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# HYDROGEN BONDED COMPLEXES—II[1]

## THE LACTAM–PHENOL RATIOS AND STRUCTURES IN LACTAM–PHENOL COMPLEXES

JOHN E. BARRY, NED E. CIPOLLINI, MANUEL FINKELSTEIN and SIDNEY D. ROSS*
Research and Development Center, Sprague Electric Company, North Adams, MA 01247, U.S.A.

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**Abstract**—Lactams form solid, isolable complexes with the three dihydroxybenzenes, *o,o'*-biphenol and 2,3-naphthalenediol, in which lactam-phenol ratios of 1:1, 2:1, 3:1 and even 4:3 were observed. These ratios can be determined with precision by a gas chromatography method which is described. IR spectroscopy indicates that the bonds linking lactam and phenol are O–H...O and/or N–H...O hydrogen bonds. Structures for the complexes are suggested.

In a previous study[1] it was shown that amides and lactams form solid, isolable complexes with the more acidic phenols, e.g. picric acid and pentachlorophenol, and that, depending on the amide structure, the amide-phenol ratio in these complexes may be 1:1, 2:1 or 3:1. Complexing of amides or lactams with phenols has been studied in dilute solution with both IR spectroscopy[2–7] and UV spectroscopy.[8] These studies permit determination of the equilibrium constants for 1:1 complexing and provide evidence that the chemical interaction involved is H-bonding, with the phenolic OH providing the donor and the amide or lactam CO oxygen serving as the acceptor.

These spectroscopic studies afford no evidence for the existence of complexes with ratios greater than 1:1. Evidence for complex formation at ratios other than 1:1 between pairs of organic solutes in solution can be obtained, in suitable cases, from dielectric constant measurements[9] or from measurements of the square of the refractive index,[10] but the most unambiguous evidence for such complexes comes from cases where the complex can be isolated as a crystalline solid and where the chemical composition of that solid can be determined by precise analytical methods.

Our interest in complexing between lactams and phenols was reawakened when, in another connection, it was observed that the addition of 3% catechol to N-methylpyrrolidinone (NMP) lowers the 25° resistivity of that solvent by an order of magnitude and that it is possible to isolate from catechol–NMP solutions a crystalline complex (m.p. 41–43°) in which the lactam–catechol ratio is 2:1. The 2:1 ratio was not unexpected, since the phenol moiety, catechol, is bifunctional, but a quick experimental investigation of complexing between lactams and the dihydroxybenzenes indicated that solid complexes in ratios of 1:1, 2:1, 3:1 and, in one case, even 4:3 were formed. Some of these complexes had been reported previously,[11,12] but with experimental evidence to support the assignment of the lactam–phenol ratios provided for only a very few of them. In the present work crystalline complexes were prepared from lactams and phenol itself, the three dihydroxybenzenes, *o,o'*-biphenol and 2,3-naphthalenediol. The lactam–phenol ratios were determined by elemental analysis and confirmed by a gc method to be described. The evidence for the structures of these solid complexes is discussed.

### RESULTS AND DISCUSSION

The complexes that were prepared are listed in Table 1, which includes the lactam–phenol ratios, the m.p. and the results obtained by elemental analysis. The complexes were generally prepared in excellent yield by dissolving the lactam and phenol, usually in a molar ratio of 2:1, in ether or ether–acetone and then adding hexane at room temperature until the solution became just slightly cloudy. Cooling resulted in slow crystallization. With one exception, a single complex having the lactam–phenol ratio indicated in Table 1 was obtained, and this result was independent of the initial lactam–phenol ratio (1:1, 2:1 or 3:1) used in the preparation.

The one exception was the NMP–hydroquinone complex. The initial preparation led to the 2:1 complex, m.p. 66–69°, and this product could be recrystallized unchanged by adding a little NMP to the crystallization solution. However, repeated recrystallization without NMP added, or preparation with the initial lactam–hydroquinone ratio 1:1 or recrystallization from 2-propanol-hexane led to formation of the 1:1 complex, m.p. 96–98°. Attempts to convert other 2:1 complexes to 1:1 complexes by comparable methods were without success.

Resorcinol forms a complex with 2-pyrrolidinone, which is a crystalline solid in the freezer but liquifies on standing at room temperature. It is, therefore, not included in Table 1. Similarly phenol forms complexes with other lactams, but only the product with ϵ-caprolactam stayed conventiently solid at room temperature.

