the 11–12 carbon–carbon bond would be required to give quantitative agreement with the observed data for the *cis* compound, and this seems unreasonable.

The moments of the 1,2-dichloroacenaphthenes are similar to those of the 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes. As before, the higher melting isomer is assigned the *cis* configuration (as it has the higher electric moment 2.97 *D*), and the lower melting isomer, with dipole moment 2.04 *D*, is *trans*. The calculated values would be 3.77 and 1.89 *D*, respectively, if the groups on the 1- and 2-carbon atoms are directly opposed. The higher melting isomer was prepared by the addition of chlorine to acenaphthalene and the lower melting isomer by reaction of acenaphthalene with iodobenzene dichloride; it was expected, on this basis, that the higher melting isomer would be *trans*.[5] Since the dipole moment results were the reverse of expectation, resolution of the isomers was undertaken[6]; partial resolution of the lower melting isomer by treatment with brucine in dioxane showed that it was the *dl-trans* modification, whereas the higher melting isomer must have the *meso-cis* structure since it was not resolved by this procedure.

Only the 124° melting isomer of 1,2-dibromoacenaphthene is known and its observed electric moment, 1.63 *D*, is close to that calculated for the *trans* isomer (about 1.75 *D*). Partial resolution by treatment with brucine in dioxane confirms the *dl-trans* structure for this compound.

The lower melting 1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate has been assigned the *cis* configuration on the basis of its larger dipole moment. However, because of the possibility of interactions between the two acetate groups, which might appreciably affect the dipole moments, this assignment is not as certain as the others. It is in agreement with the structures assigned to the corresponding diols.[7]

The single trichloroanthracene[8,9] obtained by dehydrohalogenation of the known isomer (*trans*) of 1,8,9,10-tetrachloro-9,10-dihydroanthracene[7] is shown to be 1,8,10-trichloroanthracene. The electric moments calculated for 1,8,10-trichloroanthracene and 1,8,9-trichloroanthracene are, respectively, 1.5 and 4.5 *D*.

Experimental

Materials.—The synthesis and properties for the compounds studied are given elsewhere: the *cis–trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene[2]; the *cis–trans* isomers of 1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate[10]; the *cis–trans* isomers of 1,2-dichloroacenaphthene[6]; the *trans* isomer of 1,2-dibromoacenaphthene[6] and 1,8,10-trichloroanthracene.[9] The melting points of the isomers are listed in Table I.

Benzene was fractionally crystallized twice, distilled and dried over sodium: $n^{25}\text{D}$ 1.4979, d^{25}_4 0.87350.

Measurements and Calculations.—The electric moments were determined in benzene solution at 25°. By use of apparatus and technique described previously,[11] dielectric constants and densities of from five to ten solutions, ranging in mole fraction from 0.0001 to 0.005, were measured for each compound. The molar polarizations and dipole moments were calculated by the method of Halverstadt and Kumler.[12] The constants of their equation are shown in Table I along with the calculated molar polarizations, molar refractions and dipole moments. The probable error in molar polarizations is ±4%, and the probable error in dipole moments about ±0.12 *D*.

TABLE I

EMPIRICAL CONSTANTS,[a] MOLAR REFRACTIONS,[b] MOLAR POLARIZATIONS AND DIPOLE MOMENTS AT 25° IN BENZENE SOLUTION

ϵ_{10}	α^1	V_{10}	β^1	P_2^∞	MR_D	μ
cis-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (m. p. 203–204°)						
2.2737	14.77	1.14495	−1.38	278.73	74.03	3.16
trans-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (m.p. 113.6–114°)						
2.2714	7.268	1.14488	−1.307	170.26	74.03	2.17
cis-1,5-Dichloro-9,10-dihydro-9,10-anthradiol diacetate (m. p. 246°)						
2.2725	3.65	1.14487	−1.91	133.73	88.78	1.48
trans-1,5-Dichloro-9,10-dihydro-9,10-anthradiol diacetate (m.p. 265°)						
2.2725	2.9	1.14484	−2.10	118.30	88.78	1.20
cis-1,2-Dichloroacenaphthene (m.p. 113–114°)						
2.2734	12.12	1.14474	−1.156	242.06	61.14	2.97
trans-1,2-Dichloroacenaphthene (m.p. 67–68°)						
2.2723	6.61	1.14480	−1.148	146.69	61.14	2.04
1,8,10-Trichloroanthracene (m.p. 191°)						
2.2725	4.50	1.14485	−1.59	125.15	71.58	1.62
trans-1,2-Dibromoacenaphthene (m.p. 124–125°)						
2.2732	4.60	1.14488	−2.370	118.86	64.21	1.63

