Rearrangements in the Furan Series. IV* The Reaction Between Furan-2carbaldehyde and Aniline

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Abstract

It has been shown that reaction of furan-2-carbaldehyde with three or four molecules of aniline gives rise to a substance assigned as 4-phenyl-1,6-di(phenylamino)-7-phenylimino-3a,4,4a,7,7a,7b-hexahydro-1*H*-dicyclopenta[*b*,*d*]pyrrol-2(3*H*)-one rather than the simple anil previously proposed. The use of an excess of furan-2-carbaldehyde gives not furoin anil but a compound of polymeric structure.

Introduction

The reaction of furan-2-carbaldehyde (1 mole) with aniline (2 mole) has been examined by various groups.^{1–5} In particular, the Russian workers assigned to the major product of this reaction the heterocyclic structure (1). On the basis of further evidence we established^{4,5} that the product has the structure 2,4-dianilinocyclopent-2-enone (2). Barvinok, Platonov, Kuprik and Bukhareva^{6,7} also examined the products formed when furan-2-carbaldehyde was treated with other molar proportions of aniline, and claimed to have isolated definite compounds with several ratios of reactants. With a 1:1 ratio, the anil of furan-2-carbaldehyde was formed as expected. With increasing amounts of amine (1:3 and 1:4) a new crystalline compound was isolated in relatively



* Part III, Aust. J. Chem., 1987, 40, 509.

¹ McGowan, J. C., J. Chem. Soc., 1954, 4032.

² Rombaut, J., and Smets, G., Bull. Soc. Chim. Belg., 1949, 58, 421.

³ Barvinok, M. S., Kuprik, V. S., Mazurek, V. V., and Semenov, G. I., *Zh. Obshch. Khim.*, 1961, **31**, 632.

⁴ Lewis, K. G., and Mulquiney, C. E., Chem. Ind. (London), 1968, 1249.

⁵ Lewis, K. G., and Mulquiney, C. E., Aust. J. Chem., 1970, 23, 2315.

⁶ Barvinok, M. S., Platonov, A. P., Kuprik, V. S., and Bukhareva, I. S., *J. Org. Chem., U.S.S.R.*, 1967, **3**, 1065.

⁷ Barvinok, M. S., Platonov, A. P., Kuprik, V. S., and Bukhareva, I. S., *Zh. Org. Khim.*, 1967, **3**, 1107.

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low yield and was considered to be the anil of the pyrrolinone (1). The use of a ratio of 2 mole of furan-2-carbaldehyde to 1 mole of aniline gave a product which was designated as furoin anil (3).

Discussion and Results

We were intrigued by several aspects of the above work. It was possible that the compound obtained by using the 1 : 3 ratio of aldehyde to amine was simply the anil (4) derived from the cyclic ketone (2) but Barvinok *et al.*^{6,7} in discussing their assignment stated that they were unable to obtain the anil by reaction of aniline with the compound to which they had assigned structure (1). The analyses which were reported were in agreement with such an anil structure and in discussion of the i.r. spectrum of the product they stated that it 'has absorption bands at 1648, 1621 and 1596 cm⁻¹ belonging to C=C vibrations, but lacks bands of the stretching vibrations of a carbonyl group and exhibits an absorption band at 1648 cm⁻¹ apparently corresponding to the vibrations of the C=N group (Fig. 3)'. We thought that the latter frequency might be a translation misprint for 1748 cm⁻¹ as the quoted Fig. 3 shows an intense absorption peak at *c.* 1750 cm⁻¹, but the same value appears in both the original Russian publication⁷ and the translated version.⁶

Whether or not the quoted value of 1648 cm⁻¹ (which could well be assigned to C=N) was intended, we considered that the recorded absorption peak at c. 1750 cm⁻¹ could be assigned more satisfactorily, in line with our previous work,⁴ to a cyclopentanone carbonyl absorption. This would require that the compound contain oxygen.

