean, β = 112°2', which is almost exactly the mean of the goniometer measurements, was adopted. This cell contains four molecules of $C_3N_6H_6$ and the calculated and observed (Heydrich) densities are 1.577 g./cc. and 1.573 g./cc., respectively. The

consistent extinctions, $h0l$ when h is odd and $0k0$ when k is odd, indicate uniquely[6] the space group $P2_1/a$.

Pictures for intensity data were made for the $h0l$ and $0kl$ zones with MoKα radiation since it seemed that additional reflections might be so obtained sufficient in number to materially improve the resolution of the Fourier projections. A crystal, over 1 mm. in all directions, was cemented firmly to a stiff wire in the proper orientation and the wire mounted on a goniometer head. After final adjustment for orientation the goniometer head was fastened in a lathe and the crystal turned down into a cylinder about 0.9 mm. in diameter, garnet paper being used as a cutting tool. The surface was smoothed with finer grades of abrasive. Although these cylinders are somewhat larger than cylinders usually ground for CuKα pictures, the linear absorption coefficient of melamine for MoKα is so small that no absorption correction was required and experience showed that the large crystal was necessary to bring the exposure time within reasonable limit. Both a and b axis cylinders were prepared and complete sets of 12° oscillation pictures were made for the two zones. For the b axis pictures two exposures, in the ratio of ten to one, were made for each range. Later, when the a axis pictures were made, a modification of the multiple film technique of de Lange, Robertson and Woodward[7] was used. The absorption of duplitized X-ray film for MoKα is too small to give useful reduction. The three films used were interleaved with 0.001 inch Cu foil. The ratio for one film and foil was almost exactly 4:1.

For the $hk0$ zone the additional data obtainable with MoKα radiation could be of no use in a Fourier synthesis so only a set of CuKα 15° oscillation pictures was made using a small crystal (0.2 to 0.3 mm.) and the multiple film technique.[7] From these various films the data of Tables I, II and III were obtained by visual estimation. The relative intensities were corrected for the Lorentz-polarization factor and the scale of their square roots has been adjusted in the tables to approximately absolute scale by comparison with the values calculated from the final structure.

(6) It might be well to point out here an unfortunate misstatement in the dicyandiamide paper (ref. 1) where it was inadvertently said, through confusion with melamine, that the extinctions lead *uniquely* to the space group C_2/c. Actually the extinctions indicate either Cc or C_2/c and the latter was chosen because of the crystallographic point group assignment and because a satisfactory structure was eventually based on it.

(7) De Lange, Robertson and Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

In each table the data are in order of decreasing spacing and the limit of CuKα is indicated in Tables I and II in order to emphasize the importance of using Mo radiation.

Determination of the Structure

Since there are four molecules of $C_3N_6H_6$ per cell it appears that each atom must occupy one of the four-fold general positions of $P2_1/a$: x,y,z; $\bar{x},\bar{y},\bar{z}$; $1/2 + x$, $1/2 - y$, z; $1/2 - x$, $1/2 + y,\bar{z}$. And since there are nine ponderable atoms in the molecule there are twenty-seven parameters to be evaluated.

From the high birefringence[2] ($\alpha = 1.491$, $\beta = 1.743$, $\gamma = 1.872$, D lines) one infers that the molecules, which one expects to be coplanar, are set nearly parallel with one another and approximately normal to the acute bisectrix. Moreover, one is at once impressed with the great intensity of 060, as compared with other reflections in the same spacing range, and with the fact that all other orders of $0k0$ are weak or absent. The spacing of 060 is 1.24 Å. This suggests that one of the three two-fold axes of the molecule is very nearly parallel to (010), for then it turns out that all the atoms are approximately in layers parallel to (010) and if the plane of the molecule is inclined not more than twenty to twenty-five degrees from b the spacing between these layers is about equal to 1.24 Å. (The N–C distance was taken at 1.36 Å. in these trial models.)
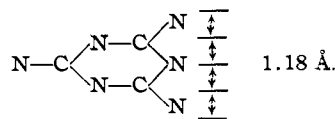
If then the center of the molecule is at some multiple of $b/12$ in the y direction, all the atoms of all the molecules will be about in phase for 060 and will likewise interfere destructively for all other orders of $0k0$ (except possibly 0,12,0). Using such a model, no fit could be obtained with many simple reflections for any x and z position of the molecular center. On further inspection of the data one notes that F_{201} is unusually large and since its spacing is fairly large too one is led to suspect that the molecules are really in layers parallel to this plane. Although this is contrary to the acute bisectrix of Heydrich, this is indeed the case. Consequently a check was made upon the position of the bisectrices. A small crystal was mounted on a microscope stage with b parallel to the optical axis of the microscope. It was ob-

served that extinction between crossed nicols did not occur at the positions required by the bisectrices given by Heydrich. The mean of four settings gave one extinction at 43 ± 2° to a in acute β and of course the other at 90° to the first. One cannot tell from this experiment which of these positions corresponds to the acute and which to the obtuse bisectrix but since the second is perpendicular to (201) to within 5° it was taken to be the acute bisectrix. These new data then placed the molecular plane 5° from the trace of (201) on (010), in the direction indicated by the extinction, and not over 20 to 25° from b. The positions of the two-fold axes of the molecule are as before. An approximate fit with the large spacing $h0l$ reflections was then easily obtained by varying the x and z coördinates of the center of the molecule. Further smaller manipulations of the orientation of the plane and the position of the center of the molecule improved the fit throughout the range of $h0l$ spectra to the point where a Fourier synthesis could be tried. The series $\rho(x,z) = \sum_h \sum_l F_{h0l}$ cos 2 $\pi(hx + lz)$ was summed using Lipson–Beevers[8] strips at intervals of $a/60$ and $c/60$, except in the final summation (Fig. 1) where the summation over h was at intervals of $a/120$. The original series employing Cu data gave three peaks, only one of which corresponded to a single atom. But inclusion of only the largest F's in the region beyond the CuKα limit produced enough resolution to show that the model in use for calculating signs was tipped a little too much from b. The final series plotted in Fig. 1 contains all observed F's with the same signs as those calculated from the final structure. Although this figure shows six of the atoms as separate peaks it is clear that most are so close to neighboring peaks that the positions of the maxima are shifted. F's calculated from parameters taken directly from the maxima show only moderate agreement with observed values and variation of the three unresolved atoms does not materially improve matters. The atoms were shifted slightly from the peaks in the directions indicated by the environment and the final positions, including those of the three unresolved atoms, were determined by what is essentially a systematization of the trial and error method.

