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PHOTOLYSIS OF 3,3'-DIAMINO-2,2'-BI-1,4-NAPHTHOQUINONYL

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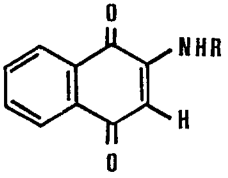
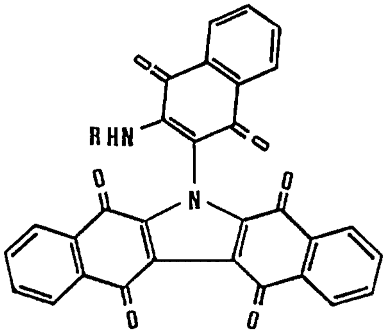
Abstract: *Pyrex filtered sunlight irradiation of an acetic anhydride of 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl unexpectedly led to the formation of 3',3':N,N-bi[3-amino-2,2'-bi-1,4-naphthoquinonyl] which contains only two secondary amino groups. The structure of the photoproduct was elucidated from a FAB mass spectrometric as well as ^{1}H and ^{13}C n.m.r. study.*

Pyrex-filtered sunlight irradiation of an acetic anhydride solution of 2-amino-1,4-naphthoquinone (1, R=H) has been reported[1] to produce the trimeric carbazole derivative 3 (R=H). It has also been shown[1] that photolysis of 1 (R=H) in acetone produces in addition to 3 (R=H) also 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl (6). Irradiation of 2 ($R=CH_3$) in acetic anhydride leads to the formation of 4 ($R=CH_3$) as well as the carbazole derivative 5. It has been observed[1] that the photolysis of 6 in acetone does not produce any photoproducts. These results persuaded us to investigate the photochemical behaviour of 6 in acetic anhydride.

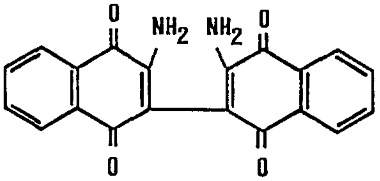


1 R = H
2 R = CH_3



3 R = H
4 R = CH_3

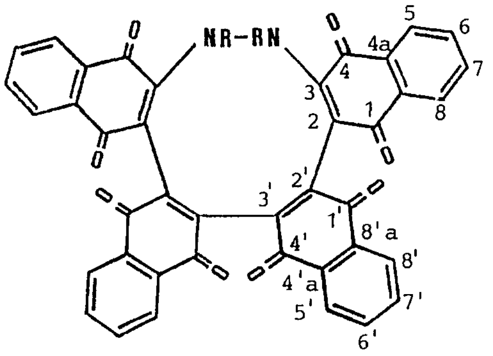
5 R = CH_3



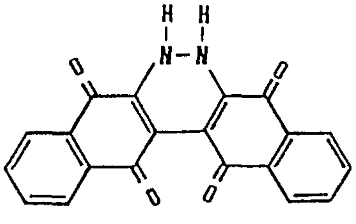
6

Pyrex-filtered sunlight irradiation of an acetic anhydride solution of 6 produced an orange-red product (7) which decomposes at 435°C. The infrared spectrum of 7 exhibits N-H stretching vibrations of secondary amino groups at 3 171 and 3 142 cm^{-1}. An absorption at 3 100 cm^{-1} can be attributed to the C-H stretching vibrations of aromatic rings. Strong carbonylic absorptions at 1 672 and 1 660 cm^{-1} correspond well with the carbonylic absorptions of 2,2'-bi-1,4-naphthoquinonyl (1 666 cm^{-1}) and differs from the carbonylic absorptions of 6 (1 606 and 1 573 cm^{-1}).

To gain more information on the structure of 7, it was subjected to a mass spectrometric investigation. Due to its thermal stability no electron impact (EI) induced spectrum could be obtained. Since the photoproduct 7 is insoluble in the conventional matrices for fast atom bombardment (FAB) mass spectrometric studies, we attempted to obtain a FAB mass spectrum by depositing a solution of 7 in nitrobenzene on a FAB target coated with a mixture (1:1) of glycerol and concentrated sulphuric acid. The sample was bombarded with a 1 mA beam of 8 kV fast xenon atoms generated in a saddle field neutral beam gun. The structurally related species was observed as a [M + H]$^+$ ion and was registered at a m/z value of 655. An elemental analysis corresponded with a molecular composition of $C_{40}H_{18}N_2O_8$. On strength of the above data it was concluded that the photoproduct of 6 probably has the structure 7.



7 R = H
8 R = CH_3



9

Supportive evidence for the correctness of the allocated structure of 7 was obtained from a ^1H and ^{13}C n.m.r. study. Compound 7 is poorly soluble in most organic solvents. Even at 500 MHz an overnight run was required to obtain a ^1H n.m.r. spectrum of 7 in DMSO-d_6 at 303 K. The 300 MHz ^1H and 75 MHz ^{13}C n.m.r. spectra of 7 were therefore recorded at 373 K from a saturated solution in DMSO-d_6 using a 10 mm n.m.r. tube and the appropriate 10 mm n.m.r. probehead. The n.m.r. data of 7 are given in Table 1.

