

TABLE I  
ENTROPY OF  $C_2F_5Cl$  FROM THERMAL DATA  
( $0^\circ C. = 273.16^\circ K.$ )

0-15°K., Debye function, $\theta = 75.7$ , six degrees of freedom	$1.91 \pm 0.02$
15-80.24°K.	$17.59 \pm .03$
Transition, 627.59/80.24	$7.82 \pm .02$
80.24-173.72°K.	$19.65 \pm .04$
Fusion, 448.9/173.72	$2.58 \pm .01$
173.72 to 234.04°K.	$9.73 \pm .01$
Entropy of liquid at 234.04°K.	$59.28 \pm .13$
Vaporization, 4639/234.04	$19.82 \pm .04$
Entropy, real gas, 234.04°K., 1 atm.	$79.10 \pm .17$
$S_{ideal} - S_{real}^a$	$0.18 \pm .03$
Entropy, ideal gas, 234.04°K., 1 atm.	$79.28 \pm .20$
$^a S_{ideal} - S_{real} = \frac{27}{32} R \frac{(T_c)^3}{T} \frac{P}{P_c}$ with $T_c = 351^\circ K.$ , $P_c = 31.7$ atm.	

were computed for the product of principal moments and for the reduced moment assuming tetrahedral angles and the usual bond lengths. The tables of Pitzer and Gwinn<sup>4</sup> were used to compute the barrier hindering internal rotation to bring the "spectroscopic" entropy into agreement with the calorimetric entropy.

The computation of the "spectroscopic" entropy is summarized in Table II which is self explanatory and leads to a barrier of 5300 cal. mole<sup>-1</sup>. This is about what is to be expected from the barriers in ethane, ethyl chloride and hexafluoroethane.

TABLE II  
ENTROPY OF PENTAFLUOROCHLOROETHANE FROM  
MOLECULAR DATA AT 234.04°K. IN E.U.

$S$ (translation)	39.809
$S$ (vibration)	8.160
$S$ (external rotation)	27.837
	75.81
$S$ int. rot. $CF_3$ , $V = 5300$	3.47
	Sum 79.28
	Obsd. $79.28 \pm 0.20$

(4) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 426 (1942).

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### The Effect of Base on the Ultraviolet Absorption Spectra of Phenylacetic Acids

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The base-catalyzed condensation of benzaldehyde with phenylacetic acid in acetic anhydride has been pictured<sup>1</sup> as an aldol-type condensation involving as an intermediate the enolate ion of the mixed anhydride of phenylacetic acid and acetic acid. The present investigation is concerned with a com-

(1) R. E. Buckles and K. G. Bremer, *THIS JOURNAL*, **75**, 1487 (1953).

parison of the change in spectra of *o*-nitrophenylacetic acid, *p*-nitrophenylacetic acid and phenylacetic acid in acetic anhydride and in 95% ethyl alcohol when an excess of the typical basic condensation catalyst triethylamine was added. In acetic anhydride the mixed anhydrides and their corresponding enolate ions would be expected to be the main absorbing species under neutral and basic conditions, respectively, and in 95% ethyl alcohol the corresponding species would be the carboxylic acids and their carboxylate ions. Of the two types of ionic species only the enolate ions would have effective conjugation of the negatively charged center with the aromatic ring, and such conjugation should enhance the absorption spectrum—especially with a nitro group in the *o*- or *p*-position.

This type of result has been observed to some extent. The most pronounced shift in the presence of the base in acetic anhydride was observed for *o*-nitrophenylacetic acid. A comparison of this shift with that observed for the formation of *o*-nitrophenylacetate ion in 95% ethyl alcohol is shown in Fig. 1. The corresponding shifts in acetic anhydride were also somewhat more pronounced than those in 95% ethyl alcohol for *p*-nitrophenylacetic acid and for phenylacetic acid, but the excessive absorption of acetic anhydride below 290  $m\mu$  limited the comparison in this solvent to a small part of the spectrum where no peaks were observed.

