

E/Z Photoisomerization of 3-Amino-3-phenylprop-2-enitriles

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The *E/Z* photoisomerization of 3-phenyl-3-(*N*-substituted amino)- and 3-phenyl-3-(*N,N*-disubstituted amino)-prop-2-enitriles was investigated by means of u.v. and ^{13}C n.m.r. spectroscopy. Informative results on the mechanism of the reaction produced by direct irradiation of 3-anilino-3-phenylprop-2-enitrile were obtained from the different effects of quenchers and heavy atoms. Neither the heavy atoms nor the quenchers had any effect on the direct photoisomerization, which involves only the singlet state, by-passing the triplet state.

Various aspects of the reactivity of 3-aryl-3-aminopropenenitriles have been investigated in our laboratory. Recent work has included studies on their dipolarophilic reactivity towards benzonitrile oxides, $^{1-3}$ as well as the ^{13}C n.m.r. spectra of (*Z*)- and (*E*)-3-(*p*-substituted phenyl)-3-aminopropenenitriles. 4

We here report the results of direct irradiation of *N*-substituted and *N,N*-disubstituted 3-amino-3-phenylpropenenitriles (**1b–f**), including a detailed study of 3-anilino-3-phenylprop-2-enitrile (**1a**), together with their ^{13}C n.m.r. spectra. We hoped to obtain mechanistic information on the *E/Z* isomerization and on the transmission of the electronic effects of the amino group, which, together with the configuration of the C=C double bond, appears to be responsible for the reactivity of the conjugated system. 2,3

Results and Discussion

The enamines (**1**) were obtained from phenylpropynitrile and the corresponding amines in ethanolic solution at reflux temperature. 1

The enamine (**1a**) consisted of a mixture of *E*- and *Z*-isomer; the enamines (**1b–g**) consisted of only one isomer (*E*-form). The isomeric characterization rests on the assumption that the cyano group carbon atom and the methine proton of the *E*-form resonate at lower field than in the *Z*-isomer, as already reported for the parent compounds. 4

Mixtures of isomers were obtained by irradiating solutions of pure *E*-isomer in ethanol or in $(\text{CD}_3)_2\text{SO}$. Relative yields and the proton chemical shifts are recorded in Table 1.

The ^{13}C chemical shifts for the enamines (**1a–g**) and (**2a–d**) are listed in Table 2. The signals of the *Z*-isomers could easily be identified in the spectra of the photoequilibrium mixtures.

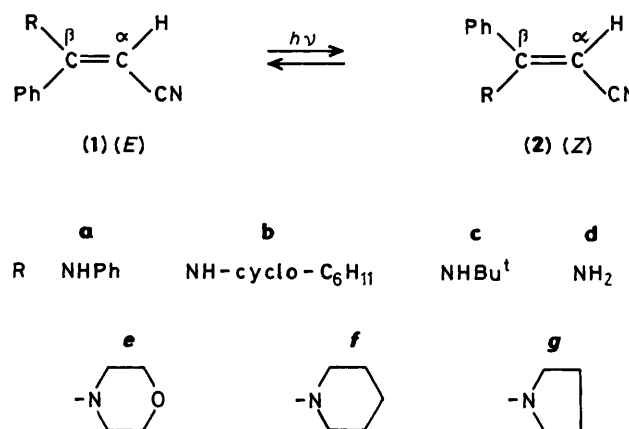
Direct Irradiation of 3-Anilino-3-phenylprop-2-enitrile (1a).—Under direct irradiation both (**1a**) (*E*) and (**2a**) (*Z*) undergo *E/Z* isomerization (Figure), and a photostationary state in which the *Z*-isomer predominates is rapidly achieved. The photoequilibration may be followed by observing the changes in the u.v. absorption spectrum; the *E*-form absorbs at lower wavelengths and has more intense absorption bands [λ_{max} 307 (ϵ 10 150) and 229.5 nm (ϵ 15 390)] than the *Z*-isomer [λ 319 (ϵ 9 750) and 250 nm (16 480)]. The composition at photoequilibrium, as established by u.v., is 8.7% *E* and 91.3% *Z*. The quantum yields are independent of the initial concentration and of the irradiating wavelength (365 or 333 nm): $\Phi_{E/Z} = 0.300 \pm 0.03$; $\Phi_{Z/E} = 0.090 \pm 0.004$. The quantum yield at 313 nm was not evaluated because of simultaneous decomposition reactions.