We had some difficulty in repeating the preparation of the 'anil' but finally obtained material⁸ that showed similar physical properties to those quoted, including an i.r. spectrum identical with that reported^{6,7} earlier. The m.p. of our product, R, was somewhat higher than that reported but was dependent on the rate of heating, and decomposition occurred at the m.p. We consider that the identity of the i.r. spectra establishes that our compound is the same as that obtained in the previous work.^{6,7} Compound R analysed for $C_{34}H_{30}N_4O$ (confirmed by accurate mass mol. wt measurement). If the substance (2) is presumed to be an intermediate then this indicates the involvement of two C_{17} units rather than one C_{17} plus a molecule of aniline. The i.r. spectrum showed bands at 3398 and 3328 cm⁻¹ assigned to NH, and absorption at 1751 (CO of cyclopentanone), also at 1653 and 1628 (C=N and C=C), and 1603 cm⁻¹ (aromatic C=C). The mass spectrum showed intense ions at positions expected for M–PhNH, M–PhNH₂ and PhNH₂, but lacked an ion corresponding to M–CO.



⁸ Mulquiney, C. E., Ph.D. Thesis, University of New England, 1971.

The loss of PhNH and PhNH₂ is typical of the β -anilino ketone portion of compounds of structure (2), while the failure to observe loss of CO speaks against structures such as (5) and similar isomers based on Diels–Alder addition of compound (2) with 2-anilinocyclopentadienone followed by anil formation.

Based on the assumption that all four nitrogen atoms derive from aniline residues, 24 carbon atoms are required and the remaining 10 could sensibly derive from two furan-2-carbaldehyde units. On a similar basis, 10 non-aromatic protons need to be accounted for. Initial ¹H n.m.r. spectra indicated the presence of 9 non-aromatic protons but these spectra were complicated by the presence of a large HOD peak from the solvent. Spin-decoupling experiments indicated the presence of a further proton, and subsequent shifting of the HOD peak revealed the presence of an extra one-proton triplet signal at $\delta 3.48$. Deuterium-exchange experiments led to the rapid disappearance of a doublet at $\delta 4.22$ (J 7 Hz) and, more slowly, of a singlet at 7.68. This behaviour is paralleled by the ease of exchange of the NH protons of the 2,4-dianilino compound (2) where the 4-NH (identified by its coupling to H4 and the downfield shift of the signal of H4 when the 4-anilino group was $acetylated^{5}$) exchanged rapidly while exchange of the NH attached to the ethylenic carbon α to the carbonyl group is much slower.⁹ The deuterium exchange also led to the simplification of the triplet at $\delta 3.48$ (splitting 8 Hz) which then appeared as a broad doublet (splitting c. 8.5 Hz). Such coupling between HN and CH is again common in the simpler compounds (2).8,9

Progressive spin decoupling experiments beginning with irradiation at $\delta 6 \cdot 16$, converted the doublet of doublets at $5 \cdot 42$ into a doublet (J 6 Hz) and subsequent irradiation at 5.42 led to collapse of the doublet of doublets at 3.81 (J 6, 2.8 Hz) to a doublet (J 2.8 Hz). Irradiation at δ 3.81 simplified the complex multiplet (intensity 2H) at 2.66. This multiplet was also simplified by irradiation at $\delta 2 \cdot 18$ (d, J 19 Hz). The removal of the large coupling left a residual doublet (J 6·4 Hz) at δ 2·70 and enabled the second proton coupled to that at 3.81 to be located as a multiplet centred on 2.66. Spin decoupling of the broadened triplet (splitting c. 6.5 Hz) at δ 4.14 converted the doublet of doublets (J 19, 6.4 Hz) at 2.70 into a doublet (J 19 Hz) while the signal at 2.66 (partly obscured) simplified, and the signals at 3.48and 2.18 sharpened. Irradiation of the broad triplet at δ 3.48 converted the doublet of the exchangeable NH proton at 4.22 into a singlet, and simplified the multiplet at 2.66 so that the doublet of doublet pattern of the proton absorbing at 2.70 became apparent, and also sharpened the pattern of the signal at $4 \cdot 14$.