The 300 MHz ^1H n.m.r. spectrum only exhibits two four spin systems (am AMPX and an ABMN spin system) characteristic for two different ortho disubstituted aromatic systems and a signal at δ 6.408 which disappeared on treatment with D_2O and is attributable to the two equivalent nitrogen protons. ^1H-{^1H}decoupling experiments were used to determine the resonances belonging to a specific spin system. The broad band proton decoupled and the nuclear Overhauser enhanced (n.O.e.) proton coupled ^{13}C n.m.r. spectra indicated that 7 consists of at least four carbonyl carbon atoms, eight methine aromatic carbon atoms and eight quaternary carbon atoms. Three of the quaternary carbon atoms exhibit no detectable splittings arising from long range (over more than one bond) (C,H)-couplings while four quaternary carbon atoms appeared as triplets with splittings of *ca* 7 Hz in the n.O.e. proton coupled ^{13}C n.m.r. spectrum. The quaternary carbon resonance at δ_C = 142.85 showed a long range (C,H) coupling of 4.4 Hz which can be originated by the nitrogen atom in 7 bearing one hydrogen atom. The individual proton resonances were correlated with the methine carbon signals from an off-resonance proton decoupled ^{13}C n.m.r. experiment. From these results it could be concluded that the two sets of six carbon atom resonances (four methine carbon resonances and two quaternary carbon signals) must arise from disubstituted aromatic rings. If the carbon signals observed for 6 (see Table 1) and those reported for 3[1] and substituted 1,4-naphthoquinones[2] are considered, 7 must consist of two different 1,4-naphthoquinone moieties. The observed ^{13}C chemical shifts of δ_C = 142.85 and δ_C = 118.07 for two quaternary carbon atoms are characteristic for an 2-amino-1,4-naphthoquinone moiety. The two quaternary carbon resonances at δ_C = 125.01 and δ_C = 135.71 which appear as singlets with no detectable long range couplings in the n.O.e. proton coupled ^{13}C n.m.r. spectrum must arise from a 1,4-naphthoquinone moiety bearing no electronegative substituents. It is clear that the n.m.r. data can only be explained if 7 exists as a dimeric compound as proposed.

Unambiguous assignments of all the ^1H and ^{13}C n.m.r. resonances could not be obtained because of the low solubility of 7 although the proton resonances have been correlated with the methine carbon resonances. If one assumes[1] that the aromatic proton resonating at lowest field for each naphthoquinone moiety are the C-5 and C-5'(C-8') protons then the assignment for the proton resonances and methine carbon resonances as given in Table 1 is obtained.

Table 1 ^{1}H and ^{13}C n.m.r. data[a] of 6 and 7

		7			6[f]		
Carbon	Assignment[c]	δ_C^b(ppm)	^1J(Hz)	$^{>1}J$(Hz)	δ_C^b(ppm)	^1J(Hz)	$^{>1}J$(Hz)
C = O	1	180.11 Sd		4.0	191.13 Sm		
	4	172.44 S			179.11 S		
	1'	175.23 Sdd		4.2			
	4'	177.11 Sm					
Quaternary	2	118.07 S			107.38 S		
	3	142.85 Sd		4.4	146.58 S		
	4a	131.63 St			130.37 St		6.7
	8a	133.56 St			133.52 St		6.8
	2'	125.01 S					
	3'	135.71 S					
	4'a	128.24 St					
	8'a	130.00 St					
Methine	5	123.86 Dd	165	7	124.71 Dd	165.7	7.1
	6	134.54 Dd	164	7	131.11 Dd	162.5	7.3
	7	129.71 Dd	164	7	133.52 Dd	163.7	7.9
	8	128.78 Dd	166	7	124.94 Dd	165.1	7.0
	5'	126.14 Dd	165	7			
	6'	132.71 Dd	162	7			
	7'	133.48 Dd	164	7			
	8'	125.19 Dd	166	7			

H-proton		$\delta_H^{d,e}$(ppm)	δ_H^d(ppm)	J(Hz)	δ_H(ppm)	J(Hz)
	5	8.358	8.426	1.4	8.105	
	6	7.765	7.773	7.6	7.705	7.4
	7	7.529	7.566	7.3	7.786	
	8	7.955	7.990	1.9	7.964	
	5'	8.096	8.107	7.3		
	6'	7.797	7.813	1.8		
	7'	7.847	7.851	1.8		
	8'	8.096	8.121	7.3		
	NH	6.408	6.783			

[a] Solvent $(CD_3)_2SO$; temperature 373 K; 300 MHz for ^{1}H and 75 MHz for ^{13}C except where otherwise indicated.