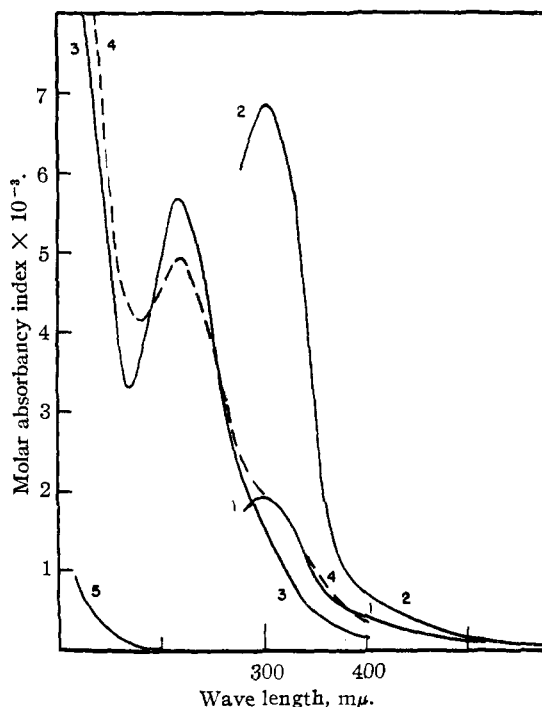


Fig. 1.—Absorption spectra of *o*-nitrophenylacetic acid, (1)  $1.00 \times 10^{-4} M$  in acetic anhydride, (2)  $1.00 \times 10^{-4} M$  in acetic anhydride containing  $2.3 \times 10^{-2} M$  triethylamine (corrected for excess triethylamine), (3)  $1.07 \times 10^{-4} M$  in 95% ethyl alcohol, (4)  $1.07 \times 10^{-4} M$  in 95% ethyl alcohol containing  $3.9 \times 10^{-3} M$  triethylamine (corrected for excess triethylamine), and of (5)  $3.9 \times 10^{-3} M$  triethylamine. Triethylamine had negligible values for the molar absorptivity index (molar extinction coefficient) in acetic anhydride above 290  $m\mu$ .

The absorption spectra data for the three phenylacetic acids in 95% ethyl alcohol are summarized in Table I. The spectrum of phenylacetic acid checks well with that reported<sup>2</sup> but has two additional inflection points that were not mentioned. No reports on absorption spectra of the nitrophenylacetic acids or of any of the phenylacetate ions could be found in the literature.

TABLE I  
MOLAR ABSORBANCY INDICES OF ABSORPTION SPECTRA  
PEAKS IN 95% ETHYL ALCOHOL

Acid	Concn., <i>M</i>	No base		Triethylamine <sup>a</sup>	
		$\lambda$	$\frac{am}{\lambda} \times 10^{-2}$	$\lambda$	$\frac{am}{\lambda} \times 10^{-2}$
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOH	1.00 × 10 <sup>-2b</sup>	241 <sup>c</sup>	1.08	...	...
		247.5	1.13	...	...
		252.5	1.47	255	1.53
		258.5	1.83	259.5	2.03
		264.5	1.40	265.5	1.58
		267.5 <sup>c</sup>	0.70	269	1.39
<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -COOH	1.07 × 10 <sup>-4d</sup>	259	56.8	258.5	49.2
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -COOH	1.19 × 10 <sup>-4d</sup>	272	96.1	284	94.9

<sup>a</sup> For phenylacetic acid the triethylamine concn. was 3.6 × 10<sup>-2</sup> *M*; for the nitrophenylacetic acids it was 3.9 × 10<sup>-3</sup> *M*. <sup>b</sup> Run in a 10-cm. cell. <sup>c</sup> Inflection point. <sup>d</sup> Run in a 1-cm. cell.

#### Experimental Part

**Materials.**—The acetic anhydride was freshly distilled, b.p. 137–139° (745 mm.). Sharples anhydrous grade triethylamine was distilled from barium oxide, b.p. 89.0° (746 mm.). Phenylacetic acid, m.p. 76–77°, *o*-nitrophenylacetic acid,<sup>3</sup> m.p. 140–141°, and *p*-nitrophenylacetic acid,<sup>4</sup> m.p. 152–153°, were used.

**Absorption Spectra Measurements.**—Stock solutions were made up by weight and diluted to concentrations suitable for measurement. Solutions of the phenylacetic acids in acetic anhydride were allowed to stand overnight in order to ensure the formation of the mixed anhydride. Most of the measurements were carried out in calibrated silica cells of path length either 1.00 ± 0.01 cm. or 10.00 ± 0.01 cm. with a Cary, Model 11, recording spectrophotometer. A few determinations were carried out with a Beckman, Model DU, spectrophotometer. The uniform nomenclature and symbology suggested by the National Bureau of Standards<sup>5</sup> has been used throughout this note.

(2) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, *THIS JOURNAL*, **69**, 880 (1947).

(3) R. E. Buckles, M. P. Bellis and W. D. Coder, Jr., *ibid.*, **73**, 4972 (1951).