Of the sixteen complexes listed in Table 1 four have been reported previously.[11] For three, the 1:1 complex from NMP and hydroquinone, the product from 2-pyrrolidinone and hydroquinone, and the complex from ϵ-caprolactam and hydroquinone, the results in Table 1 are in good agreement with the values previously reported. For the reaction of ϵ-caprolactam and phenol we report a 2:1 complex having m.p. 37–39°, whereas Randall *et al.*[11] report a 1:1 complex of m.p. 34–36°, without offering any analytical support for the 1:1 assignment.

The lactam–phenol ratio for the ϵ-caprolactam–phenol complex listed in Table 1 is 2:1. This conclusion follows from the analytical values given in Table 1 and from analysis by gas chromatography (gc), which provides a simple and precise method for determining the lactam–

Table 1.

LACTAM-PHENOL COMPLEXES

| A LACTAM | B PHENOL | A:B RATIO | M.P. °C | ANALYSES CALCD. C | H | N | FOUND C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| ε-Caprolactam | Phenol | 2:1 | 37-39 | 67.47 | 8.81 | 8.74 | 67.27 | 8.61 | 8.72 |
| N-Methylpyrrolidinone | Catechol | 2:1 | 41-43 | | | 9.09 | | | 8.93 |
| 2-Pyrrolidinone | Catechol | 4:3 | 44-46 | 60.88 | 6.91 | 8.35 | 61.09 | 7.06 | 8.33 |
| ε-Caprolactam | Catechol | 3:1 | 53-55 | 64.12 | 8.74 | 9.35 | 64.43 | 8.82 | 9:00 |
| N-Methylpyrrolidinone | Resorcinol | 2:1 | 60-61 | | | 9.09 | | | 8.94 |
| ε-Caprolactam | Resorcinol | 2:1 | 77-79 | 64.26 | 8.39 | 8.33 | 64.59 | 8.61 | 8.31 |
| N-Methylpyrrolidinone | Hydroquinone | 1:1 | 96-98 | | | 6.70 | | | 6.58 |
| N-Methylpyrrolidinone | Hydroquinone | 2:1 | 66-69 | | | 9.09 | | | 8.86 |
| 2-Pyrrolidinone | Hydroquinone | 2:1 | 129-132 | | | 9.99 | | | 9.82 |
| ε-Caprolactam | Hydroquinone | 2:1 | 115-117 | 64.26 | 8.39 | 8.33 | 64.49 | 8.48 | 8.29 |
| N-Methylpyrrolidinone | o,o'-Biphenol | 1:1 | 65-67 | | | 4.91 | | | 4.91 |
| 2-Pyrrolidinone | o,o'-Biphenol | 2:1 | 76-78 | | | 7.86 | | | 7.74 |
| ε-Caprolactam | o,o'-Biphenol | 1:1 | 75-77 | 72.71 | 7.07 | 4.68 | 72.51 | 7.15 | 4.72 |
| N-Methylpyrrolidinone | 2,3-Naphthalenediol | 1:1 | 90-92 | | | 5.40 | | | 5.35 |
| 2-Pyrrolidinone | 2,3-Naphthalenediol | 2:1 | 48-50 | | | 8.48 | | | 8.19 |
| ε-Caprolactam | 2,3-Naphthalenediol | 1:1 | 96-98 | 70.31 | 7.01 | 5.12 | 70.67 | 7.33 | 5.09 |

phenol ratios. The lactams and phenols in these complexes are held together primarily by relatively weak NH...O or OH...O H-bonds, having bond energies of ~3.5–7.0 kcal/mol.[13] When dissolved, these complexes will dissociate at least partly into the starting materials, and the dissociation process will be fully completed when the solutions are subjected to the conditions and temperatures prevalent in the injection port and on the column during gc. These observations provide the basis for a precise analytical method. The complex is dissolved in acetone or methanol, and the solution is analyzed by gc for the lactam and phenol starting materials. The validity of the method was checked by analyzing the two N-methylpyrrolidinone-hydroquinone complexes. For the 1:1 complex, the determined lactam–phenol ratio was 0.97 ± 0.01:1, and for the 2:1 complex the ratio was 1.90 ± 0.02:1. In the case of the ε-caprolactam and phenol complex, this procedure led to the observation of ε-caprolactam and phenol in a molar ratio of exactly 2.00:1.