Least Squares Refinement of Parameters

In the trial and error method one makes small adjustments of the parameters, chosen in such a

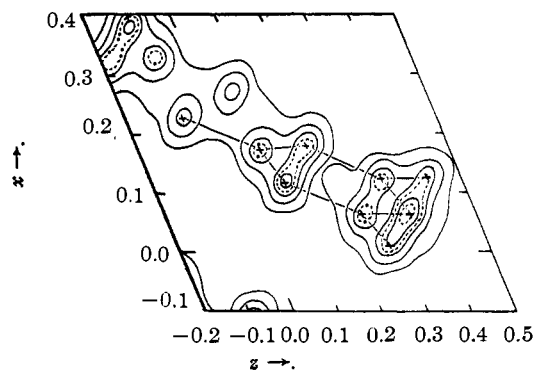(8) Lipson and Beevers, Proc. Phys. Soc., **48**, 772 (1936).

Fig. 1.—$\rho(x,z)$. Dotted contours are at half the regular contour interval. ρ is in arbitrary units. Crosses indicate final parameters.

way as to improve as many of the outstanding discrepancies as possible, and then recalculates all the F's. The process is repeated until the best possible agreement is thought to have been obtained. However, to make all possible combinations of small displacements in a multiparameter structure and show that the agreement is best for the parameters proposed would be an impossible task. The situation seems to call for the use of the method of least squares.[9] The equations connecting the F's with the parameters and scattering factors, being trigonometric, are not suitable for convenient least squares treatment. But with reasonably good trial parameters available approximate equations can be set up in the form

$$\sqrt{w_{hkl}} \sum \left[\frac{\partial F_{hkl}}{\partial x_i}\right]' \Delta x_i =$$
$$\sqrt{w_{hkl}} (F_{hkl} - F'_{hkl}) = \sqrt{w_{hkl}} \Delta F_{hkl}$$

Here the summation is over all the coördinates of all the atoms, the primes indicate that the quantities have been evaluated for the trial parameters x'_i, y'_i, z'_i and F_{hkl} is the observed structure factor. The Δx_i's are the corrections being sought. w_{hkl} is a weighting factor. The entire equation must be multiplied by its square root to allow for the fact that the absolute probable error of F_{hkl} is variable from spectrum to spectrum, depending upon the size of F, background, spot shape and other factors. In general in this work w_{hkl} was taken proportional to $1/F_{hkl}^2$, for F's more than four times the minimum observable F in that region of the film, and proportional to $^1/_{16} F_{min}^2$ for F's smaller than 4 F_{min}. This corresponds to taking the *percentage* probable error in the inten-

(9) For a general discussion of the use of least squares in multiparameter problems see, for instance, Whittaker and Robinson, "Calculus of Observations," Blackie and Son, London, 1929, Chapter IX.

sities as constant for intensities more than sixteen times the background and the *absolute* probable error constant for smaller intensities, an approximation justified chiefly by the simplicity in application.

In this way each spectrum *hkl* within the range of the wave length and camera employed supplies one observational equation for the least squares solution. These equations are of course not rigorous because the Δx_i's are not true infinitesimals. The solutions must be repeated successively until the Δ's obtained are of the order of the probable errors of the parameters.

It is to be observed that in order to start a series of successive approximations the trial parameters must be sufficiently good to fix the signs of the *F*'s and their partial derivatives for a sufficiently large number of spectra and must also give absolute values of *F* for the larger spacings of sufficient average accuracy to establish approximately the absolute scale of the observed *F*'s used. These restrictions are of the same nature, but rather more stringent than those imposed by the Fourier method. The number needed for a successful start depends upon the number of parameters and the probable errors in the observations. An accurate statement cannot be made but experience to date with visually estimated intensities from organic crystals indicates that one must have about two times the number of parameters involved. One can include unobservably small spectra when the calculated *F*'s are too large.

The method suffers certain disadvantages in comparison with the Fourier method. The chief of these are that one must establish an absolute scale and one must employ the scattering factors f_i in calculating both F'_{hkl} and $\partial F'_{hkl}/\partial x_i$. Errors in either scale or scattering factors are bound to influence the results somewhat and the scale should be checked after each refinement. However, the same difficulties occur in the ordinary trial and error method which we are trying to improve. There are also some compensating advantages over the Fourier synthesis. One must include in a Fourier synthesis all the *F*'s observed, even though one knows that some are very uncertain because of extinction, absorption or other causes for which corrections often cannot easily be made. In the least squares treatment these *F*'s may be ignored or given small weights. The omission of data beyond the range of the wave length used, which may produce troublesome diffraction

effects in Fourier syntheses, causes no difficulty in this method. The most important advantage, however, is in the matter of resolving power. In Fourier projections made with data from one zone atoms frequently project so near each other as not to be resolved. This is almost invariably true when the projection axis is of medium or great length. With CuKα data the atoms commonly occurring in organic molecules cannot be resolved at all if they are closer in the projection than about 0.90 Å. With MoKα the limit depends upon the hardness of the crystal and for melamine appears to be about 0.65 Å. The resolving limit of the least squares method is much smaller. It arises in the following way. When two atoms project near each other they of course have nearly the same parameters (except parallel to the projection axis) and the partials of F'_{hkl} with respect to these parameters tend to be approximately proportional in magnitude to the two f_i's and identical in sign. As a consequence of the method of forming the normal equations from the observational equations, the normal equations tend then to become linearly dependent so far as the coefficients of the parameters of these two atoms are concerned. If identical atoms project exactly on top of each other the equations do become related in such a way that independent solutions for the parameters of the two atoms are not possible. One can get only the position of the center of gravity of the two atoms. For atoms which are merely close in the projection independent solutions can always be obtained but the probable errors are large. But this effect becomes serious only for distances which are certainly *less* than one-half the resolving limit of the Fourier projection. For radiation of sufficiently short wave length the resolving limit of a Fourier depends upon the natural fuzziness of the atoms themselves. In this least squares method we attempt to use our theoretical knowledge of this fuzziness, as embodied in the tabulated scattering factors, to separate atoms too close to be resolved by the Fourier method. Of course by making three-dimensional Fouriers with sufficient data, any pair of atoms (excluding hydrogen) can be resolved since the distances are always greater in three dimensions than the resolving limit. But this involves a great deal of labor in collecting the necessary *hkl* data and, unless there is an exact layer structure parallel to some convenient crystal plane, the work of summing the necessary series is

practically prohibitive in a multiparameter problem.

Finally, since a least squares solution is a problem in minimizing a function it may easily be converted by the use of Lagrange's undetermined multipliers into a problem of a constrained minimum. If, for example, it is fairly certain that the molecule is coplanar the problem may be solved in such a way as to give the best possible fit with the data subject to the constraint that the molecule be kept coplanar. For details see Whittaker and Robinson.[9]

The reduction of the observational equations to normal equations can be carried through in reasonable times, say three days or less, by an ordinary electrically powered calculator when the number of parameters is about twelve or less. In the case of the $h0l$ data from melamine with over one hundred observational equations and eighteen parameters such a calculation with adequate checks might well take over a week of extremely tiresome work. The calculations were actually carried through on an International Business Machines Co. Tabulator using the Hollerith punched card system. The application of this machine to least squares problems will be described elsewhere. The cards were punched, verified, and the normal equations produced in slightly less than two days.