(4) G. R. Robertson, *Org. Syntheses*, **I**, 406 (1941).

(5) National Bureau of Standards, Letter-Circular, L. C. 857 (1947).

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### Coördination of Copper(II) in Copper 8-Hydroxyquinolate Dihydrate

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The crystal structure of copper 8-hydroxyquinolate dihydrate, Cu(C<sub>9</sub>H<sub>6</sub>ON)<sub>2</sub>·2H<sub>2</sub>O, has been determined as part of a study of the stereochemistry of copper(II). It has been found that this copper salt is isomorphous with the corresponding zinc salt whose structure has been determined by Merritt, Cady and Mundy.<sup>1</sup> This finding raises the interesting question as to whether the anhydrous

(1) L. L. Merritt, Jr., *Anal. Chem.*, **25**, 718 (1953); L. L. Merritt, Jr., R. T. Cady and B. W. Mundy, *Acta Cryst.*, **7**, 473 (1954).

copper and zinc salts are also isomorphous. Liu and Bailar<sup>2</sup> have found tetrahedral coördination of the metal in the zinc salt of 8-hydroxyquinoline-5-sulfonic acid, and it is reasonable to assume the same arrangement in the 8-hydroxyquinolate. Now since copper(II) shows such a strong tendency to square planar coördination it would be extremely unusual if the isomorphism were found to persist in the anhydrous salts.

The actual arrangement in the anhydrous copper salt remains to be investigated, but the supposition is strong that copper's coördination is not tetrahedral, but rather square planar. The ubiquitous square planar coördination of copper(II) is found in the dihydrate.

#### Experimental

Crystals of copper 8-hydroxyquinolate dihydrate were grown by permitting slow evaporation from a solution of copper nitrate and 8-hydroxyquinoline in approximately 2 *N* acetic acid. The crystals are light green and needle-like, the needle axis parallel to *b*. Oscillation photographs made with Cu K $\alpha$  radiation yielded the following lattice constants: *a* = 13.01, *b* = 5.56, *c* = 11.34 Å.,  $\beta$  = 106.1°. The space group was assumed to be P2<sub>1</sub>/c and this assumption was proved correct by the appropriate systematic absences. Intensities were measured on triple films by visual comparison with a calibrated set of time exposures. No correction for absorption was made.

The measured intensities of the *h*0 $l$  reflections were used together with signs determined by Merritt for the zinc salt to compute a Fourier density projection on (010). One hundred and ten reflections were used. The projection is one in which all atoms are resolved and it was found to be practically indistinguishable from that prepared by Merritt for the zinc salt.<sup>1</sup> Parameters obtained from the projection (in order *x, z*) are as follows: Cu at 0, 0; O (of H<sub>2</sub>O at 0.00, 0.16; O (phenolic) at 0.08, 0.92; N at 0.15, 0.09; C at 0.18, 0.95; 0.25, 0.91; 0.36, 0.96; 0.40, 0.06; 0.33, 0.10; 0.23, 0.05; 0.37, 0.18; 0.29, 0.21; 0.20, 0.17. No attempt was made to refine the values since the main purpose was to determine the nature of copper's coördination rather than accurate bond distances.

#### Discussion

Copper is at a center of symmetry so that one can readily estimate the angle between the plane of the quinolinol molecule and (010) from the known ring dimensions; and if then one assumes that the H<sub>2</sub>O–Cu–H<sub>2</sub>O axis is normal to the plane of Cu–O (phenolic) and Cu–N bonds, one obtains a Cu–O (of H<sub>2</sub>O) distance of about 2.3 Å. This distance is much larger than the other Cu–O distance in the molecule (estimated 2.0 Å.) and larger than the Cu–O distance in CuO (1.95 Å.). The density projection thus clearly shows that copper coördinates four atoms (two O and two N of 8-hydroxyquinoline) in a square plane, with two other ligands (H<sub>2</sub>O) weakly bound in the vertex positions of a tetragonal bipyramid. Copper(II) is found in this distorted octahedral environment in CuCl<sub>2</sub>, CuCl<sub>2</sub>·2H<sub>2</sub>O, K<sub>2</sub>CuCl<sub>4</sub>·2H<sub>2</sub>O, CuBr<sub>2</sub>, CuCrO<sub>4</sub> and CuSO<sub>4</sub>·5H<sub>2</sub>O, to mention only a few.

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(2) J. C. L. Liu and J. C. Bailar, Jr., *THIS JOURNAL*, **73**, 5432 (1951).