Solution and Solid-State Photochemistry of 2-Anilino-5-phenyl-2,4-pentadienenitriles

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2-(*N*-Methylanilino)-5-phenyl-2,4-pentadienenitrile (**3**) undergoes either isomerization or oxidative cleavage at the 2,3-double bond upon irradiation in solution, whereas it dimerizes in a regiospecific manner to give the [2 + 2] cycloaddition product **12** upon irradiation in the solid state. From the fluorescence spectra and semiempirical calculations, the excited state of **3** is proposed to be a twist intramolecular charge transfer species. The X-ray analysis indicates that molecules of **3b** orient appropriately with a reasonable distance for the [2 + 2] cycloaddition in the solid state. The distance between C2 and C3′ is 525 pm, the longest distance known in solid-state [2 + 2] cycloadditions. 2-(*N*-Methyl-*p*-bromoanilino)-5-phenyl-2,4-pentadienenitrile (**4**) shows behavior similar to that of **3** in the solution and solid-state photochemistry, whereas analogs **7**−**10** having nitro substituents on the 5-phenyl rings do not dimerize upon irradiation in the solid state. Semiempirical calculation of the electronic structures is used to interprete the discrepancy of reactivity.

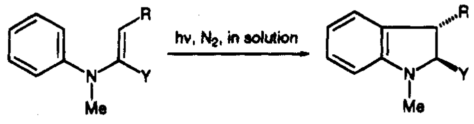
Introduction

N-Aryl enamines **1a** generally undergo photochemical reactions to give the corresponding 2,3-dihydroindoles **2a** via conrotatory cyclizations and 1,4-hydrogen migrations (Scheme 1).[1] Similar photochemical cyclizations of α-anilino alkenenitriles and dienenitriles **1b**−**e** have been observed.[2,3] The presence of the α-cyano group in **1b**−**e** can stabilize the zwitterionic intermediates and thus increase the photochemical yields of **2b**−**e**. The photochemical reactions are not changed with bromo atom or azido substituent in the R group. We found that 2-anilino-5-phenyl-2,4-pentadienenitriles **3**−**10**, however, underwent isomerization, oxidative cleavage, or [2 + 2] cycloaddition (Scheme 2), unlike the photocyclizations of analogous dienenitriles **1d**[4] or **1e**.[5] We describe herein the selective photochemical processes in **3-10** which can occur in solution or solid state with or without the presence of oxygen.

Results and Discussion

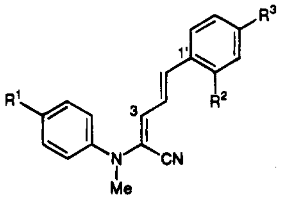
Solution Photochemistry. A benzene solution of **3a** (or **3b**, Scheme 2) was irradiated with a medium-pressure mercury lamp in the presence of oxygen to give cinnamaldehyde and a cyanoformamide (**11**) via an oxidative cleavage at the 2,3-double bond. The photochemical oxidative cleavage can be accelerated by addition of a small amount of sensitizer 9,10-dicyanoanthracene (DCA) or 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP).[6] No cleavage at the 4,5-double bond was observed. The photoreaction of **3a** in toluene also gave **11** and cinnamaldehyde, whereas irradiation in methanol only caused *E*/*Z* isomerization at the 2,3-double bond. Both oxidative cleavage and isomerization occurred when an acetonitrile solution of **3a** was irradiated.

Scheme 1



1a-1e **2a-2e**

	Y =	R =
a	H	alkyl group
b	CN	alkyl group
c	CN	C_6H_5
d	CN	$CH_2{=}CH$
e	CN	$C_2H_5CH{=}CH$



	R^1 =	R^2 =	R^3 =
3a	H	H	H
4	Br	H	H
5	H	MeO	H
6	Br	MeO	H
7	H	H	NO_2
8	Br	H	NO_2
9	H	NO_2	H
10	Br	NO_2	H

By exclusion of oxygen, irradiation of a hexane solution of **3** showed strong fluorescence. The lifetime of the