The resulting normal equations consisting of eighteen simultaneous equations in the eighteen parameters were solved by an iteration method[9] in about four hours.

Tests of the end accuracy of this method are being made and a fuller account of the details of the method and the results of further tests will be reported elsewhere. So far one check against a structure where a Fourier could be used showed in a twelve-parameter projection an average discrepancy of 0.001 between Fourier and least squares parameters and a maximum discrepancy of 0.0025 for one parameter.[10] The cell was 15.00 Å. by 13.12 Å.

After the first least squares refinement based upon the first molybdenum data Fourier there was a marked improvement in the agreement between observed and calculated F's for sin θ/λ less than about 0.60. Beyond this point, however, the discrepancies remained very bad and from an inspection of the observational equations it became clear that any changes large enough to remove the

discrepancies would undo the fit already obtained for sin $\theta/\lambda < 0.60$. It was then noticed that in general the F's which calculated high were of the type $h0l$ while those which were low were of the type $h0\bar{l}$. There seemed to be a strong anisotropy in the thermal vibrations of the molecule. The larger displacements perpendicular to the plane of the molecule are generally across $h0l$ planes while the smaller ones parallel to the plane of the molecule are generally across $h0\bar{l}$ planes. Accordingly an anisotropic temperature factor was introduced into the calculations. The equation for the scattering factor was modified from that

$$f = f_0 e - (A + B \cos^2 \varphi) \sin^2\theta/\lambda^2$$

derived by Helmholz[11] for silver phosphate. f_0 is the scattering factor of a stationary atom, A and $(A + B)$ are constants for reflecting planes parallel and perpendicular, respectively, to the direction of maximum vibration, and φ is the angle between the normal to the reflecting plane and the direction of maximum vibration. Actually in this zone the "direction of maximum vibration" is the projection on (010) of the normal to the plane of the molecule, which is in all probability the real direction of maximum vibration. The function $A + B$ $\cos^2 \varphi$ changes but slowly in the neighborhood of $\varphi = 0$ and $\varphi = \pi/2$. Planes were selected for which φ differed by no more than 5° from one or the other of these values and A and B were chosen to give the best possible agreement for these few planes. The f_0's were taken from Pauling and Sherman[12] and the f_0's for NH₂ were taken equal to those for N plus the difference between those of O and O⁻⁻. The values found for A and $(A + B)$ are 1.4 and 3.2, respectively. These correspond to a ratio between root mean square vibration amplitudes of about 3 to 2. Recalculation of all the F's using the anisotropic temperature factor eliminated all major discrepancies. A final least squares based on these parameters produced Δ's averaging less than 0.002 with a maximum of 0.004. After the y parameters had been determined some slight changes were made from these values, averaging 0.001 with a maximum of 0.003, for the purpose of improving the planarity of the molecule. The final parameters are recorded in Table IV and are shown by crosses on Fig. 1. The calculated F's based on them are recorded in Table I in comparison with the observed quantities.

(10) The $h0l$ zone of dicyandiamide, ref. 1.

(11) Helmholz, J. Chem. Phys., 4, 316 (1936).

(12) Pauling and Sherman, Z. Krist., 81, 1 (1932).

TABLE IV

	C_I	C_{II}	C_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	N_{VIII}	N_{IX}
x	0.173	0.123	0.063	0.226	0.125	0.009	0.063	0.117	0.179
y	.654	.514	.807	.651	.364	.963	.662	.808	.503
z	.075	.319	.242	.931	.424	.273	.352	.100	.180

The anisotropic temperature vibrations are further supported by the appearance of the Fourier plot. Atom 4 (see Fig. 3 for the numbering systems) which is quite well resolved is seen to be elongated in the direction of maximum vibration. Atoms 8 and 9 are just barely resolved from each other as separate peaks but are very well separated from 1 although the three distances in the projection are about equal. This is because the line joining 8 and 9 is parallel to the direction of large vibration. For the same reason atoms 2 and 3 are well resolved from 5, 6 and 7 although 2 and 3 themselves are just barely resolved, while 5, 6 and 7 are not resolved at all into separate peaks. Similar effects may be seen in the $0kl$ projection (Fig. 2).
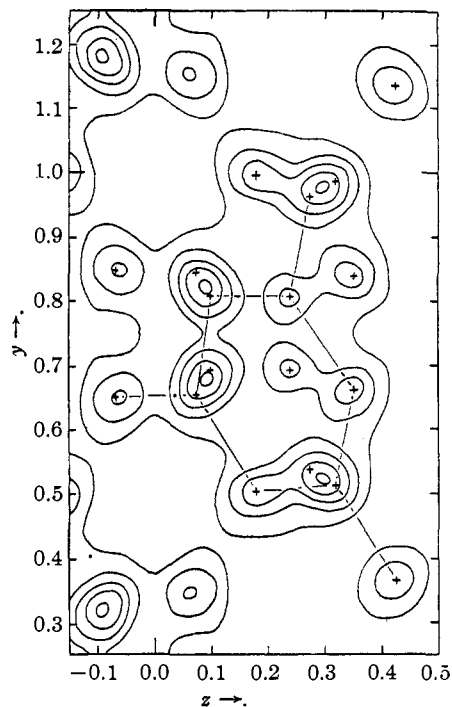
Fig. 2.—$\rho(y,z)$, in arbitrary units. Crosses indicate final parameters.

Trial y coördinates were obtained by taking a model of average expected dimensions, orienting it so that the atoms projected parallel to b fell upon the x, z positions already found, and then varying the y coördinate of the center of the molecule until a position of satisfactory packing was found. In doing this both a center of symmetry and a two-fold screw axis were tried at the origin, and the y parameter of the ring center was restricted to values near multiples of $b/12$, in order to satisfy the intensities of the $0k0$ reflections.
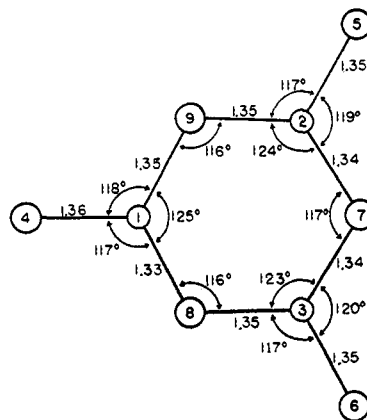

Fig. 3.—The melamine molecule: small circles carbons, large circles nitrogens, hydrogens not shown. The molecule is coplanar. Bond lengths are in Ångström units.