The above connectivities were confirmed by a ${}^{1}H{}^{-1}H$ proton correlated spectrum (cosy-45).

The ¹³C n.m.r. spectrum was dominated by the signals of the 24 aromatic carbons but the signal at δ 212 was assigned to a five-membered ring carbonyl group while that at 171 was assigned as C=N.¹⁰ In the fully coupled spectrum, five singlets were observed in the region δ 140–150 and four were assigned as aromatic quaternary carbons. The fifth, a sharp singlet at δ 141·0, was

⁹ D'Arcy, B. R., Ph.D. Thesis, University of New England, 1987.

¹⁰ Pretsch, E., Clerc, T., Seibl, J., and Simon, N., 'Spectral Data for Structure Determination of Organic Compounds' p. C90 (Springer Verlag: Berlin 1983).

assigned as a quaternary vinyl carbon shifted to lower field by the attachment of nitrogen.¹⁰ The ¹H–¹³C correlated spectrum showed that a further vinyl carbon absorbing at δ 111.5 was coupled to the protons absorbing at 6.16 and also confirmed the presence of five saturated methine carbons and one methylene carbon, and enabled assignment of all the aliphatic carbon resonances and their attached protons to be made.

Taking into account the four anilino residues and the evidence for three other units of unsaturation, the formula $C_{34}H_{30}N_4O$ requires that R be tricyclic. The infrared absorption at 1750 cm⁻¹ and the carbonyl resonance at δ 212 indicate the presence of a saturated cyclopentanone ring and the large geminal coupling constant for the protons absorbing at δ 2.18 and 2.70 establishes the methylene group as adjacent to the carbonyl.¹¹ These protons are coupled to that absorbing at δ 4.14 and this is coupled to the proton absorbing at 2.66 which is, in turn, coupled to that resonating as a doublet at 3.48 after deuterium exchange. The latter proton has no further direct coupling, which agrees with its attachment to the other carbon adjacent to the carbonyl group of the cyclopentanone ring. The low-field chemical shift (δ 4.14) of the proton vicinal to the methylene protons requires the attachment also of an electronegative group to this carbon and so part-structure (6a) may be assigned.



The doublet absorbing at $\delta 6.16$ is assigned to a vinyl proton (in agreement with its coupling to the carbon absorbing at 111.5) and this proton is coupled only to the proton absorbing at 5.42 (J 2.5 Hz). This coupling is too small to represent a *cis* coupling between two vinyl protons so, in agreement with the presence of a quaternary vinyl carbon in the ¹³C spectrum, the proton at $\delta 5.42$ is assigned as attached to a saturated carbon. The chemical shift position is attributed to its attachment to an allylic carbon bearing a nitrogen atom. The allylic proton is coupled to that resonating at $\delta 3.81$ which in turn is coupled to the proton of the cyclopentanone ring absorbing at 2.66.

Since the readily exchangeable NH has already been placed on C1 (6a) and the slowly exchanging NH is considered to be attached to a vinyl carbon, the nitrogen attached at C3a and that attached at the allylic carbon must be fully substituted. As only four nitrogens are available, a single nitrogen must fulfill both functions and part-structures (6b) and (6c) are proposed.

Attachment of the ArN=C grouping to the remaining free carbon valencies gives two possible structures (7a) and (7b) for R.

The vicinal coupling $(2 \cdot 5 \text{ Hz})$ between H4a and H5 in (7a) is similar to that (3 Hz) observed in the analogous system of (2), while in (7b) the size of the

¹¹ Cookson, R. C., Crabb, T. A., Frankel, J. J., and Hudec, J., Tetrahedron, Suppl., 1966, 7, 355.

allylic coupling between H4a and H6 would require that rather favourable conditions for allylic coupling be present. This would appear not to be so as the conformation in the model of (7b) does not seem to be particularly favourable and in addition electron delocalization, which is possible with the anilino group at C5, would be expected to give a value of the allylic coupling of 1 Hz or less.¹²