The fact that the quantum yields are the same at different wavelengths supports the hypothesis that the reaction arises from one excited intermediate state, which might be singlet or

Table 1. ^1H Chemical shifts for methine protons of (*E*)- and (*Z*)-3-phenyl-3-(*N*-substituted amino)prop-2-enitriles in $(\text{CD}_3)_2\text{SO}^a$

Compound designation	Solution of enamine ^b R	Photoequilibrium population (%) of <i>Z</i> -isomer ^c	δ (p.p.m.)	
			<i>E</i>	<i>Z</i>
a	NHPh	92	4.71	4.66
b	NH-cyclo-C ₆ H ₁₁	25	4.13	3.87
c	NHBU ^t	40	4.25	4.04
d	NH ₂	59	4.30	4.19
e	Morpholino	4	4.56	4.17
f	Piperidino	4	4.45	4.03
g	Pyrrolidino	4	4.02	3.70

^a Chemical shifts in p.p.m. relative to Me₄Si. ^b For description of the solutions see Experimental section. ^c Yields of *Z*-isomers in photoequilibrium mixtures were determined from intensity ratios of the methine proton signals.

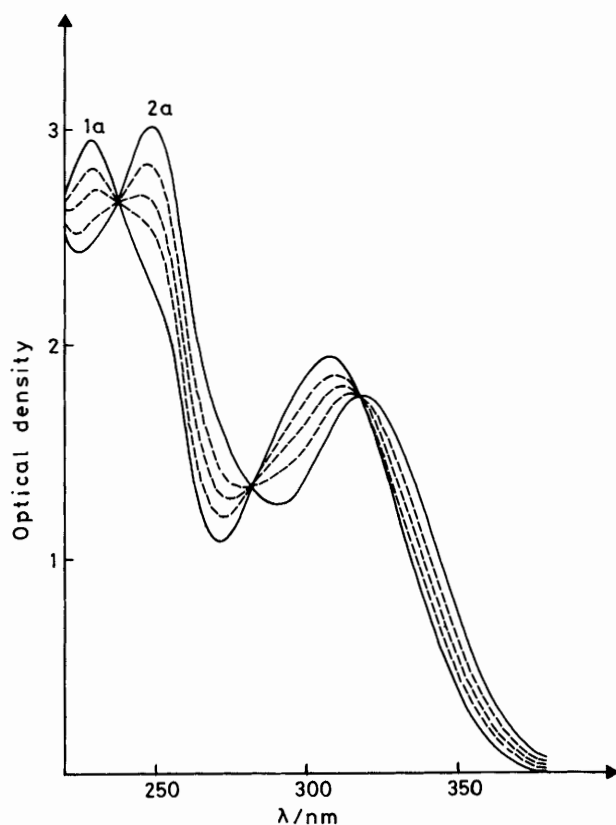


triplet. In order to elucidate this singlet/triplet distinction we carried out experiments based on the quenching of the excited electronic states and on the heavy-atom effect. A preliminary study dealt with the problem of determining the approximate energy of the triplet state. Since (**1a**) neither phosphoresces nor reveals any absorption intensity in the presence of heavy atoms (xenon or EtI) which could be assigned to absorption from the triplet state, we performed preliminary sensitization experiments which showed that chrysene (E_T 238.3 kJ mol⁻¹) was effective for *E/Z* isomerization, whereas Crystal Violet (E_T 163.0 kJ mol⁻¹) was completely ineffective for sensitization. It is evident that the lower triplet reactive state is greater than 163.0 kJ mol⁻¹. Consequently, azulene ($E_T < 155$ kJ mol⁻¹) and ferrocene ($E_T < 180$ kJ mol⁻¹) are suitable quenchers of the isomerization. Irradiation of either (**1a**) (*E*) or (**2a**) (*Z*)