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Scheme 2

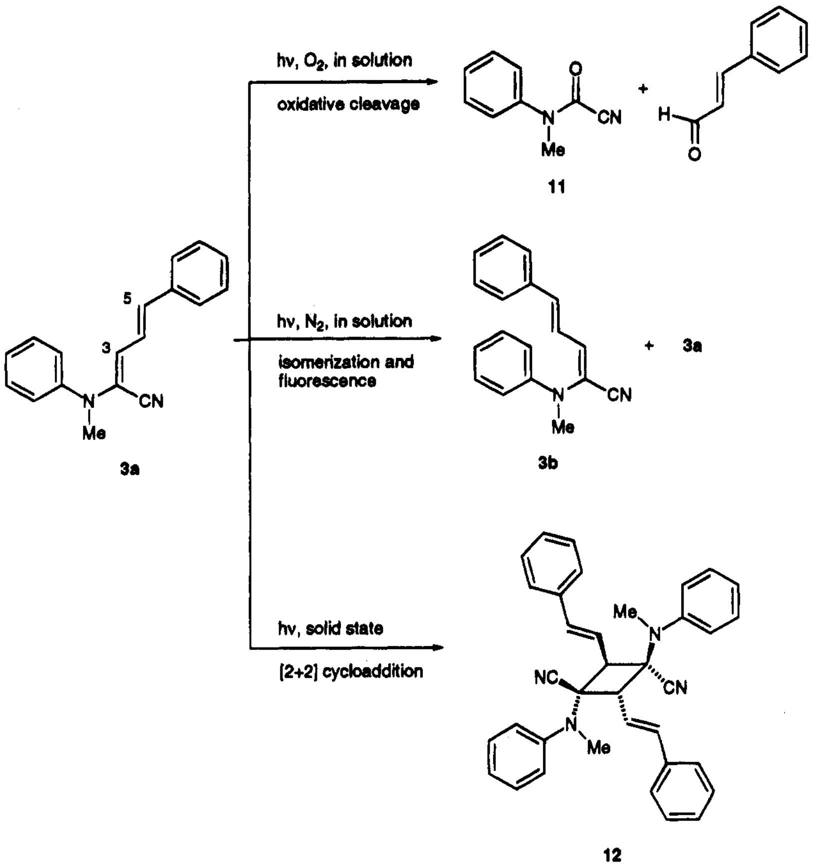

Table 1. Fluorescence Maxima upon Irradiation of α-Anilino Dienenitriles 3−10 in Various Solvents[a]

	C_6H_{14} (ϵ 1.89)	C_6H_6 (ϵ 2.28)	$CHCl_3$ (ϵ 4.81)	CH_2Cl_2 (ϵ 9.08)	Me_2CO (ϵ 20.7)
3a	481[b] (>518)[c]	522.5 (345)	530 (66)	530 (29)	541.5 (5)
3b	487 (418)	525.5 (51)	532.5 (10)	538 (5)	546.5 (1)
4	472.5 (326)	518 (38)	525 (10)	534.5 (6)	538 (2)
5[d]	482.5 (>525)	517.5 (441)	536 (97)	539.5 (49)	545 (9)
6	468 (>525)	504 (296)	526 (72)	527.5 (36)	534 (12)
7	516 (321)	533 (103)	559.5 (45)	589 (12)	598.5 (4)
8	502 (287)	532.5 (61)	550.5 (38)	558 (13)	587 (4)
9	511 (5)	*e*	*e*	*e*	*e*
10	503.5 (6)	*e*	*e*	*e*	*e*

[a] The samples **3−8** were taken as 2×10^{-4} M solutions, whereas **9** and **10** were measured as saturated solutions. The lifetimes of fluorescence in hexane are **3a**, 6.7 ns, **3b**, 10 ns, **4**, 7.7 ns, **5**, 13 ns, **6**, 5.9 ns, **7**, 7.7 ns, and **8**, 5.9 ns, respectively. [b] The wavelength of fluorescence in nm. [c] The numbers in parentheses indicate the maximum absorbance. [d] This sample is composed of the 2*E*- and 2*Z*-isomers (2:1). [e] No significant fluorescence was observed.

excited state (measured by duration of the fluorescence) was in the order of nanoseconds. For an individual α-anilino dienenitrile (**3−10**), the wavelength of fluorescence maximum increased as the dielectric constant of the solvent (benzene, chloroform, dichloromethane, and acetone) increased. The intensity of fluorescence, however, decreased as the dielectric constant of solvent increased (Table 1). No significant fluorescence released in MeOH (ϵ 32.6) or MeCN (ϵ 36.2). On the other hand, an individual dienenitrile (**3−10**) showed similar UV spectra in varied solvents (hexane, CH_2Cl_2, or MeCN).

