[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE MOLECULAR SYMMETRY OF ACETONYL PYRROLE

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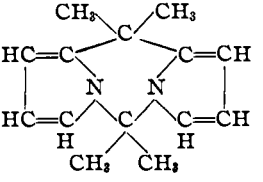
The x-ray diffraction patterns obtained from complicated organic compounds have been interpreted in several different ways. The determination of the smallest unit of structure by the use of Laue and spectrum photographs is the only one of these methods not involving questionable assumptions. As a rule a complete structure determination cannot be made but, in most cases, the minimum symmetry of the molecule can be determined. The fixing of this minimum symmetry is of great value in the study of the geometrical configurations of organic compounds.

Acetonyl pyrrole is a condensation product of acetone and pyrrole.[1] C. Liebermann and R. Kraus assigned it the following formula



Condensation supposedly takes place between two moles of acetone and two of pyrrole with the elimination of water, the hydrogen atoms being removed from the N and the α-C atoms. It has been described[2] as crystallizing in the tetragonal system with $a:c = 1:0.8343$.

The material used in this investigation was prepared by heating 10 g. of pyrrole (Eastman) with 15 g. of acetone in 300 cc. of 90% ethyl alcohol containing 4 cc. of concentrated hydrochloric acid.[1] The crystalline material was separated and recrystallized several times from acetone. Crystals several millimeters in length were obtained by crystallization from acetone solutions containing small amounts of benzene. The developed crystals were elongated octahedra showing evident pyramidal character.

Laue photographs were made with the incident x-ray beam normal to (100) and making small angles with this normal. Data obtained from one of these photographs are listed in Table I. Spectrum photographs were made on which (100) and (001) reflected as the principal spectrum. These faces were initially parallel to the x-ray beam and were oscillated through an angle of 20° with first the c- and then the b-axis in the axis of rotation in the former case and the b-axis in the latter case. It was very difficult to obtain accurate spacing measurements for d_{100} since

[1] (a) Baeyer, *Ber.*, **19**, 2184 (1886); (b) Dennstedt and Zimmerman, *ibid.*, **20**, 2450 (1887); (c) C. Liebermann and R. Kraus, *ibid.*, **40**, 2504 (1907).

[2] Fock, *Z. Krist*, **14**, 541 (1888).

TABLE I

TYPICAL LAUE PHOTOGRAPHIC DATA FROM ACETONYL PYRROLE

The incident x-ray beam was approximately normal to (100)

Plane	d_{hkl}, Å.	$n\lambda$	Intensity	Plane	d_{hkl}, Å.	$n\lambda$	Intensity
$1\bar{6}0$[a]	1.659	0.48	v.w.	1.4.13	1.465	0.45	v.w.
$1\bar{6}2$	1.643	.46	v.w.	$2\bar{9}0$	1.094	.42	v.w.
162	1.643	.38	w.	$2\bar{9}4$	1.076	.41	v.w.
$1.\bar{1}.15$	1.548	.46	v.w.	1.3.15[b]	1.431	.43	v.w.
166	1.530	.35	w.	$1.3.\overline{14}$	1.499	.47	v.w.
1.3.14	1.499	.45	v.w.	1.4.14	1.395	.45	v.w.

[a] The indices used in this publication are referred to the space group axes.

[b] Data from a second photograph.

it was impossible to determine whether or not reflections from (100) were present. The data listed for (100) in Table II were obtained by

TABLE II

TYPICAL SPECTRUM PHOTOGRAPHIC DATA FROM ACETONYL PYRROLE, MO K RADIATION

Plane	Line	Order	d_{hkl}, Å.	Intensity[a]
001	MoKβ	4	...	s.
	α_1	4	24.30	v.s.
	α_1	8	...	abs.
	α_1	12	23.72	m.
	α_1	16	...	v.w.
100	α_1	2	10.48	
	α_1	3	10.10	
	α_1	4	10.12	
	α_1	5	10.19	

[a] The following abbreviations are used throughout this paper: v.s., very strong; s., strong; m.s., medium strong; m., medium; m.w., medium weak; w., weak; v.w., very weak.

measurements to the mid-point of the zone for which h is a constant. In these photographs (100) reflected as the principal spectrum and the crystal, with its b-axis in the axis of rotation, was oscillated through an angle of 20°. Spacing measurements were made on reflections from (001), sodium chloride being used as a reference substance (transmission). The spacing d_{001}/n obtained from these measurements is 5.975 Å. in agreement with the value 5.950 Å. calculated from d_{100}/n = 10.09 Å. and the observed axial ratio. The smallest unit of structure compatible with the Laue and spectrum data has $a_0 = b_0 = 10.09$ Å., $c_0 = 23.85$ Å. The density calculated on the basis of this unit containing 8 $C_{14}H_{18}N_2$ is 1.132 in agreement with the density 1.162 determined by the Retgers suspension method.

The observation that a Laue photograph made with the incident x-ray beam normal to (100) shows only a horizontal plane of symmetry requires the structure to be isomorphous with one of the point groups $4c$, $4C$ or $4Ci$. Reflections were obtained in the first order from planes having

$(h + k + l)$ both odd and even. The underlying lattice is therefore the simple tetragonal one.