Table 2. ^{13}C Chemical shifts for (*E*)- and (*Z*)-^a 3-phenyl-3-(*N*-substituted amino)prop-2-enitriles in $(\text{CD}_3)_2\text{SO}^b$

Carbon	(1a)	(2a)	(1b)	(2b)	(1c)	(2c)	(1d) ^c	(2d) ^c	(1e)	(1f)	(1g)
CN	121.2	(-2.6)	122.4	(-1.2)	122.1	(-0.6)	122.4	(-1.8)	120.0	120.5	120.9
α	65.1	(+5.4)	58.3	(-0.8)	61.4	(+2.6)	60.4	(-1.2)	66.2	64.5	60.3
β	160.5	(-2.3)	161.7	(-2.0)	161.1	(-1.9)	164.4	(-2.1)	164.6	164.3	161.4
<i>ipso</i>	135.4	(+0.5)	136.4	(+1.9)	137.6	(+2.0)	134.6	(+1.2)	133.3	134.3	134.6
<i>ortho</i>	128.7	(-0.1)	128.3	(-0.9)	128.2	(-0.1)	127.9	(-1.3)	127.8	127.5	126.9
<i>meta</i>	128.7	(-0.1)	128.3	(-0.9)	128.6	(-0.3)	128.6	(+0.1)	127.8	127.8	127.6
<i>para</i>	130.5	(+0.1)	130.0	(+0.1)	129.7	(+0.3)	130.3	(+0.3)	128.9	128.7	128.4
Others	140.2	(+1.1) ^d	51.8	(+0.5) ^h	51.7	(+2.4) ⁱ			46.8 ^h	47.6 ^h	47.9 ^h
	122.6	(0.0) ^e	31.3	(+1.4) ⁱ	28.1	(+2.2) ^m			64.4 ⁱ	23.8 ⁱ	23.8 ⁱ
	129.4	(0.0) ^f	24.3	(0.0) ^j						22.5 ^j	
	124.3	(0.0) ^g	25.2	(0.0) ^k							

^a Reported in parentheses, as substituent chemical shifts with respect to the corresponding shifts of the *E*-isomers. ^b Chemical shifts in p.p.m. relative to Me_4Si , calculated by adding 39.6 to the shift relative to the centre peak of $(\text{CD}_3)_2\text{SO}$. ^c From ref. 4. ^d *ipso*-Carbon. ^e *ortho*-Carbon. ^f *meta*-Carbon. ^g *para*-Carbon. ^h α' -Carbon. ⁱ β' -Carbon. ^j γ' -Carbon. ^k δ' -Carbon. ^l Quaternary carbon. ^m Methyl.

**Figure.** Changes in u.v. absorption on photoisomerization of (1a) in ethanol by irradiation at 365 nm

containing ferrocene or azulene led to photoisomerization with the same quantum yields as those found on irradiating the substrate solution in the absence of quenchers: therefore these quenchers do not affect the photoreaction.

Since the observed inefficiency could be due to the fact that the excited states do not have a sufficiently long lifetime to be intercepted, the effect of heavy atoms was also examined, in order to identify any singlet-triplet intersystem crossing. Experiments were carried out in benzene solutions saturated with xenon and in acetonitrile solutions containing 10^{-2}M - NEt_4Br . The results show that the heavy atom does not affect the quantum yields of the photoisomerization. In a series of experiments both heavy atoms and quenchers were used to

ensure that the absence of an overall effect was not the result of the quantum yields from the singlet and triplet states being almost equal; the inefficiency of both perturbors ruled out this possibility.