The only reasonable structure resulted when a symmetry center was at the origin and the molecular center at about $y = {}^2/_3$. This trial structure gave very good agreement in general with the $0kl$ and $hk0$ spectra and the signs obtained were used in preparing the a axis Fourier projection. This was summed at intervals of $b/60$ and $c/60$. The plot shown in Fig. 2 is based on signs identical with those obtained from the final parameters. Although five atoms are represented by separate maxima, only one is far enough from all others to give reliable parameters. This is not surprising, considering that we are here projecting through 10.54 Å. This one atom, number 5, confirmed the previously determined z parameter and suggested a considerable change in y. This change was confirmed and others found also by least squares solutions for y's only based on $hk0$ and $0kl$ reflections. The final approximation based on one hundred reflections yielded Δ's which were negligibly small. The final y's are in Table IV and are shown by crosses on Fig. 2. The calculated F's for the $hk0$ and $0kl$ zone are shown in Tables II and III. For the $hk0$ reflections the anisotropic temperature factor is of no great im-

<div style="text-align:center">

TABLE V

INTERATOMIC DISTANCES

</div>

Chemical Bonds		Hydrogen Bonds		van der Waals contacts N—N	
1–4	1.36 Å.	A5—C7, A7—C5	3.00 Å.	A4—F6	3.20 Å.
1–8	1.33	A9—D4, A4—D'9	3.02	A6—A'5	3.26
1–9	1.35	A8—B'6, A6—B'8	3.05	A9—F'6	3.30
2–5	1.35	A8—D'4, A4—D8	3.10	A6—C'6	3.42
2–7	1.34			A5—E8	3.53
2–9	1.35			A4—B5	3.63
3–6	1.35			A9—B9	3.69
3–7	1.34			A8—B'8	3.70
3–8	1.35				

portance since only CuKα data are involved. For both zones the anisotropy is not great since the normal to the plane of the molecule is inclined at a fairly large angle to the plane of either projection. The normals for the molecules are not all parallel to each other in these projections and in an exact calculation one should compute the contribution of each molecule separately with its own temperature factor. This tedious method was not used. For each zone the two directions parallel and perpendicular to (010) were taken as the average principal directions of anisotropy for all molecules and values of A and B were calculated from those used in the $h0l$ zone and the known angles between the different directions. Some small errors at high orders may exist in the $0kl$ calculations because of this approximation but the agreement is quite satisfactory. Although both observed and calculated F's of all the tables are rounded to the nearest integer, they were carried to one decimal place in the least squares calculations. The most serious intensity discrepancy is for 005, calculated 12, observed 16. Changes sufficient to correct this would cause several equally bad discrepancies elsewhere. It seems likely that this low value is due to the approximate way in which the hydrogens are taken into account in the scattering factors.

Discussion

The molecule thus arrived at is shown in Fig. 3. The interatomic distances are shown there as well as in Table V. The bond angles are recorded only on the figure. The displacements of the atoms from the average plane of the molecule are all within the limits of the probable error, which is estimated to be about ±0.015 Å. for the position of an atom and about ±0.02 Å. for the length of a bond. It is thus not very likely that any bond length is in error by more than 0.05 Å. Three atoms, 4, 7 and 9, were displaced from the least

squares positions by about 0.02 Å. each to achieve the close planarity of the molecule. The deviations before shifting were well within the limit of error for the position of an atom. The bond lengths shown correspond to almost complete resonance of the three double bonds about the three carbon atoms, the three principal structures being, if we overlook for the present the hydrogens
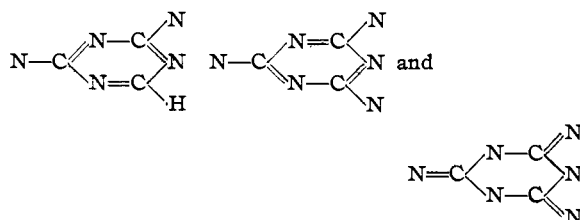
If each structure contributes equally the calculated[13] bond lengths, neglecting formal charge effects, come to about 1.343 Å. The average of the nine bonds, 1.346 Å., is almost exactly this. The three extra-ring bonds average 1.353 Å., slightly, but not significantly, higher. These lengths agree well within experimental errors with the corresponding lengths about the guanidine carbon atom in dicyandiamide[1] where the distances are 1.34, 1.36 and 1.37 Å., average 1.356 Å. In the tricyanmelamine ion[14] Hoard used the value 1.36 Å. for the bond lengths in the cyanuric ring and obtained reasonable agreement between calculated and observed intensities. But he made no serious effort to refine parameters. His assumed distance 1.40 Å. for C–N from ring to cyanimino group seems high. In cyanuric acid[15] likewise the parameters have not been carefully fixed and the cyanuric ring dimensions, although in satisfactory agreement with those presented here, so far as distances are concerned, are in

(13) Pauling. "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca. N. Y., 1940. p. 171.

(14) Hoard, THIS JOURNAL. 60, 1194 (1938).

(15) Wiebenga and Moermann. Z. Krist., 99, 217 (1938).

rather poorer agreement so far as angles are concerned. In cyanuric triazide[16] Miss Knaggs' structure suggests that the asymmetry of the attached azide groups has in some way stabilized one Kekulé form of the ring somewhat with respect to the other so that it contributes more to the resonance. There are alternate long and short bonds about the ring of 1.38 Å. and 1.31 Å. length, respectively. The average of these, 1.345 Å., is very close to the present value and the bond angles about the ring are likewise distorted from 120° in the same directions as in melamine.
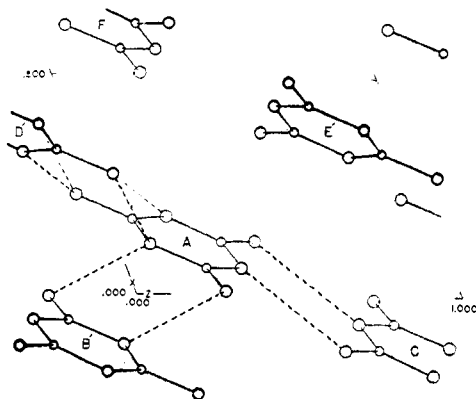
Fig. 4.—A portion of the structure projected normally onto (010). Dotted lines indicate hydrogen bonds for molecule A. Bonds ending in arrows are directed at an atom one y repeat below the atom indicated.

The discrepancy between the alternate bonds in the ring in the triazide is a surprisingly large effect to be produced by merely attaching three asymmetric groups and one might well inquire into its reality. The crystal is almost ideal for the Fourier method and the intensities have been measured quantitatively on an absolute scale. The most likely source of error lies in the possibility of lack of convergence of the series. Although reflections from some half dozen forms which may be seen on heavily exposed CuKα photographs have not been included, the most important place to expect missing spectra is beyond the range of CuKα, because one very important reflection is known to occur just at the CuKα limit. MoKα photographs of this substance have recently been prepared here and although there are some spectra to be found beyond the Cu limit it does not seem likely that all the spectra omitted from Miss Knaggs' synthesis can greatly change the results.

(16) Hughes, *J. Chem. Phys.*, **3**, 1 (1935); Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935).