In our previous work[1] the amide–phenol or lactam–phenol ratio was determined by a simple neutralization equivalent. In that work the phenols involved were relatively strong acids, e.g. picric acid and pentachlorophenol, and a simple acid–base titration precisely defined the ratio. In the present work the phenols involved, e.g. phenol itself and the dihydroxybenzenes, are all weak acids. A neutralization equivalent can be obtained with a pH titration, but the method does not provide the precision given by the gc procedure.

The ε-caprolactam–catechol complex is of interest because of its atypically high lactam–phenol ratio of 3:1. It was first prepared from ε-caprolactam (5.65 g; 0.05 mole) and catechol (5.51 g; 0.05 mole). This combination of starting materials can, in principle, lead to 0.05 mole (11.16 g) of the 1:1 complex, or 0.025 mole (8.41 g) of the 2:1 complex or 0.0167 mole (7.49 g) of the 3:1 complex or to some mixture of products. The crude product had m.p. 50–55°, suggesting that it was very probably not a complex mixture, and weighed 7.25 g a weight consistent with any one of the three possible complexes and representing a 96% yield of the 3:1 complex. Starting with 0.04 mole of the lactam and 0.02 mole of catechol the yield was 5.55 g (92% for the 3:1 complex) of the same compound; m.p. 53–55° after two recrystallizations. The analytical results, in particular the value for %N, are consistent only with the 3:1 complex. The calculated %N's are 6.27 for the 1:1 complex, 8.32 for the 2:1 complex and 9.35 for the 3:1 complex, to be compared with the 9.00 value found. Gc analysis of this product was in precise agreement with the 3:1 assignment for the lactam–phenol ratio.

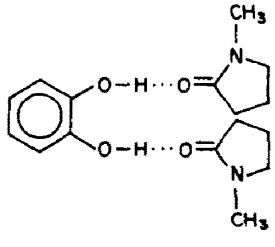
Of even greater interest is the complex from 2-pyrrolidinone and catechol, with its 4:3 lactam–phenol ratio, a value which properly induces skepticism. The complex was prepared from ether–hexane or ether–acetone–hexane with 2-pyrrolidinone and catechol in initial molar ratios of 1:2, 1:1, 3:2 and 2:1 and recrystallized from the same solvent combinations. All the preparations led to the same solid complex; m.p. 44–46° after recrystallization. The yields were in all cases reasonable, e.g. 79% when starting with the reactants in a 1:1 molar ratio and 57% when the starting materials were in a molar ratio of 2:1. The analytical values shown in Table 1 are consistent with the 4:3 lactam–phenol ratio, and this ratio was confirmed by gc analysis.

It is conceivable that the complex as prepared above is a constant mixture of the 1:1 complex and the 2:1 complex, with the two present in a molar ratio of 2:1. To assure ourselves that this is not the case, the complex was prepared from acetonitrile–hexane and recrystallized from acetonitrile–hexane. In addition samples of the complex, originally prepared from ether–hexane, were recrystallized from acetone–hexane, from 2-propanol–hexane and from benzene–hexane. In these recrystallizations, seeds were needed to induce crystallization, but the amount of hexane added was limited to ensure slow crystallization and prevent the amount recovered from exceeding 75% of the starting materials. In no case was the melting point or composition of the complex altered. By gc analysis the complex prepared from ether–acetone–hexane was found to have a lactam–phenol ratio of 3.98 ± 0.01 to 3. For the preparation from acetonitrile–hexane the ratio obtained from gc was 3.93 ± 0.02 to 3. The sample prepared in ether–hexane gave lactam–phenol ratios of 3.97 ± 0.01 to 3 after recrystallization from acetone–hexane and 3.95 ± 0.02 to 3 after recrystallization from 2-propanol–hexane. These results support the conclusion that the 2-pyrrolidinone–catechol complex is a single, pure compound having a lactam–phenol ratio of 4:3.

To obtain structural information on these complexes attention was focused on the lower melting complexes, where the IR spectrum of the complex could be obtained NEAT as a melt. In addition, IR spectra of the starting materials for these complexes and the complexes themselves were obtained in carbon tetrachloride using a 1.0 mm sealed cell. In these studies attention was focused on the range 4000–3000 $cm^{-1}$.