The results indicate that aryldienes **3−10** exist as unpolarized species in the ground state (no obvious UV shifts)[7] but exist as charge separated species in excited state (variable fluorescence maxima).[8] The dipole moment (μ) of the excited state, presumably a twist intramolecular charge transfer state (TICT), can be estimated from the variation of fluorescent emission maxima ν_{max} (cm^{-1}) with solvent polarity[9]

$$\nu_{max} = \nu_0 - 2\mu^2/hca^3[(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)]$$

where ν_0 is the hypothetical gas phase emission frequency, h is Planck's constant, a is the solvent cavity radius (approximately 450 pm), n is the refractive index of the solvent, and ϵ is the dielectric constant of the solvent. From the linear plot of the ν_{max} vs $2(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)$, the dipole moments are obtained: **3a**, 6.86 D, **3b**, 6.89 D, **4**, 7.46 D, **5**, 7.46 D, **6**,

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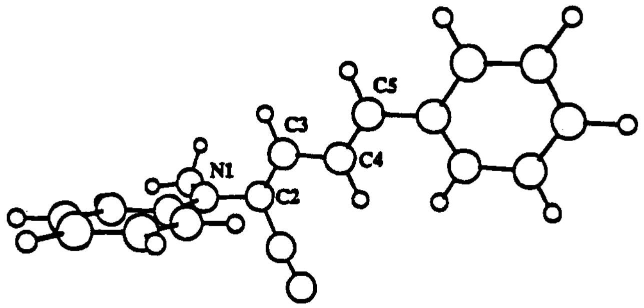


Figure 1. Perspective view for the excited state conformation of **3a** optimized by PM3. It is noticed that the plane containing CH_3–N1–C(Ph) is perpendicular to that of the phenyl–diene moiety (C2–C3–C4–C5).

7.89 D, **7**, 8.61 D, and **8**, 8.13 D. The degree of charge separation is estimated to be 25% by taking N1 and C1′ atoms as two poles 620 pm apart (see the X-ray diffraction analysis). The direction of dipoles is, however, not obviously defined as the aryldienes **3**–**8** contain both the electron-withdrawing cyano group and the electron-donating amino group at C-2.

On the TICT States. According to the crystal structures of **4** and **7**–**10** in general, the substituents of N1 are roughly coplanar with the phenyl–diene moiety. In the HOMOs of these molecules, the N1 lone pair is delocalized on the conjugated π orbital. The LUMO is, however, primarily a π^* orbital of the phenyl–diene without significant involvement of the N1 lone pair.

Upon photoexcitation a (n, π^*) transition is assumed. There are at least two immediate consequences after the absorption: first is the weakening of C2–C3 bond and second the reduction of n–π orbital overlap. The former is well known to be responsible for *E*/*Z* isomerization, while the latter induces an alternate twisting along the N1–C2 bond. The geometry optimized by PM3[10] for the excited state of **3a** reveals that for the most stable conformation the Ph–N1–CH_3 plane is twisted perpendicular to the NC–C2–C3 plane (Figure 1). In this conformation the Ph–N1 moiety and the NC–C2–C3–R moiety may be taken as isolated chromophores, the radical cation and anion, respectively. Such a structure may be described as a TICT state, while the twisting prevent the charges from annihilating readily. The fluorescence observed should have been emitted from such a state, consistent with observed high polarity of the excited species. The estimated dipole of the TICT state of **3a** is 8.99 D in the gas phase, which is comparable to that measured in the solutions (6.86 D). On the other hand, the dipole moment of **3a** in the ground state is calculated to be 3.64 D using the crystal geometry of **4** where Br is replaced by H.