The ¹H chemical shift values of the two vinylic protons of (7a) and (7b) would also be expected to be substantially different. The values calculated from the empirical rules of Simon and coworkers¹³ for the corresponding carbonyl systems (C=O for C=NPh) are $\delta 6.3$ for H5 in the (7a) analogue and 5.45 for H6 for the (7b) analogue. The observed value for H5 of $\delta 6.16$ is in better agreement with (7a). The slow exchange of the proton of the NH at C6 in (7a) parallels that of the 2-NH of (2) whereas the 5-NH of (7b) is part of the nitrogen analogue of the enolic form of a β -diketone and as such should exchange its proton readily. In a model compound, 5,5-dimethyl-3-phenylaminocyclohex-2-enone, the vinyl proton absorbed at $\delta 5.35$, the allylic coupling between H2 and H4 was *c*. 1 Hz and the NH proton underwent rapid deuterium exchange.

Compound R is thus assigned structure (7a) and named as 4-phenyl-1,6di(phenylamino)-7-phenylimino-3a,4,4a,7,7a,7b-hexahydro-1*H*-dicyclopenta[*b*,*d*]pyrrol-2(3*H*)-one.

The ${}^{1}H{-}^{13}C$ correlated spectrum is in agreement with structure (7a) and the connectivities obtained from a ${}^{1}H{-}^{13}C$ correlated spectrum optimized for long-range couplings indicated that both protons attached to C3 were coupled to the carbonyl carbon while the proton absorbing at $\delta 2 \cdot 18$ was also coupled to C3a. In addition, the vinyl proton H 5 was coupled to the carbon absorbing at $\delta 171$. The assigned geometry is based upon the magnitudes of the couplings at the ring junctions and the observation of a long-range coupling (c. 1 Hz) of protons H1 and H3a, indicating approach to a favourable planar W conformation. It is of interest to note that the same product (7a) is obtained when 3 or 4 mole of aniline are used for each mole of initial aldehyde and that the product, in fact, requires an aldehyde to amino ratio of only 1 : 2.

A reexamination of the preparation⁵ of the cyclopent-2-enone (2) by using the 1:2 ratio led to the isolation of a small amount of product (7a).

A tentative mechanism for the formation of (7a) is outlined in Scheme 1. Compound (2) forms quite rapidly from furan-2-carbaldehyde and aniline at

¹² Rottendorf, H., and Sternhell, S., Aust. J. Chem., 1964, 17, 1315.

¹³ Matter, U. E., Pascual, C., Pretsch, E., Pross, A., Simon, N., and Sternhell, S., *Tetrahedron*, 1969, **25**, 691.

room temperature.⁵ It is postulated that (2) then undergoes self-condensation in a fashion similar to the observed displacement of the 4-arylamino group of the *p*-methyl homologue of (2) by other aromatic amines¹⁴ to form a product with a new 4-arylamino substituent. It should be noted that while the 4-anilino substituent of (2) functions as a normal secondary amine and may be readily acylated, the 2-anilino group is unaffected, presumably as it is part of the enamine system.⁵ In consequence, reaction between two molecules of (2) involves loss of the 4-anilino group of one molecule and attack upon the more reactive 4-anilino group of the other to form the condensation product (8). It is proposed that ring closure occurs through the enamine system¹⁵ as indicated to give initially the tricyclic system (9). It is known that cyclopentane-1,2-dione, because of unfavourable electrostatic repulsions, exists as 2-hydroxycyclopent-2-enone^{16,17} and presumably the adjacent carbonyl equivalents in (9) would be also disfavoured. It is predicted that formation of a double bond to the carbon of the ring junction would introduce a degree of strain not present if it was the carbonyl group which enolized. Finally, in the presence of an excess of aniline the enol would be converted into the enamine.^{5,8}

Repetition of the reaction carried out by Barvinok *et al.*^{6,7} with aldehyde/amine in the ratio of 2:1 produced a brown resinous product sparingly soluble in methanol but readily soluble in chloroform. The Russian workers quoted m.p. 230–235° with analysis $C_{16}H_{13}NO_3$ and claimed their product had an i.r. spectrum identical with that of furoin anil (3) which they described as a brown powder, m.p. 130–135°, 'similar in appearance to the resin obtained above'.