[a] The observed dielectric constants ϵ_{12}, and specific volumes, V_{12}, of the solutions were plotted graphically against mole fraction of solute. The points fall, within experimental error, on straight lines with slopes α^1 and β^1, respectively, and the intercepts at zero mole fraction are ϵ_{10} and V_{10}, respectively. The molar polarizations are infinite dilution P_2^∞, and the dipole moments μ, expressed in Debye units, were calculated from these constants. [b] Molar refractions were calculated from empirical atomic refractions.

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The Preparation of O-Phenylcarbamyl Benzohydroxamate Through the Lossen Rearrangement

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In May, 1954, Hurd and Bauer[1] reported the formation of substituted O-carbamyl hydroxamates by treatment of sodium salts of hydroxamic acids with aromatic sulfonyl chlorides

$$2\,\text{RCONHONa} + \text{RSO}_2\text{Cl} = \text{RCONHOCONHR} + \text{RSO}_2\text{ONa} + \text{NaCl}$$

At the time of this publication we were in the

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[1] C. D. Hurd and L. Bauer, THIS JOURNAL, **76**, 2791 (1954).

process of submitting a report of our own discovery of this reaction. It is an interesting coincidence that a reaction, which had remained unnoticed for the eighty years since Lossen first published his observations on the rearrangement of O-acylated hydroxamic acids, has now been discovered independently by two groups of workers.

We should like to add certain additional information concerning the reaction between the sodium salt of benzohydroxamic acid and benzenesulfonyl chloride which yields O-phenylcarbamyl benzohydroxamate, $C_6H_5CONHOCONHC_6H_5$ (I).[2,3] This reaction proceeds in a satisfactory manner not only in chloroform suspension, as described by Hurd,[1] but also in aqueous solution or in pyridine. In addition to sulfonyl chlorides, the acyl chlorides of other strong acids (*e.g.*, *o*-nitrobenzoyl chloride and picryl chloride[4]) also react with benzohydroxamic acid in aqueous alkaline solution to yield I.

Marquis[5] attempted unsuccessfully to prepare I by treating benzohydroxamic acid with thionyl chloride. However, he reported that he could obtain I by reaction of equimolar amounts of benzohydroxamic acid with phenyl isocyanate in pyridine.

We obtained an identical product when this reaction was carried out in slightly alkaline aqueous acetone solution. It would appear that alkaline conditions are necessary for the reaction to take place. This supposition is supported by Hurd's[6] failure to observe this reaction in neutral solvents.

All the samples of I prepared by the methods mentioned above and also by that of Marquis[5] proved to be identical by infrared spectra. The decomposition point was 176–177° (uncor.) confirming Hurd and Bauer who reported decomposition at about 180°, but differing from Marquis who reported 209–210°.

Support for the assumption that the formation of I occurred *via* Lossen rearrangement was obtained by a study of the reaction between benzohydroxamic acid and *o*-nitrobenzoyl chloride. Hauser and co-workers[7] in their exhaustive investigation of the Lossen rearrangement of acylated aromatic hydroxamic acids found that O-(*o*-nitrobenzoyl) benzohydroxamate was particularly susceptible to rearrangement. When benzohydroxamic acid incompletely reacted with *o*-nitrobenzoyl chloride under conditions which were similar to those described for benzenesulfonyl chloride, we were able to isolate from the reaction mixture I, O-(*o*-nitrobenzoyl) benzohydroxamate (II) and diphenylurea.