The orientation of the plane of the melamine molecule can be specified by the angles made by the normal to the plane with a, 47.2°, b, 73.6°, and c', 47.4° (c' is normal to a and b). The projection of the first angle on (010) is 44.9° and is in satisfactory agreement with the position of the acute bisectrix, which is at 47 ± 2°. The second angle does not check very well with the tip calculated from Heydrich's refractive indices. The latter lead to 62°, which is over 11° low. It is possible that Heydrich has made some error not only in the position but also the dimensions of the indicatrix. The interaction of neighboring molecules could hardly produce such a deviation in indicated position. One of the three two-fold axes of the molecule makes an angle of 1.2° with (010).

The perpendicular distance from the origin to the plane of the molecule specified by the parameters of Table IV is 2.81 Å. This molecule is marked A in Fig. 4, which is a normal projection of part of the structure on (010). Surrounding molecules are indicated by other letters. Unprimed letters indicate molecules which lie over half in the y parameter range 0 to 1. Primes indicate molecules one b translation above unprimed molecules. Figure 5 is an oblique projection of one unit cell and nearby molecules. The horizontal axis is c, the oblique axis is b while the vertical direction makes an angle $\beta - 90°$ with a.
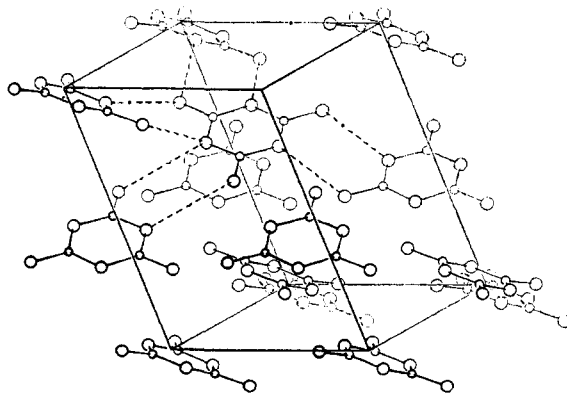

Fig. 5.—An oblique projection of one unit cell and neighboring molecules. a' is the vertical, c the horizontal and b the oblique axis. Dotted lines indicate hydrogen bonds for one molecule. One molecule in the near upper right corner of the cell has been omitted.

The smaller distances between atoms on different molecules are recorded in Table V. In this table the letters indicate molecules as in Figs. 4 and 6 while the numbers are as in Figs. 3 and 4. Of these distances all but four pairs are satisfac-

tory van der Waals distances, or larger. These four short pairs of lengths, 3.00, 3.02, 3.05 and 3.10 Å., are taken to be hydrogen bridges and are indicated in Figs. 4, 5 and 6 by dotted lines. Figure 6 shows more clearly the disposition of these short distances about one molecule. It is an oblique projection in which the normal to the plane of molecule A is the oblique axis. Molecules B' and C, being related to A by symmetry centers, are parallel to A, but in different levels. Molecules D and D', on the other hand, are related to A by a two-fold screw axis and their planes are inclined at about 33° to the plane of A and hence to the principal plane of the drawing. The lettering and numbering on this drawing conform to the earlier figures and to Table V.

The lengths of these hydrogen bonds are comparable with those found elsewhere between nitrogen atoms, 2.94 and 2.99 Å. in ammonium azide,[17] 2.94, 3.02, 3.04, 3.15 and 3.16 Å. in dicyandiamide.[1]

Unfortunately the number and disposition of these hydrogen bridges do not determine uniquely the positions of the hydrogens. It is presumed that a hydrogen attached to a ring nitrogen would lie in the plane of the molecule and the N–H bond would coincide with the extension of the ring diagonal passing through the nitrogen in question. It is also expected that hydrogens attached to extra-ring nitrogens would also lie in the plane of the molecule and the N–H bonds would make angles of about 120° with the extra-ring C–N bonds. These nine possible N–H bond directions are indicated for molecule A by lines on Fig. 6 and the angles between these directions and the hydrogen bridge directions are recorded there. Some of the positions are mutually exclusive. For instance a hydrogen may be on A5 directed at C7, or on A7 directed at C5 but both positions may not be occupied simultaneously since there would then be by symmetry operations two hydrogens directed at each other and only separated by about 1 Å., which is less than half the required separation. If there is a hydrogen on A8 it must be forming a bifurcated bridge[18] to B'6 and D'4 and it excludes hydrogens from each of these positions. Likewise A4 to D'9 and A9 to D4 are mutually exclusive. Upon trying all possibilities we find that the iso-melamine structure is impossible

(17) Hughes. Thesis, Cornell University. 1935; Frevel, Z. Krist.. 94, 197 (1936).

(18) Albrecht and Corey. THIS JOURNAL. 61, 1087 (1939); ref. 1, p. 1265; ref. 13, footnote, p. 286.
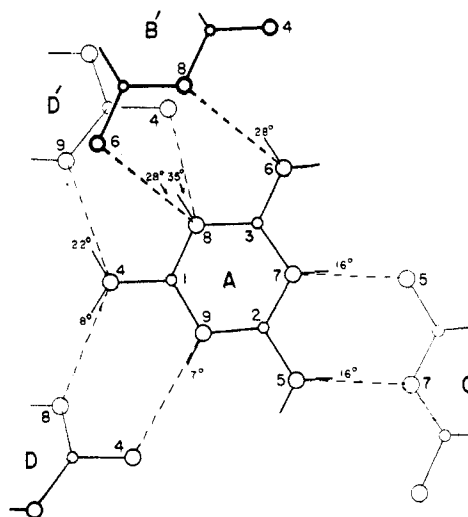

Fig. 6.—An oblique projection of a portion of structure about molecule A. The normal to the plane of molecule A is the oblique axis. Molecules A, B' and C are parallel to the plane of the projection, and molecules D and D' are inclined 33° to it.