[b] Relative to internal TMS; measured from internal $(CD_3)_2SO$ and corrected by using the expression $\delta(TMS) = \delta[(CD_3)_2SO] + 39.5$. Symbols in capital letters refer to patterns resulting from directly bonded protons and lower case letters to (C,H)-couplings over more than one bond. S = singulet, D or d = doublet, t = triplet and m = multiplet.

[c] Suggested assignments. See text.

[d] Relative to internal TMS; measured from internal $(CD_3)_2SO$ and corrected by using the expression $\delta(TMS) = \delta[(CD_3)_2SO] + 2.49$.

[e] 500 MHz; 303 K.

[f] The n.m.r. resonances of 6 are given next to the carbon atoms which correspond with those of 7.

Support for the correctness of the allocated structure of 7 was obtained from methylation[3] and pyrolysis experiments. Treatment of 7 with formaldehyde and an excess of formic acid at 100°C produced 8 in high yield. The FAB mass spectrum (glycerol-sulphuric acid-nitrobenzene matrix) of 8 showed a pseudo molecular ion ($[M+H]^+$) at m/z 683 indicating that both amino groups in 7 suffered methylation. The infrared spectrum of 8 exhibits no absorptions in the 3 100 - 3 400 region confirming that alkylation indeed occurred on both amino groups. Characteristic methyl group absorptions appear at 2 927 and 1 376 cm^{-1}.

Additional support for the structure of 7 was obtained from pyrolysis of 7 at 450°C. Only one pyrolysis product could be isolated. The mass spectrum of the pyrolysis product shows a molecular ion at m/z 342. The infrared spectrum exhibits absorptions bands at 1 639 and 1 688 cm^{-1} associated with two different carbonyl groups as well as an absorption at 3 271 cm^{-1} which can be attributed to the N-H-stretching vibrations of a secondary amino group. The 300 MHz ^1H n.m.r. spectrum (DMSO-d_6) only exhibits resonance signals characteristic of ortho disubstituted aromatic systems (δ 7.950 - δ 8.358) and a signal at δ 6.41 which disappeared on treatment with D_2O and can be assigned to exchangeable nitrogen protons. On strength of the above data, as well as an elemental analysis which corresponds with a molecular composition of $C_{20}H_{10}N_2O_4$, structure 9 was allocated to this product.

Attempts to acetylate both the amino groups in 7 failed, probably as a result of steric hindrance.

EXPERIMENTAL

Infrared spectra (KBr disc) were recorded on a Nicolet 5 DX FT-spectrophotometer. FAB mass spectra were recorded on a VG Analytical 7070-E mass spectrometer equipped with a Ion-Tech FAB gun, operating at 8 keV accelerating potential, resolving power approximately 1000 and scanned at 10 s per decade in the positive ion mode. Elemental analyses were performed on a Hewlett-Packard analyser. N.m.r. spectra were recorded on a Bruker WM 500 FT and a Bruker AC 300 spectrometer as indicated.

Photolysis of 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl (6)

A solution of 6 (0.5 g) in acetic anhydride (200 cm^3) was sealed in Pyrex test tubes and exposed to direct sunlight for a period of 5 days. The orange-red crystalline product was filtered off, refluxed in acetone to remove impurities and recrystallised from nitrobenzene to give 7 (0.38 g, m.p. 435°C dec.). ν_{max} 3 171, 3 142, 3 100, 1 672, 1 660, 1 499, 1 294, 1 081, 958, 917, 777, 720 and 687 cm^{-1}; FAB-MS m/z 655 ($[M+H]^+$); Calc. for $C_{40}H_{18}N_2O_8$: C, 73.39; H, 2.75; N, 4.28%. Found: C, 73.35; H, 2.98; N, 4.24%.

Methylation of 7

A mixture of 7 (0.6 g), 90% formic acid (15 cm^3) and 37% formaldehyde solution (1 cm^3) was boiled under reflux for 16 hours. After the addition of 0.5 cm^3 concentrated hydrochloric acid and removal of most of the formic acid under reduced pressure, the residue was made alkaline and the product 8 (0.43 g, m.p. 380°C) filtered off. ν_{max} 2 927, 1 665, 1 654, 1 592, 1 508, 1 376, 1 289 and 1 261 cm^{-1}. FAB-MS m/z 683 ($[M+H]^+$); Calc. for $C_{42}H_{22}N_2O_8$: C, 73.90; H, 3.23; N, 4.11%. Found: C, 73.88; H, 3.21; N, 4.10%.

Pyrolysis of 7

7 (0.5 g) was heated (450°C) in a sealed tube for 0.5 hours. The product 9 (0.05 g, m.p. 396°C) sublimed as an orange coloured solid and was collected from the walls of the tube. ν_{max} 3 271, 2 918, 2 853, 1 688, 1 639, 1 495, 1 285, 765 and 680 cm^{-1}; EI-MS m/z 342; Calc. for $C_{20}H_{10}N_2O_4$: C, 70.18; H, 2.92; N, 8.19%. Found: C, 70.16; H, 2.89; N, 8.17%.

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