The simplest case is represented by the 2:1 NMP–catechol complex. In carbon tetrachloride NMP shows no absorption in the 4000–3000 $cm^{-1}$ range. At half the above NMP concentration catechol shows two sharp absorption bands of almost equal intensity (free OH at 3617 $cm^{-1}$ and H-bonded OH at 3568 $cm^{-1}$). In the spectrum of the complex, the intensity of the doublet due to the OH groups in catechol is decreased significantly, and a new, broad absorption band, with a maximum at ~3200 $cm^{-1}$, appears in the spectrum. In the spectrum of the complex as a melt, the bands due to the catechol OH groups have disappeared and only the broad band centered at 3200 $cm^{-1}$ remains.

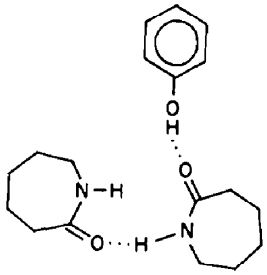
These observations are fully consistent with a structure for the complex in which catechol and two NMP molecules are held together by two "weak" O–H...O H-bonds[14] as shown in I.




I

For the 2:1 ε-caprolactam–phenol complex as well, only a H-bonded structure is probable. In dilute carbon tetrachloride phenol shows a single absorption at 3614 $cm^{-1}$ (free OH stretching). ε-Caprolactam shows four absorptions in the N–H stretching region—a very sharp absorption at 3430 $cm^{-1}$ (free N–H) and slightly

broader absorptions at 3300, 3215 and 3085 $cm^{-1}$ (H-bonded NH). In the solution spectrum of the complex, the absorption at 3614 $cm^{-1}$ is greatly decreased, the absorption at 3430 $cm^{-1}$ is not noticeably changed, and the remaining three bands in the 3300–3085 $cm^{-1}$ region are broadened. In the spectrum of the melt the absorptions due to free OH and free NH are gone, and a single broad band from 3300 to 3200 $cm^{-1}$ is observed. All of these lactam–phenol complexes are held together by weak H-bonds,[14] and a reasonable representation for the 2:1 $\epsilon$-caprolactam–phenol structure is II.

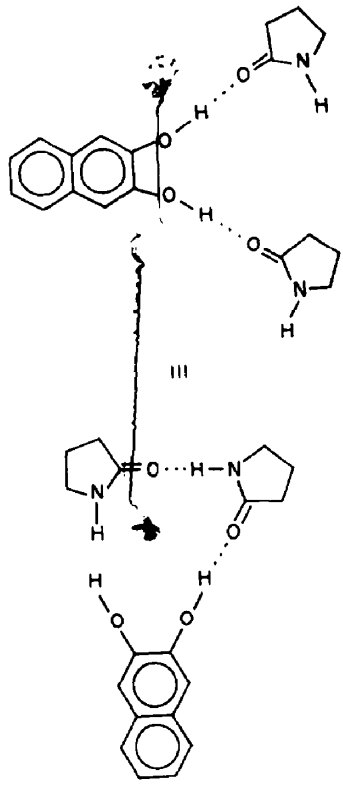


II

The 3:1 $\epsilon$-caprolactam–catechol complex in solution shows spectral characteristics which are superficially similar to those observed with the above phenol complex. There is a significant decrease in the intensity of the catechol doublet, the free N–H absorption at 3430 $cm^{-1}$ is not noticeably altered, and the bands in the 3300–3000 $cm^{-1}$ region are broadened. In the melt the catechol doublet and the band for free NH are absent. One observes three centered at 3290, 3230 and 3080 $cm^{-1}$ effectively merged into one broad band. A reasonable structure would have one catechol OH H-bonded to an $\epsilon$-caprolactam molecule and the other OH H-bonded to an $\epsilon$-caprolactam dimer.

The 2-pyrrolidinone-2,3-naphthalenediol complex and the 2-pyrrolidinone–catechol complex have similar IR spectral characteristics despite the fact that the former is a 2:1 complex and the latter a 4:3 complex. In carbon tetrachloride the 2,3-naphthalenediol spectrum is similar to the catechol spectrum in the region 4000–3000 $cm^{-1}$—two peaks of nearly equal intensity at 3605 $cm^{-1}$ (free OH) and 3563 $cm^{-1}$ (H-bonded OH). 2-Pyrrolidinone shows three bands in the NH stretching region—a very sharp absorption at 3460 $cm^{-1}$ (free NH) and two slightly broader bands at 3200 and 3110 $cm^{-1}$ (H-bonded NH). In the solution spectra for both complexes the OH absorptions are significantly diminished in intensity and the remaining bands (3460–3110 $cm^{-1}$) are broadened. As melts, the two complexes provide spectra in the 4000–3000 $cm^{-1}$ region similar enough to be superposable. In both cases the OH bands are not seen, and a strong, broad absorption band at 3300–3200 $cm^{-1}$ appears.