The most characteristic feature of the spectrum photographs was the presence of reflections from (001) in only the 4th, 8th, etc., orders (Fig. 1). The only space groups based upon a simple tetragonal lattice and having the symmetry of one of the point groups $4c$, $4C$ or $4Ci$ explaining this

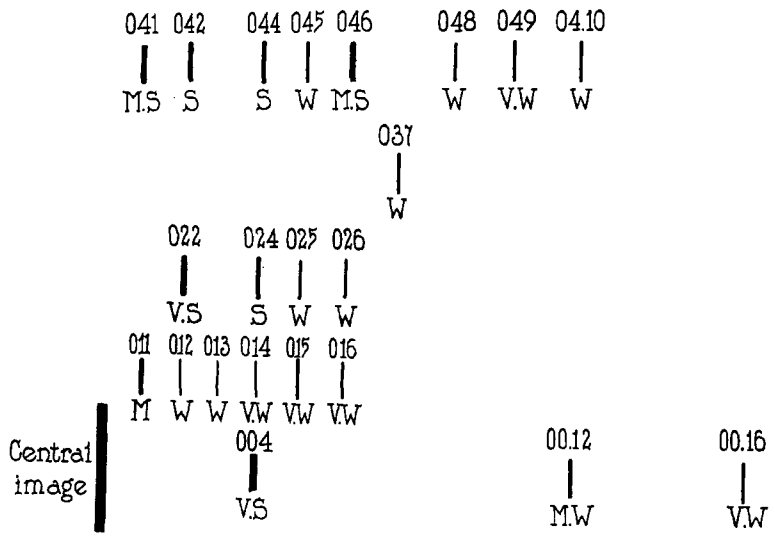


Fig. 1.—A reproduction of a spectrum photograph showing reflection from (001) in the equatorial zone. The b-axis of the crystal was vertical. Only the Mo Kα lines are shown; 20° oscillation.

observation are $4C$-2 and $4C$-4. The possible molecular centers in these two cases[3] are

$4C$-2 (a) $xyz;\ \bar{y},x,z+\frac{1}{4};\ \bar{x},\bar{y},z+\frac{1}{2};\ y,\bar{x},z+\frac{3}{4}$
$4C$-4 (a) $xyz;\ \bar{y},x,z+\frac{3}{4};\ \bar{x},\bar{y},z+\frac{1}{2};\ y,\bar{x},z+\frac{1}{4}$

In either case there can be only four equivalent molecules in the unit of structure. It is thus possible that if $C_{14}H_{18}N_2$ is the structural molecule there are two sets of such molecules. It is more probable, however, that the real structural molecule is $C_{28}H_{36}N_4$ corresponding to a condensation product of four moles of pyrrole with four of acetone.

An investigation of the literature showed that the original formula had been assigned without a molecular weight determination being made. For this reason it was necessary to make such a determination. The previously described differential vapor pressure method[4] was used, benzene

[3] R. W. G. Wyckoff, "An Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, No. 318, Washington, **1922**, p. 80.

[4] Menzies, THIS JOURNAL, **43**, 2309–2314 (1921); Menzies and Wright, *ibid.*, **43**, 2314–2323 (1921).

being used as the solvent; 0.656 g. of acetonyl pyrrole in 100 cc. of the solvent at the boiling point gave an equivalent boiling point elevation of 0.052°, corresponding to a molecular weight of 403. The molecular weight calculated for $C_{28}H_{36}N_4$ is 428. It thus seems very probable that $C_{28}H_{36}N_4$ is the structural molecule. These molecules, since their centers are in the general positions, do not necessarily have an element of symmetry.

The formula $C_{28}H_{36}N_4$ depends upon the analysis of Dennstedt and Zimmerman.[1] It is possible that the hydrogen content of the molecule is not correctly given. Such a possibility does not influence the correctness of the above conclusions concerning the molecular symmetry and the number of molecules associated with the unit of structure.

Summary

Laue and spectrum photographs have been obtained and analyzed from crystals of acetonyl pyrrole. The unit of structure containing four $C_{28}H_{36}N_4$ molecules has the dimensions $a_0 = b_0 = 10.09$ Å., $c_0 = 23.85$ Å. The space group is $4C$-2 or $4C$-4, the molecules being in the general positions and thus not necessarily having an element of symmetry. The molecular weight is twice that corresponding to the previously assigned formula. A determination of the molecular weight by a differential vapor pressure method gave a value in agreement with the formula $C_{28}H_{36}N_4$.

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PHENYLETHYLMALONIC METHYL ESTER. A NEW METHOD OF SYNTHESIS

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There appeared recently a paper[2] in which there was described a method of preparation of phenylethylmalonic methyl ester, $(C_6H_5)(C_2H_5)C(CO_2CH_3)_2$, by a procedure summarized as follows.

$$(C_6H_5)CH_2(CN) + NH_2Na + C_2H_5I \longrightarrow (C_6H_5)(C_2H_5)CH(CN) + NaI + NH_3\uparrow \quad (1)$$

$$2(C_6H_5)(C_2H_5)CH(CN) + 2Na \longrightarrow 2(C_6H_5)(C_2H_5)C{=}C{=}NNa + H_2\uparrow \quad (2)$$

$$(C_6H_5)(C_2H_5)C{=}C{=}NNa \rightleftharpoons (C_6H_5)(C_2H_5)(CN)CNa \quad (3)$$

$$(C_6H_5)(C_2H_5)(CN)CNa + ClCO_2CH_3 \longrightarrow (C_6H_5)(C_2H_5)(CN)C(CO_2CH_3) + NaCl \quad (4)$$

$$(C_6H_5)(C_2H_5)(CN)C(CO_2CH_3) + CH_3OH + HCl \longrightarrow (C_6H_5)(C_2H_5)(C{=}NH_2Cl)C(CO_2CH_3) \quad (5)$$

$$(C_6H_5)(C_2H_5)(C(OCH_3){=}NH_2Cl)C(CO_2CH_3) + HOH \longrightarrow (C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + NH_4Cl \quad (6)$$

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[1] This paper describes work done by Tsoh-Wu Zee in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago, 1926.

[2] Rising and Zee, THIS JOURNAL, 49, 541 (1927).