- ¹⁴ D'Arcy, B. R., Lewis, K. G., and Mulquiney, C. E., Aust. J. Chem., 1987, 40, 509.
- ¹⁵ Szmuszkowicz, J., in 'Advances in Organic Chemistry' (Eds R. A. Raphael, E. C. Taylor and H. Wynberg) p. 1 (Interscience: New York 1973).
- ¹⁶ Cumper, C. W. N., Leton, G. B., and Vogel, A. I., J. Chem. Soc., 1965, 2067.
- ¹⁷ DePuy, C. H., Lyons, C. E., and Rodewald, L. B., J. Chem. Eng. Data, 1966, 11, 102.

In our hands 'furoin anil' formed orange-yellow crystals (m.p. 95°) which were quite soluble in methanol. The i.r., ¹H n.m.r. and mass spectra showed that it possessed not the hydroxy anil structure (3) but the α -phenylamino ketone structure (10) as has been established in other similar cases.^{18–20}

The ketone (10) showed in its i.r. spectrum a typical aromatic carbonyl absorption at 1663 cm⁻¹ while that of the brown product had a weak broad band at 1710 and an intense peak at 1610 cm⁻¹, presumably corresponding to aromatic C=C. The two spectra were quite different and that of the α -phenylamino ketone showed sharp absorption bands while the peaks for the brown product were quite broad.

The methanol-insoluble residue was chromatographed over alumina. Early and late fractions did not melt below 300° and showed closely similar i.r. spectra. A further portion of the insoluble resin was purified by precipitation from chloroform solution, when it analysed for $C_{28}H_{29}NO_5$ but gave a mol. wt (osmometric) of 2000.

A portion of the whole resin was subjected to flash chromatography over silica and the major fraction further chromatographed. The first major fraction showed mol. wt 750 with later ones giving values rapidly rising to 1800.

The ¹H n.m.r. spectra (300 MHz) of the methanol-soluble and methanolinsoluble portions of the resin showed only broad unresolved absorption in the region δ 6–8. The ¹³C n.m.r. spectrum of the insoluble material also showed only broad unresolved signals in the aromatic region.

The material isolated by treating furan-2-carbaldehyde (2 mole) with aniline (1 mole) is thus not 'furoin anil' and would appear to be a mixture of polymer types, and no further investigation of it is proposed.

Experimental

General

For experimental details see an earlier paper.⁵ N.m.r. spectra were recorded on a Jeol JNM FX 200, a Bruker 270 or, more recently, on a Bruker AC-300 spectrometer. Molecular weights were determined on a Knauer vapour pressure osmometer with chloroform as solvent.

Isolation of 4-Phenyl-1,6-di(phenylamino)-7-phenylimino-3a,4,4a,7,7a,7b-hexahydro-1H-dicyclopenta[b,d]pyrrol-2(3H)-one (7a) from Reaction of Furan-2-carbaldehyde with an Excess of Aniline

To a mixture of furan-2-carbaldehyde (6.5 ml, 0.078 mol) and aniline (25 ml, 0.275 mol) was added conc. HCl (1 drop). The mixture, which became deep red and warmed up, was allowed to stand with occasional shaking for 4 h. The dark oil was then warmed on the water bath for 30 min and allowed to stand for 1 month. The resultant viscous gum was diluted

¹⁸ Julian, D. L., Meyer, E. W., Magnani, A., and Cole, W., *J. Am. Chem. Soc.*, 1945, **67**, 1203.
¹⁹ Cowper, R. M., and Stevens, T. S., *J. Chem. Soc.*, 1940, 347.
²⁰ Heyns, K., and Stumme, W., *Chem. Ber.*, 1956, **89**, 2833.