since three hydrogens on the ring leave open, by the above arguments, only places for two of the three remaining hydrogens. The ordinary melamine or cyanuric triamide formula is satisfactory on this basis but so too are three other arrangements which involve a combination of amide and imide groups. Two of these, which have one imide and two amide groups, are identical chemically except for the orientation of the hydrogen on the imide group, while the third shows two imide groups and one amide group. The existence of any of these unsymmetrical forms seems intuitively somewhat doubtful and it will hereinafter be presumed that the triamide structure is the correct one. The chief resonating forms are
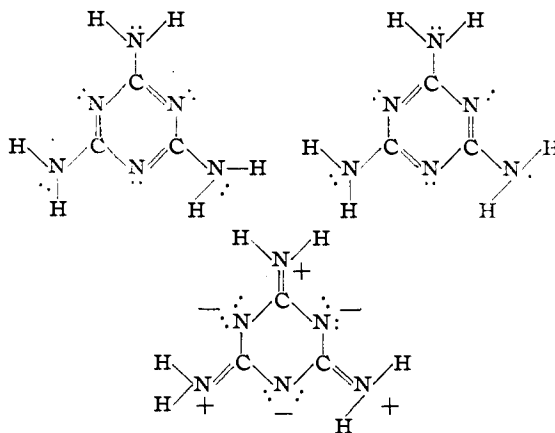
Many less symmetrical structures may also make contributions, one set being
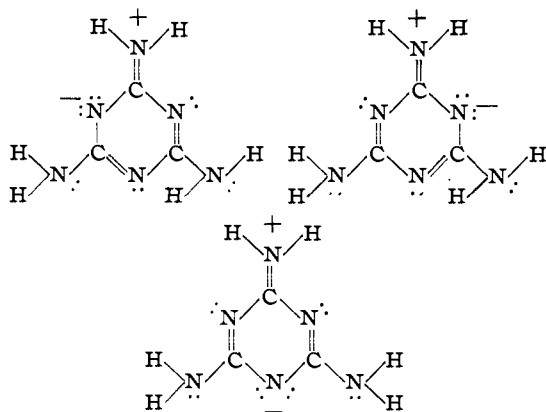
and others in which the double bond is to other amino groups. These numerous structures are of equal energy as long as the hydrogens are symmetrically disposed and would then contribute considerably to the resonance stabilization. It is for this reason that the structures unsymmetrical as to hydrogens seem unlikely. Inspection of "Beilstein" shows that although either eso or exo trisubstituted melamines are of frequent occurrence, there is no example of a mixed eso-exo trisubstituted melamine except where the substituents are aromatic groups. Because of the marked ability of aromatic radicals to conjugate with nitrogen, with resultant additional stabilization, they are hardly comparable with hydrogen. The apparent non-existence of aliphatic unsymmetrically trisubstituted melamines supports the view that the above auxiliary structures are of importance and that the hydrogens are symmetrically distributed in melamine.

The two hydrogen bonds converging upon atom 8 are longer than the remaining two, 3.10 and 3.05 Å. compared with 3.02 and 3.00 Å. This is to be explained by the fact that resonance between the resonating structures postulated will place on 8 an average of one and one-third unshared electron pairs to serve for the two bonds, or only two-thirds of a pair per bond. At both 7 and 9 the full electron density is available for only one bond.

The chemical behavior of melamine depends markedly upon the environment. In liquid ammonia solution it behaves as an acid, reacting with alkali metals or alkali amides to form salts.[19] But in water they are at once hydrolyzed to melamine and the alkali hydroxide and with aqueous acids melamine is a very weak base. In most of its well-known salts with acids it is monovalent, as in $C_3N_3(NH_2)_2NH_3Cl \cdot 1/2H_2O$, but some divalent

compounds have been reported, such as $C_3N_3NH_2$-$(NH_3)_2PtCl_6$. No trivalent salts have been obtained from water solutions but Barnett[20] has shown that the crystals slowly take up dry hydrogen chloride to form first the monohydrochloride and then the di- and finally the trihydrochloride. Barnett also states that a dihydrochloride may be crystallized from concentrated hydrochloric acid solutions but gives no preparational or analytical data.

The addition of a proton to an amide group to form a cation would completely exclude that group from conjugation with the ring and there would be a consequent reduction in resonance stabilization. Thus in liquid ammonia where the proton affinities of the solvent and solute are about equal this resonance effect completely dominates the situation and melamine takes no protons from ammonia. But neither does it give up appreciable numbers, for the electrical conductivity is so very small that it may be due entirely to impurities.[21] The alkali melamine salts which may be formed in liquid ammonia solution are obtainable only because of their insolubilities and the small dissociation of the solvent. In water these salts are at once completely hydrolyzed.

The proton affinity of an amino group in water is greater than that of a hydroxyl group, as is evidenced by the fact that primary amines remove protons extensively from water to form substituted ammonium hydroxides. These are weak bases, supposedly because the hydroxyl ions are bound to the cations by hydrogen bonds. In water solution melamine behaves similarly but the resonance effect counteracts the proton affinity of the amino groups to a great extent. The amount of melamine hydroxide formed is relatively much less and consequently there is even a smaller ratio of dissociated base to total solute than for amines. The addition of a second or third proton to form the di- or trivalent base will be even more difficult and it is not surprising that salts of these bases can be so rarely crystallized from solution.

In the reaction with dry hydrogen chloride gas to form an ionic crystal the proton affinity of amines seems much greater than that of a chloride ion and very stable salts are formed. For melamine the resonance effect seems unable to overcome this affinity and the three hydrochlo-

(19) Franklin. THIS JOURNAL. 44. 505 (1922).

(20) Barnett. J. Phys. Chem., 34, 1497 (1930).

(21) Smith. THIS JOURNAL, 49. 2162 (1927).

TABLE VI

|	$C_3N_3(NH_2)_3$	$C_3N_3(NH_2)_2Cl$	$C_3N_3Cl_3$	$C_3N_3O_3H_3$	
				Norm.	Iso.
$\Delta H_{obsd.}$, kcal.	1213	1059	722	1126	
$\Delta H_{calcd.}$, kcal.	1076	926	627	968	999
Difference, kcal.	137	133	95	158	127
$\Delta H_{sub.}$	32	35	24	32	
Empirical res. energy	105	98	71	126	95
Calcd. res. energy	5.83 β	5.26 β	4.13 β	5.15 β	5.15 β
β, kcal.	18.0	18.6	17.2	24.5	18.4

β is the C-N exchange integral.

rides formed are quite stable, with vapor pressures of 2 to 3 mm. at room temperature. But they are not stable with respect to water. A sample of the monohydrochloride has been found to be quite hygroscopic, probably forming the hemihydrate, and water solutions of the latter are acid to litmus.

Barnett proposed[20] a structural formula which he thought might account for what he regarded as an abnormal slowness in the formation of the hydrochlorides from hydrogen chloride gas.
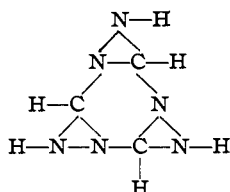
This arrangement not only is, as he says, repugnant to organic chemists, but is quite incompatible with the X-ray results.

The heats of formation of a number of cyanuric derivatives are recorded in the "International Critical Tables" and in "Beilstein." The molal heats of formation of these substances from gas atoms as derived from these data are recorded in the first row of numbers in Table VI. The corresponding theoretical values for gaseous molecules, calculated from the bond energy values of Pauling,[22] are shown in the second row. The differences between these, in the third row, are to be attributed chiefly to resonance stabilization, but partly to heats of sublimation. The latter can be estimated roughly. Data in the "Critical Tables" indicate a heat of sublimation of about 8 kcal./mole for CNCl and we take three times this value for $C_3N_3Cl_3$. The corresponding values for melamine and cyanuric acid will be less so far as van der Waals energies are concerned and are estimated at 20 kcal. But there will be in addition for these substances the energy of breaking hydro-

gen bonds. The NH — N bonds of melamine will be greater than the 1.3 kcal. observed in solid ammonia and the NH — O bonds of cyanuric acid somewhat larger, but probably less than 5 kcal. At 3 and 4 kcal., respectively, the values shown in row four of the table were obtained for the heats of sublimation. The empirical resonance energies finally obtained in row five are certainly not very accurate but ought not to be off by more than ±10 kcal. For $C_3N_3(NH_2)Cl$ the crystal structure is not known and the number of hydrogen bonds has been arbitrarily taken equal to the number of hydrogens.