These results suggest that the lactams and phenols in these complexes are held together by bonds of the same general type and strength, and that these bonds are weak H-bonds (O–H...O, OH...N or N–H...N). For the 2:1, 2-pyrrolidinone-2,3-naphthalenediol complex, III, which has two O–H...O H-bonds, or IV, which has one O–H...O bond and one N–H...O bond, can be suggested.



III IV

In either case, the joining bonds are weak H-bonds, and our results do not permit a choice between III and IV. For the 4:3 2-pyrrolidinone-catechol complex we would suggest V, where P is a

P–C–P–C–P–C–P

V

2-pyrrolidinone and each C a catechol. Each P–C bond would be an O...H–O bond, and each C–P bond would be an OH...N bond. It should, of course, be recognized that other modes of organization for the lactams and phenols in the complex are possible, and that the actual organization is determined by crystalline dimensions and geometric considerations not presently available to us. The one thing clearly indicated by the results is that the joinings are via weak H-bonds.

Structures II, III, IV and V all have been written with a free NH or OH bond, despite the fact that no free NH or OH is observed in the IR spectra of the melts. It is conceivable that these structures should contain an additional H-bond so that no free NH or OH remains. It is, however, more probable that these free NH or OH bonds are tied up in intermolecular rather than intramolecular H-bonds.

## EXPERIMENTAL

*Materials.* 2-Pyrrolidinone, Eastman practical grade, was distilled *in vacuo*; b.p. 121° at 8 mm. N-Methylpyrrolidinone, Baker analyzed, was distilled at 14 mm; b.p. 92–94°. $\epsilon$-Caprolactam, Eastman practical, was crystallized from hexane; m.p. 68–70°. Catechol, Eastman, was crystallized from benzene; m.p. 103–105°. Hydroquinone, Eastman, was crystallized from water; m.p. 174–176°. 2,3-Naphthalenediol, Aldrich, was crystallized from MeOH–water; m.p. 164–165°. Phenol, Mallinckrodt AR, was

sublimed *in vacuo*; m.p. 37–40°. *o,o'*-Biphenol, Aldrich, was crystallized first from MeOH–water and then from toluene; m.p. 109–110°. Resorcinol, Eastman, was used as received.

*The N-methylpyrrolidinone-o,o'-biphenol complex.* This procedure is typical. A soln of *o,o'*-biphenol (9.3 g; 0.05 mole) in ether was treated with N-methylpyrrolidinone (10.3 g; 0.104 mole). Hexane was added until a slight turbidity appeared. The soln was cooled in the freezer, where white crystals slowly appeared. The yield was 12.7 g (89%) of the 1:1 complex; m.p. 65–67°.

*Gc studies.* A Hewlett-Packard Model 5840 microprocessor based gas chromatograph was used. The column, a 6 ft × 1/8 in. OD SS, 10% OV-101 on 80/100 chromosorb WHP was used isothermally at either 150° or 180° with helium at 25 ml/min as the carrier gas and flame ionization detection.

For quantitative studies standard solns of the starting materials were prepared in a suitable solvent, either acetone or MeOH, and compared chromatographically to a soln of the complex in the same solvent. The HP5840GC is a self-calibrating instrument requiring only that a standard be run and the composition entered through the keyboard for calibration. A standard soln was prepared containing each of the components of interest at known concentrations approximating those expected on the sample being analyzed. A response factor normalization technique was used to correct for differences in detector behavior, and area rejection coupled with time programming was used to reject the solvent peak.

*IR measurements.* A Perkin–Elmer Model 281B IR Spectrophotometer was used. The soln spectra in $CCl_4$ were obtained using a 1.0 mm sealed liquid cell. Spectra were obtained of the complexes and of the individual components.

For those complexes, which are low-melting solids the spectra were also obtained NEAT as melts. Samples were prepared by placing a small amount of the complex on a NaCl plate and warming under an IR lamp until the complex melted. The sample was then treated as a normal liquid sandwiched between NaCl plates. The spectra were taken immediately, and heat in the sample compartment was sufficient to maintain the liquid state throughout the IR scan.

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