with acetone and stirred for several hours and the solution filtered. The insoluble residue was washed well with cold acetone to give $4 \cdot 3$ g of off-white solid. This material crystallized nicely from a large volume of acetone or from nitromethane. Several recrystallizations from acetone gave 4-phenyl-1,6-di(phenylamino)-7-phenylimino-3a,4,4a,7,7a,7b-hexahydro-1Hdicyclopenta[b,d]pyrrol-2-(3H)-one (7a) as fine pale pink needles, m.p. 248-250° (dec.). T.l.c. of this product on silica showed that it was homogeneous. It had $R_F 0.49$ with benzene/chloroform (1:1) as solvent, 0.69 with chloroform and 0.81 with acetone/benzene (1:10) (Found: C, 79.9; H, 6.0; N, 10.9; O, 3.5%; M+•, 510.2406. C₃₄H₃₀N₄O requires C, 80.0; H, 5.9; N, 11.0; O, 3.1%; M⁺, 510.2418). ν_{max} 3398, 3328, 1751, 1653, 1628, 1603, 1538, 1504, 1449, 1377, 1302, 751, 690 cm⁻¹. ¹H n.m.r. [(CD₃)₂SO] δ 2 · 18, 1H, d, Jgem 19 Hz, H3; 2.66, 1H, m, J 8.5, 6.5, 2.8 Hz, H7b; 2.70, 1H, dd, Jgem 19, Jvic 6.5 Hz, H3; 3·48, 1H, approx. t, J 8·5, 7, 1 Hz, H1; 3·81, 1H, dd, J 6, 2·8 Hz, H7a, 4·14, 1H, br t, J 6.5, 6.5, 1 Hz, H3a; 4.22, 1H, d, J 7 Hz, NH (exch.); 5.42, 1H, dd, J 6, 2.5 Hz, H4a; 6.16, 1H, d, J 2.5 Hz, H5; 6.3-7.3, m, aromatics; 7.68, 1H, s, NH (exch.). ¹³C [(CD₃)₂SO)] δ 212 · 7, 1C, C 2; 170 · 8, 1C, C 7; 149 · 4, 1C; 147 · 0, 1C; 145 · 9, 1C; 141 · 9, 1C; 141 · 0, 1C, C6; 129.0, 6C (arom., m to N); 128.3, 2C (arom., m to N); 124.0, 1C (arom., p to N); 120.8, 1C (arom., p to N); 119.7, 2C (arom., o to N); 118.2, 1C (arom., p to N); 117.3, 2C (arom., o to N); 116.3, 3C (arom., 2×o to N, 1×p to N); 112.7, 2C (arom., o to N); 111.5, 1C, C5; 65·0, 1C, C4a; 62·0, 1C, C1; 54·6, 1C, C3a; 47·6, 1C, C7b; 43·8, 1C, C7a; plus in C₅D₅N, 40.0, 1C, C3. Mass spectrum m/z 510 (M, 3%), 508 (3), 419 (9), 418 (28), 417 (21), 416 (10), 390 (8), 297 (3), 272 (4), 271 (17), 247 (25), 246 (100), 245 (14), 169 (4), 168 (5), 167 (4), 130 (5), 118 (6), 104 (14), 93 (32), 77 (36), 66 (8), 65 (7), 51 (7).

Reaction Between Furan-2-carbaldehyde (1 mole) and Aniline (2 mole)

The reaction was carried out as described earlier.⁵ The crude material (20 g) that separated from the ether solution was boiled with benzene (100 ml) and the insoluble material was filtered off and washed with hot benzene and then with acetone to give crude (7a) (1 g, c. 5%). Recrystallization from acetone gave pale pink needles, m.p. 246–248° (dec.) identical with compound (7a) above.

