

TABLE I
SOLUBILITIES OF ACETYLENE AT A PARTIAL PRESSURE OF 1
ATMOSPHERE IN ORGANIC SOLVENTS

Compound	Temp., °C.	Mole fraction	
		Obsd.	Calcd.
Acetal, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$	-10	0.200	0.04
Methylal, $\text{CH}_2(\text{OCH}_3)_2$	-10	.192	.04
Acetaldehyde, CH_3CHO	-10	.177	.04
Ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$	-10	.168	.04
Ethyl formate, HCOOC_2H_5	-10	.144	.04
Methyl acetate, $\text{CH}_3\text{COOCH}_3$	-10	.163	.04
Methyl formate, HCOOCH_3	-10	.142	.04
Isoamyl acetate, $\text{CH}_3\text{COOC}_5\text{H}_{11}$	-10	.166	.04
Isoamyl formate, $\text{HCOOC}_5\text{H}_{11}$	-10	.095	.04
Acetic acid, CH_3COOH	18	.0150	.0245
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	18	.0151	.0245
Benzene, C_6H_6	4	.0252	.0342
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	4.2	.0223	.034
Dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	0.3	.037	.0382
Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	3.8	.0223	.0345
Cyclohexane, C_6H_{12}	3	.0175	.0352
Acetone, CH_3COCH_3	0.0	.092	.038
Acetone, CH_3COCH_3	15	.074	.026
Acetone, CH_3COCH_3	15	.490	.312 ^a
Acetone, CH_3COCH_3	25	.0402	.0206

^a Pressure of acetylene 12 atmospheres.

stituted formamides than in N-disubstituted acetamides.

A further test of this idea is being made by means of vapor pressure-composition studies and by measuring the heats of mixing of a monosubstituted acetylene (phenylacetylene) with a number of donor solvents.

Figure 1 shows the heat evolved at 3° per mole of solution as a function of the mole fraction of phenylacetylene when it is mixed with, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, and methyl acetate. The calorimeter and method of making the heat measurements were described previously by Zellhoefer and Copley.⁸ The maxima of the curves in Fig. 1 occur very close to a mole fraction of 0.5 and indicate that in each case an equimolar complex is formed. Curve A is a plot of the heat of mixing data for chloroform and diethyl ether obtained by McLeod and Wilson.⁹ Comparison of curves A and C shows that the hydrogen of chloroform is a better acceptor than the hydrogen of phenylacetylene, although the latter is more acidic, and thus emphasizes the influence of different groups on the carbon to which the active hydrogen is attached. Gordy¹⁰ has observed that when CH_3OD is mixed with ethers, esters, or ke-

tones, the largest shift in the OD fundamental band is shown with ethers. The somewhat larger amount of heat obtained here with dimethyl ether than with methyl acetate or acetone also indicates that with phenylacetylene an ether oxygen is a better electron donor than an ester or ketone oxygen.

As would be expected from previous solubility measurements⁴ on monofluorodichloromethane in ethers and N-disubstituted amides, considerably more heat is evolved on mixing phenylacetylene with N,N-dimethylacetamide than with diethyl ether. The nitrogen atom of N-disubstituted amides appears to be the best electron donor atom for forming hydrogen bonds.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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The Preparation and Melting Point of 1-Iodoanthraquinone

BY ALBERT E. GOLDSTEIN

In the course of an investigation involving halogenated anthraquinones,¹ it became necessary to prepare 1-iodoanthraquinone. Investigation of the literature revealed but one procedure for the purpose—the method of Laubé.² The recorded yield of crude product appears as 27 g. (90%). It was found that, if the reported procedure were carefully followed, the crude yield invariably amounted to 7–8 g. If the procedure of Laubé is modified in the light of an observation made by Scholl and Mansfeld,³ then the results obtained are in agreement with those of Laubé.

The melting point of 1-iodoanthraquinone is given by Laubé as 177°. Brass and Eichler⁴ give the melting point as 176°. Nowhere is any mention made of the color of the compound. The repeated preparation of 1-iodoanthraquinone by the author and by others in these Laboratories invariably has yielded a crude compound melting at 195–197°. Two recrystallizations of the crude material yielded a compound melting at 204–205° instead of 177° as given by Laubé. Nitrobenzene has been found to be a more satisfactory solvent for the recrystallization than glacial acetic acid. The color of the product varies from brownish-yellow to dark brown.

(1) A. E. Goldstein with J. H. Gardner, *THIS JOURNAL*, **56**, 2130 (1934).

(2) Laubé, *Ber.*, **40**, 3566 (1907).

(3) Scholl and Mansfeld, *ibid.*, **43**, 1739 (1910).

(4) Brass and Eichler, *ibid.*, **67B**, 785 (1934).