The following sequence of reactions explains the formation of these products in aqueous alkaline solution[8]

$$C_6H_5CONHOH + ACl \xrightarrow{OH^-} \underset{II}{C_6H_5CONHOA} + HCl \quad (1)$$

$$C_6H_5CONHOA \xrightarrow{OH^-} C_6H_5NCO + AOH \quad (2)$$

$$C_6H_5CONHOH + C_6H_5NCO \xrightarrow{OH^-} \underset{I}{C_6H_5CONHOCONHC_6H_5} \quad (3)$$

where, A = RCO, RSO_2, picryl

Diphenylurea presumably is formed by the normal reaction of phenyl isocyanate with its hydrolysis product, aniline. Phenyl isocyanate is produced by reaction 2 and also by the decomposition of I

$$C_6H_5CONHOCONHC_6H_5 \xrightarrow[\text{or heat}]{OH^-} C_6H_5NCO + CO_2 + C_6H_5NH_2$$

Complete reaction between benzenesulfonyl chloride and an excess of benzohydroxamic acid at a maintained *p*H of 7.6 should require the addition of 2.85 to 2.90 molar equivalents of alkali (based upon benzenesulfonyl chloride); one mole each for neutralization of the benzenesulfonic and hydrochloric acids, respectively, and the remainder to adjust for the acidity produced in the conversion of two moles of benzohydroxamic acid, pK_a 8.8, to one mole of I, pK_a 6.4.[9] Thus, the proposed reaction series is susceptible to further check based upon the quantity of alkali required to maintain a constant *p*H during the course of reaction. The difficulty caused by the competitive solvolysis reaction of benzenesulfonyl chloride which yields only two moles of acid was overcome by studying the reaction at two different levels of benzohydroxamic acid concentration (in each case, in large excess over amount required for reaction) and determining thereby the competition factor for the two competing reactions. An average value of 275 for the competition factor[10] was obtained for reaction at *p*H 7.6 which was used for the calculation of the expected amount of acid produced in the reaction. The close agreement between the calculated and found values for the alkali required, as indicated in Table I, provides additional confirmation for the proposed reaction series.

TABLE I

MOLES OF ALKALI PER MOLE OF BENZENESULFONYL CHLORIDE REQUIRED TO MAINTAIN *p*H 7.6[11]

Concn. of benzohydroxamic acid, *M*	Alkali Calcd.	Alkali Found
0.135	2.34	2.37
0.60	2.64	2.61

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(2) Hurd and Bauer[1] referred to this compound as benzo-(phenylcarbamylhydroxamic) acid. It is believed that the name herein suggested is in closer conformity with established systems of chemical nomenclature.

(3) Isomeric substances which give identical elemental analyses are excluded on the following bases: The benzoyl ester of α-phenyl-β-hydroxyurea, $C_6H_5NHCONHOCOC_6H_5$, which has almost the same m.p. as I (179°), unlike I, is insoluble in dilute alkali. Similarly, the failure of I to give a positive color test with ferric chloride (indicative of the structure RCON(R′)OH) eliminates N-phenylcarbamyl benzohydroxamic acid, $C_6H_5CON(CONHC_6H_5)OH$.

(4) Studied by R. Plapinger and O. O. Owens. O-Picrylated oximes readily undergo the Beckman rearrangement; B. Jones, *Chem. Revs.*, **35**, 335 (1944).

(5) R. Marquis, *Compt. rend.*, **143**, 1163 (1906).

(6) C. D. Hurd, THIS JOURNAL, **45**, 1472 (1923).

(7) C. R. Hauser, and W. B. Renfrow *ibid.*, **59**, 2308 (1937); R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

(8) For purposes of clarity, acids have been written in their protonated form.

(9) At *p*H 7.6, benzohydroxamic acid is 5% neutralized, while I is 95% in its salt form. Hence, the conversion of two moles of the hydroxamic acid to one mole of I should require 0.85 molar equivalent of alkali. Side and sequential reactions which yield carbon dioxide might tend to increase this value to a maximum of 0.90.