Pauling and Sturdivant[23] have calculated by the method of molecular orbitals the resonance energies of some cyanuric derivatives. These are shown in row six of Table VI in terms of β, the resonance integral of one electron between two adjacent C and N atoms. The value for $C_3N_3Cl_3$ is their value for the C_3N_3 nucleus, it being assumed here that the conjugation of Cl with the ring is negligible. The value for $C_3N_3(NH_2)_2Cl$ is obtained by subtracting from their value for melamine the average conjugation energy of one amino group, which they give. Division of the values of row five by those in row six gives the empirical values for β shown in row seven. Leaving out the value calculated from the normal form of cyanuric acid we obtain an average of about 18 kcal. for β. The corresponding value for benzene derivatives where β represents C–C interaction is 20 kcal.

The above calculations have been carried through separately for the normal and the isoform of cyanuric acid. In the first place we note that the iso form has a calculated heat of formation some 31 kcal. greater than the normal form and this fact alone indicates that the acid should exist as the iso form. This supposition is further supported by the values obtained for β. That obtained assuming the iso form is in good agreement with the other calculations, while that ob-

(22) Ref. 13, pages 53 and 131.

(23) Pauling and Sturdivant, Proc. Nat. Acad. Sci., 23, 615 (1937).

tained from the regular form seems impossibly large. An error of about 33 kcal. in the empirical resonance energy would be required to account for the discrepancy. The calculated resonance energies of the two forms are identical to within the approximations made in applying the molecular orbital method. A difference would arise only if one allows for the effect upon the electronegativity of N and O of changing the positions of the hydrogens. The empirical resonance energies of the iso and normal forms of melamine itself are identical as the same number of each kind of bond occurs in each.

The crystal structure of cyanuric acid[15] further supports the iso formula for this substance. The two hydrogen bridges between O and N atoms which bind the crystal together in the [101] direction make angles of about 120° with both the N–C and the O–C bonds and are otherwise arranged so that the hydrogens might be either on O or N without contravening any accepted stereochemical principles. But the third bridge linking molecules along the [010] direction makes an angle of about 120° with the C–N bonds but 180° with the C–O bond. If the H were on the O atom it would point away from the N atom to which it is supposed to be attracted by an angle of at least 60° and probably more. If on the N atom on the other hand it will be directed exactly at the O atom to which it is bridged.

Although this argument fixes only one of the three hydrogens definitely on the ring it seems unlikely that the others could be different for the same reasons already cited for melamine. Although both tri-N esters and tri-O esters of cyanuric acid are well known, there is no established example of a mixed N and O tri-ester despite efforts to prepare them (see Sidgwick's "Organic Chemistry of Nitrogen," Oxford, 1937, p. 344). Even aromatic esters do not occur in mixed positions as they do for melamine. This no doubt is due to the smaller conjugating power of oxygen in an ester as compared with nitrogen in a similar situation. O esters on heating tend to change into N esters.

Melamine Monohydrochloride Hemihydrate

This substance, referred to above, is easily obtained by adding an equivalent amount of concentrated hydrochloric acid to a melamine solution saturated at about 40°. On cooling slowly fine needles are obtained. The faces are so small that

only poor signals result on the goniometer. Eight faces occur in the prism zone and these appear within experimental error to be {100}, {010} and {110} forms of the orthorhombic system. Laue photographs normal to (100) and (010) and oscillation photographs with CuKα radiation about a and c show symmetry mmm, confirming the orthorhombic assignment. The unit cell has the dimensions a = 16.75 Å., b = 12.29 Å., c = 6.93 Å. (±0.5% CuKα, λ = 1.539). The length of b was not confirmed by an oscillation photograph but a complete set about c was satisfactorily indexed using the length given. With eight molecules per cell the calculated density is 1.587 g./cm., which is reasonable. The extinctions, hkl, h + k odd and h0l, l odd, indicate space groups Cmcm or Cmc (or C2cm). A pyroelectric experiment with liquid air gave negative results but the crystals are so small that great weight cannot be given this result. There is no obvious relationship to the melamine structure and the investigation has not been carried further.

The Work of Knaggs and Lonsdale

In a note in a recent number of the *Proceedings of the Royal Society* which arrived in Pasadena after this investigation had been completed and most of this paper written, Knaggs and Lonsdale[24] have given a preliminary report on the crystal structure of melamine, accompanied by a note on the optical properties, by Wood and Williams. Their unit cell, a = 10.54 Å., b = 7.48 Å., and c = 7.28 Å., β = 112°16′ (Heydrich) is in good agreement with that given here. They have not given any parameters but illustrate the structure which they suppose to be approximately correct by drawings of projections on (010) and (201). Although their projection on (010) is qualitatively in agreement with the structure described above, their structure as a whole is quite different since the positions of the centers of the four molecule, as shown in their projection on (201), are two at y = 0 and two at y = 1/2 (the origin being in a center of symmetry), whereas in the present structure the molecules are at approximately y = 1/6, 2/6, 4/6 and 5/6. Neighboring molecules related by a center of symmetry are displaced relative to one another by one-third of a cell length and the packing and disposition of hydrogen bonds between these molecules would be entirely different in the two structures. Using the

(24) Knaggs and Lonsdale, *Proc. Roy. Soc.* (London), A177, 140 (1940).

x parameters of Table IV and y parameters taken to coincide with their illustration, the structure factors shown in Table VII were calculated for the larger spacings of the $hk0$ zone. The disagree-

TABLE VII

TEST OF THE STRUCTURE PROPOSED BY KNAGGS AND
LONSDALE

$hk0$	$F_{obsd.}$	$F_{calcd.}$
110	16	59
210	47	19
020	5	1
120	14	3
310	68	45
220	< 1	32
320	31	23
130	12	9
410	11	30
230	10	8
420	9	18
330	16	18
510	4	0

ment between these and the observed values is so great that there can be no doubt that their structure is not even approximately correct, except of course as to x and z parameters.

The magnetic and optical data which they give are in excellent agreement with the structure arrived at in this investigation. From the magnetic anisotropies, assuming the melamine molecule to be uniaxial, they obtain for the three angles which the molecule plane normal makes with a, b and c', the values 48.8°, 74.0° and 45.5°, respectively. The values from the structure are 47.2°, 73.6° and 47.4°. The position of the acute bisectrix from the optical experiments is at 45°45′ ± 1° from a in obtuse β. The value reported above is 47 ± 2° and the value from the structure is 44.9°. Wood and Williams also remeasured the refractive indices for sodium light and found a value for β appreciably different from that of Heydrich, a possibility suggested above. Using the new index one calculates for the angle of tip from b the value 76.3°, which differs greatly from the 62° calculated from Heydrich's result, and differs slightly in the opposite direction from the value 73.6° derived from the structure. All the deviations of the angles calculated using optical data from those derived from the structure are in the direction to be expected for the errors introduced by neglecting, in the calculations, the interactions with neighboring molecules. The discrepancies are generally less for the magnetic calculations since these are less subject to such interactions.