Solid-State Photochemistry. The α-anilino dienenitriles **3**, **4**, and **7**–**10** are crystalline. When crystals of **3b** were irradiated with a medium-pressure mercury lamp, a head-to-tail [2 + 2] cycloaddition product **12** was obtained in quantitative yield (based on about 20% conversion). The cycloaddition occurred at both the 2,3-double bonds of two molecules of **3b**. The photoreaction of the 2*E*-isomer **3a** also gave the same cycloadduct. The efficacy of photocycloaddition was unchanged by prior treatment of the sample (**3a** or **3b**) with a small amount of MeOH followed by evaporation to dryness. Experiments show that the [2 + 2] cycloaddition is due to a monochromic 366 nm light (generated from a 1000 W high-pressure mercury lamp), but not 308 nm or 350 nm light. The photoreaction of **4** in the solid state gave [2 + 2] cycloaddition product **13**, whereas crystals of **7**–**10** simply underwent *E*/*Z* isomerization at the 2,3-double bonds upon irradiation.

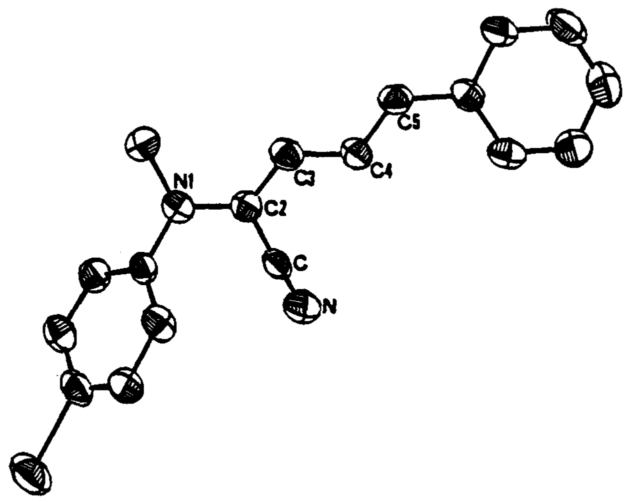
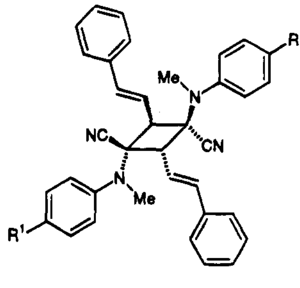


Figure 2. ORTEP drawing of **4**.



12 R¹ = H

13 R¹ = Br

Crystallographic Interpretation. The X-ray diffraction analyses of **3**, **4**, and **7**–**10** were carried out.[17] The N1 atom is sp^2 hybridized with the lone pair of electrons parallel to the π-electrons of the 2,3-double bond. Appropriate orientation of molecules in **4**, for example, is shown to account for the [2 + 2] cycloaddition. Such topochemical control on [2 + 2] cycloadditions has been illustrated in solid-state photochemistry of cinnamic acid and its related systems.[11] The upper limit of intermolecular distance for a [2 + 2] cycloaddition has been suggested to be 500 pm. In the present cases, the intermolecular distance between C2 and C3 of the closest molecules is, however, varied from 381 pm in **7** to 698 pm in **10**. Two compounds (**3b** and **4**) which gave [2 + 2] cycloaddition products after photoreaction in the solid state do not have the shortest distance, *i.e.*, 525 pm in **3b** and 468 pm in **4**. As for packing orientation,

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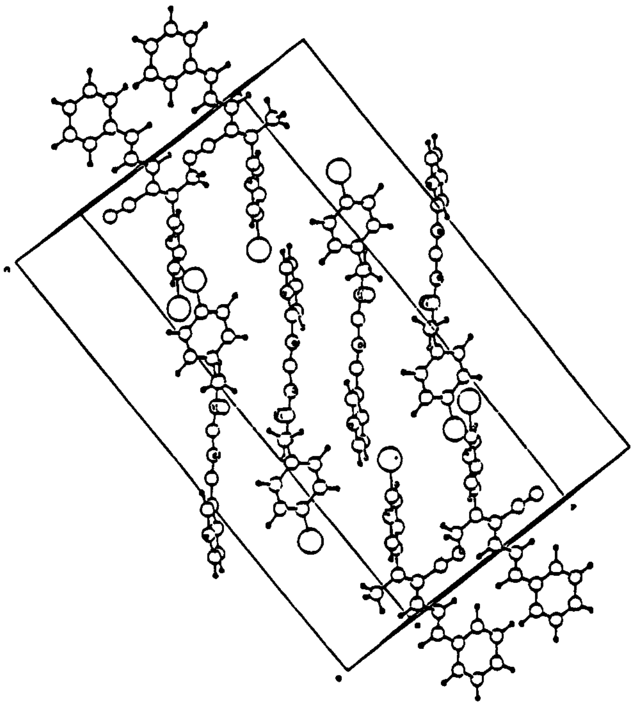

Figure 3. Crystal packing diagram of **4**.