(10) Competition factor = molar reactivity of benzhydroxamic acid with benzenesulfonyl chloride/molar reactivity of H_2O with benzenesulfonyl chloride.

(11) Studied by R. Swidler and S. Seltzer.

Hurd[6] reported the preparation of O,N-bis-(phenylcarbamyl)-N-benzoylhydroxylamine, $C_6H_5CON(CONHC_6H_5)OCONHC_6H_5$ (III), by reaction of a large excess of phenyl isocyanate with benzohydroxamic acid. The same product would be expected from the reaction of I with phenyl isocyanate. When the latter reaction was performed the product obtained had a melting point very close to that reported by Hurd and an elemental analysis corresponding to formula III. Repetition of Hurd's synthesis with benzohydroxamic acid and phenyl isocyanate yielded a product having similar properties and a satisfactory nitrogen analysis; however, the carbon and hydrogen values were too high. Apparently unidentified by-products were formed in this preparation.

Experimental

O-Phenylcarbamyl Benzohydroxamate (I). A. Reaction of Benzenesulfonyl Chloride with Benzhydroxamic Acid. (a) In Aqueous Solution.—A suspension of 1.0 g. (0.0072 mole) of benzohydroxamic acid in 100 ml. of water was adjusted to *p*H 7.6 with sodium hydroxide and the resulting solution diluted to 125 ml. One ml. of benzenesulfonyl chloride (0.0073 mole) was added and the *p*H maintained at 7.6 by automatic addition of *N* NaOH using the Beckman Autotitrator. Ten minutes after the addition of the benzenesulfonyl chloride, a precipitate started to form which increased in quantity during the next hour. The reaction slowed appreciably and during the next two hours produced only a small amount of acid.

The mixture was filtered and the precipitate washed with cold water. Diphenylurea was removed by dissolving the crude product in sodium hydroxide, filtering the very small quantity of the insoluble material and acidifying the filtrate with hydrochloric acid. The resulting precipitate, after drying, weighed 0.7 g., equivalent to a yield of 75%. (A large quantity of diphenylurea and a smaller yield of O-phenylcarbamyl benzohydroxamate was obtained when the reaction mixture was permitted to stand at *p*H 7.6 overnight.) The reaction product, which was soluble in sodium hydroxide, sodium bicarbonate, alcohol and ether, but insoluble in water and dilute acid, was recrystallized from aqueous alcohol and dried over phosphorus pentoxide in vacuum. The resulting white needles decomposed at 176–177°, with evolution of carbon dioxide, and finally melted at 234° (m.p. diphenylurea, 238°). The substance is an acid, having pK_a of 6.4. The analysis and neutralization equivalent correspond to O-phenylcarbamyl benzohydroxamate.

Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.6; H, 4.7; N, 10.9; equiv. wt., 256. Found: C, 65.7; H, 4.6; N, 11.2; equiv. wt., 253.

The same product was obtained when one-half the molar quantity of benzenesulfonyl chloride was added to benzohydroxamic acid. The yield, however, was reduced to 0.5 g., 53%, based upon benzohydroxamic acid.

(b) In Pyridine.—A solution of 2.0 g. (0.015 mole) of benzohydroxamic acid in 50 ml. of dry pyridine was cooled and 1.96 ml. (0.015 mole) of benzenesulfonyl chloride was added with stirring. A reaction occurred immediately with the evolution of heat. The solution became cherry-red and was stirred for an hour at room temperature. No color reaction with ferric chloride was obtained after this time. The pyridine was vacuum stripped, the resulting dark red viscous residue dissolved in sodium hydroxide and an orange precipitate was obtained upon acidification with hydrochloric acid. The product was decolorized with charcoal in alcohol. Upon dilution with water, there were obtained white needles which decomposed at 176–177°, with the evolution of carbon dioxide, and finally melted at 230°.