The magnetic measurements show that melamine has a molecular anisotropy practically equal to that of cyanuric triazide and these authors argue therefore that melamine cannot have the iso formula. This result agrees with that proposed here. The argument is open to some objection, however, since it neglects the effect of resonance. The anisotropy arises from the two Kekulé-like structures chiefly and these will contribute almost as much to the isomelamine structure as to the normal one. While on the other hand for cyanuric triazide the supposed partial stabilization of one Kekulé structure ought to reduce the anisotropy to a certain extent. It would be difficult to say in advance how different the three anisotropies ought to be. The anisotropies of the eso- and exo-trimethyl melamines would be of interest in this connection.

In conclusion I must thank Professor Pauling for continued encouragement and advice.

Summary

The crystal structure of melamine has been investigated. The monoclinic unit has $a = 10.54$ Å., $b = 7.45$ Å., $c = 7.25$ Å., $\beta = 112°2′$. The space group is $P2_1/a$ and there are four molecules per cell.

A new method for refining parameters, based upon least squares, has been described and was used in conjunction with Fourier syntheses to locate the atoms. The positions of the atoms correspond to a molecule which is a resonance hybrid, chiefly between structures
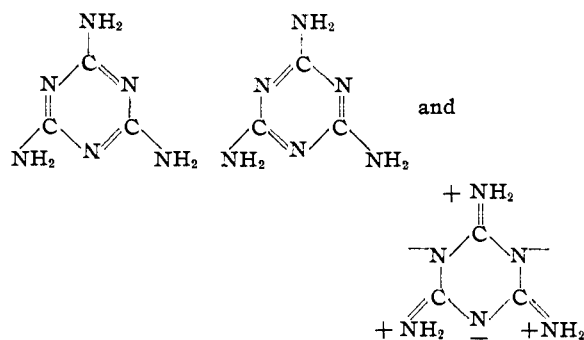
although other positions for the hydrogens may be possible. The packing of the molecules is dominated by hydrogen bonds. The properties of the compound have been discussed briefly in relation to the structure and the empirical resonance energies of melamine and other cyanuric derivatives have been calculated from data in the literature and

compared with quantum mechanical calculations. Melamine monohydrochloride hemihydrate has been briefly examined and found to be orthorhom-

bic, $a = 16.75$ Å., $b = 12.29$ Å., $c = 6.93$ Å., space group, $Cmcm$, Cmc or $C2cm$.

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Vapor Pressures of Binary Liquid Mixtures*

BY J. R. LACHER AND ROY E. HUNT

A measurement of the total and partial pressures of a binary liquid mixture leads to information concerning the chemical potentials of the liquid phase components provided certain thermodynamic properties of the gaseous phase are known. A knowledge of these chemical potentials is important for the development of theories concerning the structure of liquids and liquid mixtures. In the present paper are reported measurements on mixtures of chlorobenzene–ethylene bromide and 1-nitropropane–ethylene bromide.
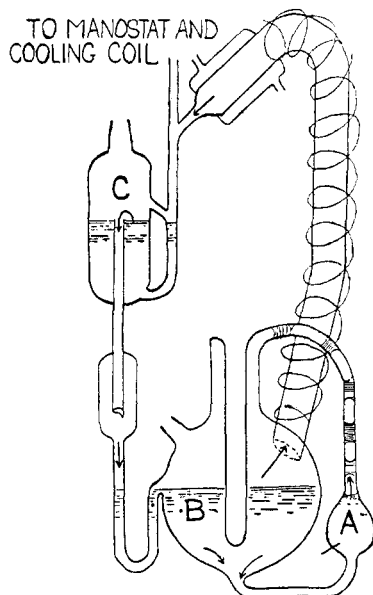

Fig. 1.

Experimental Details.—The apparatus, which is quite similar to that used by Sameshima,[1] is shown diagrammatically in Fig. 1. Instead of boiling the liquid in B by means of an electrically heated wire, a small pump A, of dimensions recommended by Swietoslawski[2] was used to force liquid and vapor over a thermometer well in B. This well was made quite long in order to permit the detection of any temperature gradients in B. A and B were

heated electrically. The vapors in B passed up a heated tube of large diameter, condensed, and returned to the reservoir via a hold-up trap C. The drop counter below C indicated the speed of circulation of the vapor. The heated parts of the apparatus were insulated with asbestos and shielded with aluminum foil. C and B are fitted with mercury sealed ground glass caps and liquid samples were removed for analysis in ice-jacketed pipets.

A cooling coil connected the still to a manostat and pump. Most of the condensation occurred in the water cooled condenser, but the cooling coil was necessary to prevent a slow diffusion of vapor out of the still. The manostat had a 45 l. capacity and was thermally insulated. Dry air was used as the confining gas. Pressures were read with a mercury manometer using a calibrated paper scale. The individual pressure readings could be made to 0.2–0.3 mm. However, all the pressures reported in this paper represent the average of a large number of individual readings. The pressure in the apparatus did not drift provided the cooling coil was maintained at a sufficiently low temperature and that the temperature of the manostat did not change. A tenth degree mercury thermometer read with a good telescope permitted temperature measurements accurate to a few hundredths of a degree.

Experiments performed on pure liquids and mixtures of ethylene bromide–chlorobenzene and ethylene bromide–1-nitropropane (whose components have almost identical vapor pressures) showed that the boiling temperatures were independent of a three-fold variation in electrical energy supplied to pump A. There was a long region of constant temperature in the upper part of the thermometer well. The temperature at the bottom depended on the heating current supplied to B. For most runs this current was adjusted so that all temperature gradients along the well vanished. However, their presence has no effect on the final experimental data which, for the above mixtures, satisfy the Margules equation.

When mixtures of ethylene chloride–sym-tetrachloroethane were boiled in the still, the temperature of boiling increased with increasing pump speed and reliable measurements could not be made. The vapor pressures of the pure components differ by almost a factor of ten in this case. Ethylene bromide–sym-tetrachloroethane and chlorobenzene–sym-tetrachloroethane mixtures are made of components whose vapor pressures differ by a factor of two; their boiling temperatures were independent of the pumping speed. However, a comparison of the data with the requirements of the Margules equation showed that the mole fraction of the more volatile component in the vapor

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* Original manuscript received December 6, 1939.

(1) J. Sameshima, THIS JOURNAL, **40**, 734 (1918).

(2) "Ebulliometry," W. Swietoslawski, Jagellonian University Press, 1936.