(8) Zellhoefer and Copley, *THIS JOURNAL*, **60**, 1343 (1938).

(9) McLeod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

(10) Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

References to the preparation and melting point of 1-iodoanthraquinone found in the chemical literature are all based on the results reported by Laubé and consequently require revision.

Experimental

1-Iodoanthraquinone.—Twenty grams of 1-aminoanthraquinone, Eastman (Technical), was dissolved in 80 g. of concentrated sulfuric acid. To this solution 6 g. of sodium nitrite was added a little at a time at room temperature. The mixture was stirred mechanically during the addition of the sodium nitrite and for an additional two-hour period. This solution was then poured slowly into 1 liter of ice water with continual stirring. The mixture was stirred mechanically for one hour. The solution was next filtered and to the filtrate 10 g. of potassium iodide was added. This mixture was allowed to stand at room temperature for three hours and then heated for one hour on a steam-bath. After adding 10 cc. of a saturated sodium bisulfite solution, the mixture was filtered, and the residue was washed with distilled water and dried at 100°. The crude 1-iodoanthraquinone was light chocolate-brown; yield 7.5 g. (25%); m. p. 195.5–197.5°.

The residue from the first filtration mentioned above was put into 1 liter of water and stirred mechanically at room temperature for thirty minutes. The mixture was filtered and the filtrate treated with 10 g. of potassium iodide. By continuing the procedure as described above, an additional yield of crude product was obtained, light brown in color, weighing 19.5 g. (65%), m. p. 195.5–197.5°.

Two recrystallizations of the combined crude product from nitrobenzene produced a yellowish-brown crystalline compound, m. p. 204–205°.⁵

Anal. Calcd. for $C_{14}H_7O_2I$: I, 37.99. Found: I, 38.02.

(5) All melting points are corrected.

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
ST. LOUIS, MISSOURI

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Note on the Molecular Structure of 1,2,4,5-Tetrabromocyclohexane (m. p. 185°)

By E. HALMÖY AND O. HASSEL

In some papers from the Oslo Institute of Physical Chemistry dealing with the structure of cyclohexane and its derivatives¹ investigations carried out on the 1,2,4,5-tetrabromocyclohexane of melting point 185° have been referred to. Although these investigations have not yet been brought as far as we could have wished in the case of the X-ray crystallographic part, we should not like to delay publication much longer, and

(1) A list of previous papers is found in a paper published by J. G. Gudmundsen and O. Hassel, *Z. physik. Chem.* **B40**, 326 (1938); see also O. Hassel and A. M. Sommerfeldt, *ibid.*, **B40**, 391 (1938).

are therefore publishing our results now, in a preliminary form.

The substance was obtained from the 1,4-dibromo compound of melting point 111° on eliminating two moles of hydrogen bromide and adding two moles of bromine to the 1,4-cyclohexadiene thus obtained. The crystals were rather well developed, having a size suitable for examination by the simple single crystal methods. They were found to be orthorhombic with axial ratios 1.010₃:1:0.997₇, and the following faces were observed: {110}, {101}, {011}, and in some cases also {001}. The optical axes were nearly perpendicular to (110) and (1 $\bar{1}$ 0).

The X-Ray Examination.—Approximate determinations of axial lengths (using the layer line method) gave the values $a = 7.92$ Å., $b = 7.85$ Å., and $c = 7.88$ Å. More accurate values were obtained from Bragg photographs on (001), (110), and (011) combined with the goniometrically determined axial ratios given above. We found $a = 7.98$ Å., $b = 7.90$ Å., $c = 7.89$ Å.

From our X-ray data (chiefly using Weissenberg photographs) we found that no other systematic extinctions can be observed than those of ($h00$) and ($0k0$), h or k being odd. The only space group of the orthorhombic system characterized by the absence of these reflections and showing no other regular extinctions is the Schönflies group $D_2^3-P2_12_12$. This space group contains only twofold and fourfold positions, the former being characterized by the point symmetry C_2 (twofold axis of symmetry) and one degree of freedom, the latter by three degrees of freedom. The density of the crystals being 2.66, the number of molecules in the unit cell must be 2 (calculated 2.01) and the single molecule must have a twofold axis of symmetry. The coordinates of the bromine atoms are of the form xyz , etc., four and four being crystallographically equivalent. It is not possible to evaluate the parameters of the bromine atoms with any accuracy, neglecting the influence of the carbon atoms, but a rough estimate of their positions can be made and this was found useful when trying to interpret the structure with the help of classical conceptions of the configuration of the cyclohexane ring using newer data concerning the interatomic distances. Assuming the carbon-carbon distance to be 1.54 Å. and the carbon-bromine distance to be 1.93 Å., the distribution of the bromine atoms was found to be in fairly