The Structure of the Stereoisomeric 3-Amino-2,4-diphenyl-2-butenenitriles

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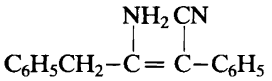
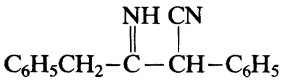
The β-amino- (*1*) or β-iminonitrile (*2*) formed by base-catalyzed dimerization of phenylacetonitrile [2] has been a subject for structure considerations several times in the literature. In older literature [1,2] the compound was always named β-iminonitrile although the structure was believed to be β-aminonitrile because hydrogenation gave a diamino compound.[2] Later,[3] on basis of UV investigations, the structure of a crystalline modification was determined as the amino compound and that of an oily form was believed to be the imino tautomer with the former predominating in solution.



1



2

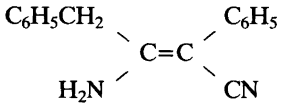
Since then the structures of the isomers have not been investigated specifically and the compounds are generally believed to be 3-amino-2,4-diphenyl-2-butenenitrile *1*.[4] The presence of two isomers with identical constitution formula has never been noticed.

The question regarding the two isomers came up because the dimer after purification by distillation [1] could be separated into two fractions by recrystallization, an oily and a crystalline fraction. The two fractions gave identical elemental analyses and hydrogenation products.[2]

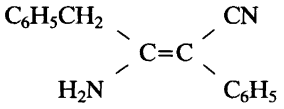
We have found that the dimer when analyzed on an HPLC Partisil 10 ODS column with acetonitrile–water as eluent gave two close but discrete peaks indicating the presence of two compounds in the ratio 2:1. Each isomer gave the same isomer distribution when analyzed on HPLC, indicating the isomerization to be very fast in that solvent. In chloroform, however, the isomerization was fairly slow so each isomer could be studied. The IR spectra of the two isomers recorded in $CHCl_3$ were almost identical. There were some small differences in band intensities. The most prominent differences were two absorptions at 1285 and 1270 cm^{-1} in the crystalline form missing in the oily modification. These dissimilarities can be ascribed to small differences in the carbon skeleton. Stretching vibrations at 3500 and 3400 cm^{-1} indicate that both isomers are amino compounds *1*. The C≡N stretch vibration at 2195 cm^{-1} is strong and indicates the nitrile is conjugated. No imino stretching vibration expected around 1660–1680 cm^{-1} was seen.

The ^1H NMR spectra of the two isomers also showed that only the amino form *1* was present in $CDCl_3$. The chemical shift value for the amino group was 4.81 ppm (2H). No CH signal from an imino form *2* was seen around 4.87 ppm, where the CH resonance for 3-oxo-2,4-diphenylbutanenitrile is found. The CH could, however, be covered by the amino signal but demasking with D_2O did not show any CH signal.

Since the IR and NMR spectroscopic evidence shows that both isomers are amino forms the two compounds must be *Z*/*E* isomers.



Z



E

The rotation is less hindered than the rotation around the normal CC double bond because the electron-donating and electron-attracting substituents attached to each end of the double bond is stabilizing the dipolar transition state for the rotation.

The significance of these resonance forms is stressed by the great diamagnetic shift for the ^{13}C NMR chemical shift for C-2 which is found at 81.1 ppm. The C-2 chemical shift for butenedinitrile is found at 120 ppm.[9]

The ^1H NMR spectra of the two isomers are almost identical except for the chemical shifts of

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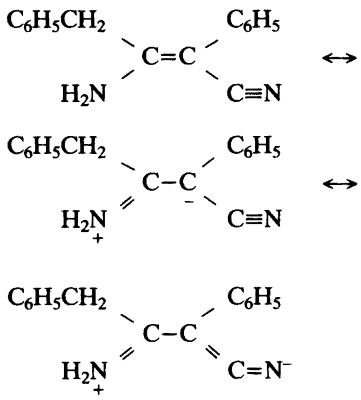

the methylene groups. For the crystalline isomer it was found at 3.65 ppm and for the oily isomer at 3.83 ppm. A solution of the crystalline isomer in $CDCl_3$ changes by standing at room temperature for 1–2 months into a 6:1 mixture of the two isomers with the oily isomer dominating. The oily isomer, on standing in solution is transformed into a mixture of the isomers in the same ratio giving an NMR identical with the NMR obtained for the crystalline isomer on standing in chloroform solution.

The oily isomer having the methylene group at lowest field must therefore be the *E*-form because of the greater deshielding effect of the cyano group compared to the phenyl group as seen for *e.g.* 2-methylbenzonitrile [5] and 2-methylbiphenyl [6] where the methyl chemical shifts are 2.51 and 2.18 ppm, respectively. For *cis* and *trans* 4-phenyl-2-butenenitrile the methylene group was found at 3.68 and 3.47, respectively,[7] also showing the deshielding effect of the cyano group. For *cis* and *trans* 2-benzyl-3-phenyl-2-butenenitrile [8] the methylene group was found at 3.70 and 3.43 ppm, respectively, demonstrating the shielding effect of the phenyl group.

In the ^{13}C NMR spectra the same trend is seen, the methylene carbon signal being shifted downfield from 37.1 ppm in the crystalline isomer to 40.3 ppm for the oily isomer. The phenyl group *cis* to the benzyl group causes more sterical pertubation than the cyano group [9] and is therefore shielding the methylene group.

From the spectroscopic evidence it can be seen that the compound formed by base catalyzed dimerization of phenylacetonitrile is 3-amino-2,4-diphenyl-2-butenenitrile. The isomers discussed in the literature for this compound are consequently not the amino–imino tautomers but the *Z*/*E* isomers with the oily *E* isomer dominating in chloroform solution.

Experimental. The experimental equipment was reported earlier.[10] Melting points are uncorrected, IR spectra were recorded on a Perkin Elmer model 298 grating spectrograph. 3-Amino-2,4-diphenyl-2-butenenitrile was prepared in accordance with the previously published method,[2] and purified by vacuum distillation. The two isomers were separated by recrystallization from ethanol.

3-Amino-2,4-diphenyl-2Z-butenenitrile. M.p. 103–108 °C. Anal. $C_{16}H_{14}N_2$: C, H, N. ^1H NMR ($CDCl_3$): δ 3.65 (2 H, s), 4.75 (2 H, broad), 7.05–7.45 (10 H, m). ^{13}C NMR ($CDCl_3$): δ 158.1, 135.8, 133.7, 129.4, 129.2, 128.9, 128.7, 127.3, 126.8, 120.3, 81.0, 37.1. IR ($CHCl_3$, cm^{-1}): 3500 (m), 3400 (m), 3000 (m), 2195 (s), 1625 (s), 1580 (s), 1495 (m), 1285 (m), 1270 (m).

3-Amino-2,4-diphenyl-2E-butenenitrile. B.p. 190–195 °C/0.5 mmHg. Anal. $C_{16}H_{14}N_2$: C, H, N. ^1H NMR ($CDCl_3$): δ 3.60 (0.3 H, s), 3.83 (1.7 H, s), 4.76 (2 H, broad), 7.05–7.45 (10 H, m). ^{13}C NMR ($CDCl_3$): δ 158.3, 157.0, 135.9, 133.3, 129.4, 129.2, 128.6, 128.8, 128.5, 127.3, 127.1, 126.9, 122.1, 120.3, 81.1, 40.3, 37.0. IR ($CHCl_3$, cm^{-1}): 3500 (m), 3400 (m), 3000 (m), 2195 (s), 1625 (s), 1580 (m), 1495 (m).

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