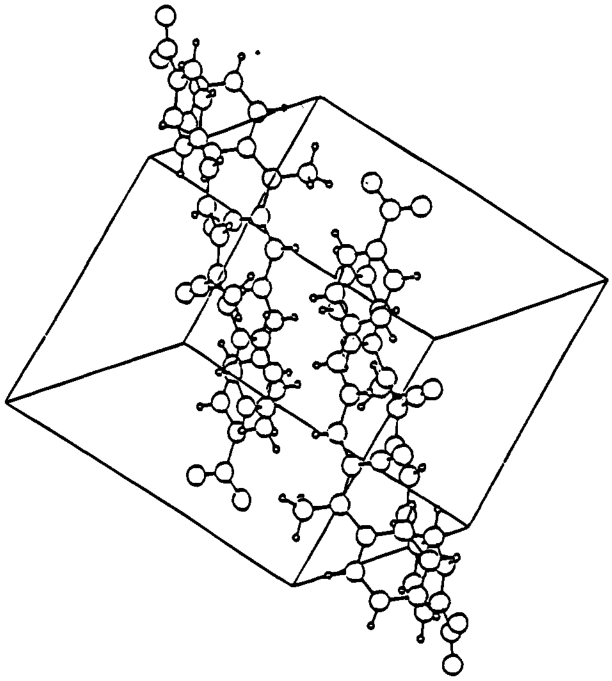

Figure 4. Crystal packing diagram of **7**.

compound **4** (Figure 3) is apparently in a proper orientation for [2 + 2] cycloaddition, the pair of C2−C3 π-orbitals are related with $\bar{1}$ symmetry, *i.e.*, parallel to each other. Although compounds **8** and **9** both have proper orientation and reasonable short intermolecular distances (399 and 489 pm), the photochemical cycloaddition did not occur. In **3b**, the pair of C2−C3 π-orbitals are parallel to each other but not related by a $\bar{1}$ symmetry. The two π-orbitals in **7** are, however, perpendicular to each other (Figure 4).

It is noted that compounds **7**−**10** all have a NO_2 group on the 5-phenyl ring, which might have some inductive effect. A semiempirical calculation based on the AM1 method was made on **3b**, **7**, and **9** using the geometries from X-ray analyses. The orbital energy levels are shown in Figure 5, where the HOMO is mainly a combination of the lone pair on N1 and the π-orbital of phenyl−diene, whereas the LUMO is characterized as π* of the phenyl−diene. There is, however, another phenyl−diene π* orbital near the LUMO for **7** and **9**, indicating the π* character on C4−C5 of the resonance structure induced by the nitrophenyl ring. This might make a difference on the (n,π*) photoexcitation and lead to a facile *E*/*Z* isomerization to dissipate energy of the incident light as in solution photochemistry. Some (2*Z*,4*E*)-isomers were indeed obtained after the solid-state photoreactions of **7**, **8**, or **10** having the (2*E*,4*E*)-configuration.

The crystal structure of **3b** having the (2*Z*,4*E*)-configuration shows an interesting feature (Figure 6). As previously mentioned, **3b** is obtained from **3a** upon photoexcitation through an *E*/*Z* isomerization along the C2−C3 bond. After rearrangement in the excited state, the molecule cannot return to its original conformation, *i.e.*, coplanar for the N1 bondings and the diene π-system, due to a steric hindrance between the *N*-methyl group and the C4 hydrogen atom. It therefore maintained a geometry similar to that of the TICT state, which is unique with respect to all other (2*E*,4*E*)-isomers resolved by crystallography.