These results show that neither the heavy atoms nor the quenchers have any effects on the direct photoisomerization process, and also that the photoisomerization pathway bypasses the triplet state. A possible mechanism, which agrees with the present results, is as follows. The molecule, excited to the lowest singlet state, undergoes rapid relaxation with concomitant twisting to a minimum on the potential energy surface where it acquires a geometry intermediate between the *E*- and *Z*-configurations. From this minimum, decay occurs to the ground *E* and *Z* states. As the sum of quantum yields $\Phi_{E/Z}$ and $\Phi_{Z/E}$ is less than unity, deactivation of the singlet state also includes other important radiationless decay processes, which occur with retention of geometric configuration. For the compounds studied, all radiationless decays are too rapid for intersystem crossing to be a competitive deactivation path; this conclusion is supported by the observation of negligible fluorescence and phosphorescence.

Unfortunately it was not possible to make a systematic study of the photoisomerization for compounds (1b-f); all attempts to separate the *Z*-forms by chromatography were unsuccessful; nevertheless qualitative studies showed that direct *E/Z* isomerization was operative. In fact, irradiation of the enamines (1b and 1c) and (1e-g) in the pure *E*-form produced an *E/Z* equilibrium mixture, as confirmed by a bathochromic shift in the u.v. absorption maximum (due to *E/Z* isomerization), by the presence of an isobestic point, and by the ^1H n.m.r. spectra of the reaction mixtures which showed signals at higher fields attributable to the methine hydrogen atom of the *Z*-form. Relative yields and $\text{CH}=\text{n.m.r.}$ shifts are reported in Table 1.

¹³C N.m.r. Spectra.—We have recently reported that for (*E*)- and (*Z*)-3-(*p*-substituted phenyl)-3-aminoprop-2-enitriles,⁴ α -ethylenic carbon atoms are deshielded by 12 p.p.m. with respect to the analogous carbon atoms of cinnamionitriles, β -carbon atoms are shielded by 35 p.p.m., and nitrile carbon atoms are deshielded by 4 p.p.m., in agreement with variations in local electron density.

In (*E*)-3-phenyl-3-(*N*-substituted amino)prop-2-enitriles (1a-g), nitrile and β -ethylenic carbon atoms, as well as the methine protons, resonate at lower field than in the *Z*-isomers. This downfield shift for nitrile carbon atoms of the *E*-forms is in agreement with the shift observed for 3-amino-3-(*p*-substituted phenyl)propenenitriles,⁴ and the reverse with respect to that of unsaturated nitriles.⁵ The downfield shift of nitrilic and β -

carbon signals can be conveniently used for the assignment of the configuration of these compounds, provided that both isomers are available.

The shifts of α -ethylenic carbons are not diagnostic of configuration, those of the (*Z*)-anilino (**2a**) and *t*-butylamino (**2c**) derivatives being higher than those of the corresponding *E*-isomers. α -Carbon shifts have already been shown to be influenced by the electron-donating character of substituents in the benzene ring attached to the β -ethylenic carbon, which causes an upfield shift.⁴

α -Carbon shifts of the present series (**1a–g**) vary in the order: cyclohexylamino < pyrrolidino < NH₂ < NHBu^t < piperidino < NPh < morpholino. This sequence does not parallel the order of basicity of the corresponding amines RH in water⁶ (pyrrolidine > piperidine, cyclohexylamine > *t*-butylamine > ammonia > morpholine > aniline), probably because of steric effects in the *t*-butyl derivative (**1c**) and in (**1e–g**), where the nitrogen atom is part of a saturated ring.

Experimental

M.p.s were determined with a Kofler apparatus. I.r. absorption spectra were determined with a Perkin-Elmer 684 spectrophotometer. The u.v. absorption spectra were measured with a Perkin-Elmer 330 spectrophotometer. The ¹³C n.m.r. spectra were obtained with a Bruker WP 80 Fourier transform spectrometer operating at 20.11 MHz and 300 ± 2 K. Typical conditions were: spectral width 5 kHz; data points 16 K; pulse width 1.0 μ S (15°); decoupler frequency 6 kHz; decoupler power 2 W; pulse repetition time 0.82 s. The accuracy of the ¹³C chemical shift measurements was ± 0.1 p.p.m. ¹H N.m.r. spectra were measured at 80 MHz with the same instrument. Chromatographic separations were carried out with a Varian HPLC 5000 instrument. The n.m.r. spectra of mixtures of *E*- and *Z*-isomers were recorded after solutions of pure *E*-isomers [0.5M in (CD₃)₂SO] were irradiated directly in quartz sample tubes with a 450 W Hanovia lamp equipped with a uranium glass filter for 4 h.