Formation of 2-Phenylamino-1,2-di(2-furyl)ethan-1-one (10) from Furoin and Aniline

Initial attempts to prepare 'furoin anil' under the conditions described by Barvinok *et* $al.^{6,7}$ were unsuccessful. In one experiment furoin, m.p. 133°, was recovered. Finally, a modification of the conditions of Heyns²⁰ gave the required product. Furoin (3 · 9 g) and aniline (2 · 0 g) were dissolved in ethanol (35 ml), and conc. HCl (2 drops) was added. The mixture was heated under reflux for 4 h. The cooled solution was neutralized with solid potassium carbonate and then evaporated to dryness under vacuum. The residue was treated with methanol (10 ml) and filtered. The filtrate deposited an orange solid (3 · 6 g) which was recrystallized several times from methanol to give *2-phenylamino-1,2-di(2-furyl)ethan-1-one* (10) as deep yellow needles, m.p. 95–96° (Found: C, 71 · 6; H, 5 · 0; N, 5 · 4. C₁₆H₁₃NO₃ requires C, 71 · 9; H, 4 · 9; N, 5 · 2%). v_{max} 3370, 3120, 1663, 1600, 1580, 1458, 1425, 1395, 1380, 1320, 1295, 1235, 1215, 1150, 1080, 1035, 1015, 990, 800, 780, 740 725 cm⁻¹. ¹H n.m.r. δ 5 · 1, br d, *J* 6 Hz, 1H, NH (exch.); 5 · 9, d, 1H, *J* 6 Hz, C**H**NH; 6 · 23–7 · 67, 11H, complex m, aromatic. Mass spectrum *m/z* 267 (M, 2%), 173 (12), 172 (100), 170 (7), 104 (13), 95 (13), 77 (24), 51 (7), 39 (10). Mol. wt (osmometric) 275.

Reaction Between Furan-2-carbaldehyde (2 mole) and Aniline (1 mole)

Concentrated HCl (1 drop) was added to a mixture of furan-2-carbaldehyde (14.5 g, 0.15 mol) and aniline (6.6 g, 0.072 mol). The mixture became red and then deep brown. After 12 months at room temperature a hard glassy mass had formed which was ground to a powder in a mortar. The brown resin was extracted with cold methanol to give methanol-soluble and methanol-insoluble fractions. No suitable solvent or solvent mixture could be found for the crystallization of these.

(a) The methanol-insoluble material (400 mg) was dissolved in benzene/chloroform (1:1) and chromatographed over alumina (20 g). The fraction eluted with benzene/chloroform

(1:1) did not melt below 300°. I.r. spectrum v_{max} 3350, 1710, 1630sh, 1610, 1510, 1380, 1300, 1160, 1085, 1030, 900, 770, 710 cm⁻¹. The gum eluted with acetone solidified on treatment with methanol. It did not melt below 300° and its i.r. spectrum was identical with that of the first fraction.

(b) The insoluble brown fraction was dissolved in chloroform and precipitated by the addition of methanol. An analytical sample was prepared in this way (Found: C, 73 · 2; H, 6 · 3; N, 3 · 1. Calc. for $(C_{28}H_{29}NO_5)_n$: C, 73 · 2; H, 6 · 4; N, 3 · 1%). Mol. wt (osmometric) 2000. v_{max} 3350, 1710, 1630sh, 1610, 1510, 1380, 1300, 1160, 1090, 1030, 900, 780, 710 cm⁻¹. ¹H n.m.r. δ 6-8, one broad absorption band. ¹³C n.m.r. δ 151, 142, 129, 120–118, 113, 110. The methanol-soluble material was recovered by precipitation with water. The dried solid had mol. wt (osmometric) 750. I.r. spectrum identical with that of the insoluble part. ¹H n.m.r. δ 6-8, broad absorption.

(c) A portion of the whole resin (2 g) was adsorbed on silica (2 g) and placed on top of a silica bed for flash chromatography. The major portion $(1 \cdot 28 \text{ g})$ eluted with 5–50% acetone/chloroform was rechromatographed. Fraction 3 [eluent: chloroform/benzene (3 : 1)] mol. wt 700; fraction 5 (eluent: chloroform) mol. wt 900; fraction 8 [eluent: acetone/chloroform (1 : 20)] mol. wt 1200; fraction 10 [eluent: acetone/chloroform (1 : 1)] mol. wt 1800.

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