B. Reaction of *o*-Nitrobenzoyl Chloride with Benzhydroxamic Acid.—To a mixture of 1.9 g. (0.012 mole) of sodium benzohydroxamate in 250 ml. of water and 50 ml. of dioxane which was adjusted to *p*H 9.0, there was added a solution of 1.1 g. (0.006 mole) of *o*-nitrobenzoyl chloride in 20 ml. of dioxane. The *o*-nitrobenzoyl chloride was almost insoluble in the reaction mixture and upon mechanical stirring formed small globules of oil. During the next five hours, the solution was maintained at *p*H 9.0 by the addition of base using a Beckman Autotitrator. In the course of the reaction the volume of acid chloride diminished considerably and by the time the reaction was stopped the remaining insoluble material had become a solid.

The aqueous solution was decanted, acidified and the precipitate that formed filtered and dried. There was obtained 0.49 g. (32%) of a white solid which decomposed at 174–177°, with evolution of carbon dioxide, and finally melted at 220–225°. A mixed melting point with an authentic sample of O-phenylcarbamyl benzohydroxamate obtained from the reaction of benzohydroxamic acid with phenyl isocyanate gave no depression.

The insoluble fraction was dried under vacuum; it melted at 126–130°. The melting point of O-(*o*-nitrobenzoyl) benzohydroxamate is 131–132°. The yield of this material was 0.3 g., equivalent to 17% of theory based upon benzohydroxamic acid.

Formation of Diphenylurea from O-Phenylcarbamyl Benzohydroxamate.—A small quantity of O-phenylcarbamyl benzohydroxamate was heated for 30 minutes, at 180–190°, and the carbon dioxide which was evolved was passed into a solution of barium hydroxide and precipitated as barium carbonate. The residual solid was insoluble in sodium hydroxide. After recrystallization from 95% alcohol, its melting point was 238–240°. A mixed melting point with an authentic sample of diphenylurea gave no depression.

O,N-Bis-phenylcarbamyl Benzohydroxamate (III). A. Addition of One Mole of Phenyl Isocyanate to One Mole of O-Phenylcarbamyl Benzohydroxamate.—An excess (3 ml.) of phenyl isocyanate was added to 0.2 g. of O-phenylcarbamyl benzohydroxamate, and the mixture was heated cautiously over a free flame until solution occurred. The resulting oil was permitted to stand at room temperature for an hour, after which 60 ml. of dry ligroin (b.p. 30–65°) was added. When this mixture was cooled in a Dry Ice–acetone-bath, a precipitate formed which was filtered and washed with ligroin. The product was recrystallized from benzene and ligroin. Upon treatment with 2% sodium bicarbonate solution, a small amount of the crystalline product dissolved. The insoluble residue was washed with water and with ligroin.

The product shrinks at 118–120°, and evolves carbon dioxide at 148°.

Anal. Calcd. for $C_{21}H_{17}O_4N_3$: C, 67.2; H, 4.6; N, 11.2. Found: C, 67.2; H, 4.8; N, 11.1.

B. Reaction of Excess Phenyl Isocyanate with Benzohydroxamic Acid.—A mixture of 0.3 g. of benzohydroxamic acid and 2.5 ml. of phenyl isocyanate was heated and the reaction product isolated according to the method of Hurd.[6] The product shrinks at 115° and evolves carbon dioxide at 148°.

Anal. Calcd. for $C_{21}H_{17}O_4N_3$: C, 67.2; H, 4.57; N, 11.2. Found: C, 72.1; H, 5.1; N, 11.6.

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A System for Paper Chromatography of 3,4-Benzpyrene, Some Derivatives and Other Polycyclic Aromatic Hydrocarbons[1]

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During a study[2] of the nature of the fluorescent material which is chemically bound to the skin protein of mice after painting with 3,4-benzpyrene,[3] it was necessary to develop a system for paper

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[2] D. S. Tarbell, E. G. Brooker, P. Seifert and T. J. Hall, Abstracts of the N. Y. Meeting of the American Chemical Society, September, 1954, p. 5N.

[3] E. C. Miller, *Cancer Research*, **11**, 100 (1951).