Starting Materials.—The enamine (**2d**) is commercially available and its isomerization to (**1d**) has been previously reported.⁴ The enamines (**1a–c**) and (**1e–g**) in the *E*-form were obtained from phenylpropynitrile and the corresponding amines in ethanolic solution at reflux temperature.¹ Most enamines were obtained as pure *E*-isomers, with the following m.p.s: (**1b**), 107 °C (lit.,³ 106–107 °C); (**1c**), 115 °C (lit.,¹ 113–115 °C); (**1e**), 66 °C (lit.,⁷ 65–66 °C); (**1f**), 87 °C (lit.,⁸ 86–87 °C); (**1g**), 105 °C (lit.,⁸ 103–105 °C).

The enamine (**1a**) was obtained together with its isomer (**2a**). The isomers were separated by analytical h.p.l.c. [preparative column (Whatman M9 1025) packed with Partisil; *n*-hexane-ethyl acetate (82:18) as eluant]. The first component isolated was a white solid, m.p. 148–149 °C, identified as the *Z*-isomer (**2a**) on the basis of its spectral properties; i.r. λ_{\max} (KBr) 3.05 (NH), 3.26, 4.54 (CN), 6.19, 6.25, 6.29, 6.65, 6.89, 7.1, 7.93, 12.73,

12.98, 13.51, 14.49, 15.87, and 18.5 nm; u.v. λ_{\max} (ethanol) 319 (ϵ 9 747) and 250 nm (16 482); δ_{H} [(CD₃)₂SO] 4.66 (1 H, s), 6.94–7.44 (10 H, m), and 9.1 (1 H, s) (Found: C, 81.8; H, 5.4; N, 12.7%). C₁₅H₁₂N₂ requires C, 81.8; H, 5.5; N, 12.7%).

The second fraction contained a white solid, m.p. 137–138 °C, identified as the *E*-isomer (**1a**) on the basis of its spectral properties: i.r. λ_{\max} (KBr) 3.07 (NH), 3.20, 3.26, 4.56 (CN), 6.21, 6.29, 6.36, 6.51, 6.57, 6.66, 7.16, 9.80, 12.98, 13.33, 14.28, 16.12, and 20.0 nm; u.v. λ_{\max} (ethanol) 307 (ϵ 10 147) and 229.5 nm (15 390); δ_{H} [(CD₃)₂SO] 4.71 (1 H, s), 7.01–7.58 (10 H, m), and 8.96 (1 H, s) (Found: C, 81.8; H, 5.5; N, 12.7%).

Apparatus for Irradiation.—A low-pressure mercury vapour lamp (Hanau Q 400) equipped with an interference filter (Schott) was used to produce radiation of wavelengths 333 and 365 nm. The intensity of the incident light was measured using a potassium ferrioxalate actinometer and was of the order of 10⁻⁷–10⁻⁸ einstein min⁻¹.

Direct Irradiation of 3-Anilino-3-phenylprop-2-enitrile (1a).—Solutions of pure (**1a**) isomers in benzene or ethanol (concentration range 10⁻³–10⁻⁵ M) were maintained at 25 °C and irradiated at 333 or 365 nm in a standard spectrophotometric cell after deaeration with nitrogen. The photochemical reaction was followed spectrophotometrically in a suitable absorption region. Quantum yields were calculated from the initial rate of the reaction or by the method of Zimmerman *et al.*⁹ A stationary state was attained without side reactions. In the experiments carried out with quenchers or heavy atoms, the relative concentrations of substrate and of quenchers or heavy atoms were such that the light was almost completely absorbed by the substrate.

Acknowledgements

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