Conclusion. Dienes have historically played an important role in organic photochemistry.[11] We have illustrated a new photochemical system using the substrates 2-anilino-5-phenyl-2,4-pentadienenitriles equipped with captodative substituents. The fluorescence study of **3**−**10** in various solvents is consistent with the existence of charge separated species in excited state. The captodative substituents at C-2 accounted for the selective photochemical oxidation of **3**−**10** at the 2,3-double bonds without cleavage at the 4,5-double bonds. The photochemical [2 + 2] cycloadditions of **3** and **4** appear to be under proximity control in the solid state.[12] However, appropriate topochemical relationship does not ensure the cycloaddition as shown in the case of **8** or **9** which contain a nitrophenyl substituent at C-5.

Experimental Section

Melting points (Yanaco micro melting point apparatus) are uncorrected. The ^1H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra were recorded at 50 or 75 MHz. The mass spectra were recorded at an ionizing voltage of 70 eV. The X-ray diffraction data were collected on a CAD-4 diffractometer. The analyses were carried out on a microVAX III computer using NRC SDP software.[13] The dienes **3**−**10** were prepared by condensation of equimolar amounts of 2-(*N*-methylanilino)acetonitrile [or 2-(*N*-methyl-4-bromoanilino)-acetonitrile] with cinnamaldehyde (or the substituted cinnamaldehyde) via the Peterson procedure previously described.[14] 2-(*N*-Methyl-4-bromoanilino)acetonitrile, mp 35−36 °C (from hexane), was prepared by treatment of 2-(*N*-methylanilino)-acetonitrile with *N*-bromosuccinimide in CCl_4 at room temperature for 2 h.[15] DCA was prepared from anthracene by bromination and a subsequent substitution with CuCN.[16]

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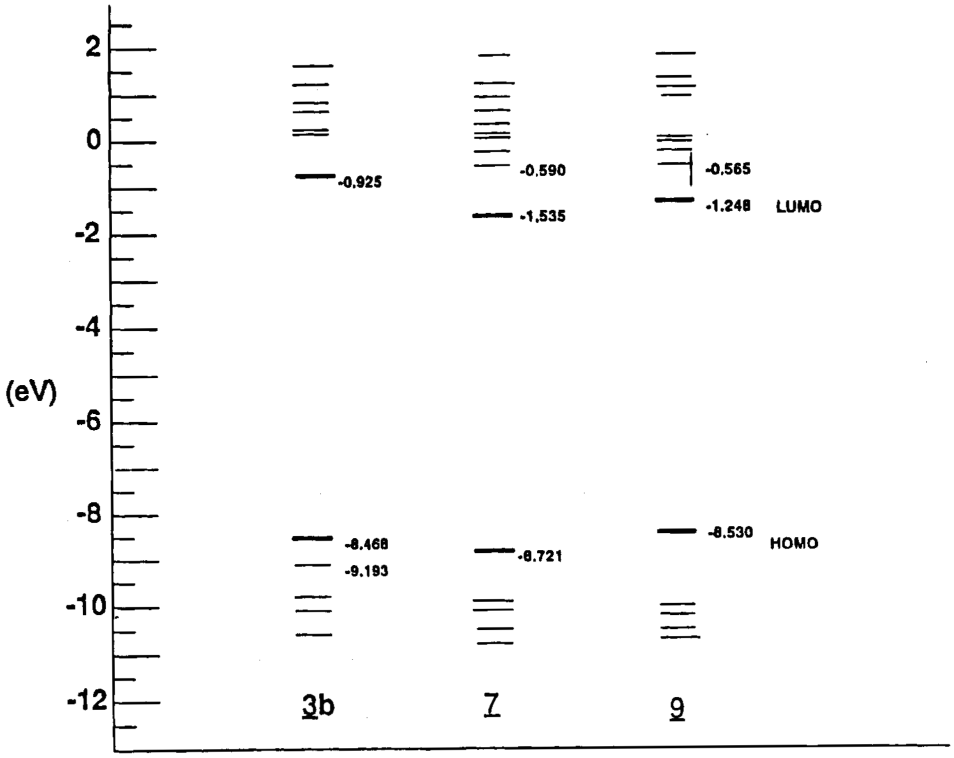

Figure 5. Orbital energy levels of **3b**, **7**, and **9** by semiempirical calculation based on the AM1 model using the geometries from X-ray analysis.

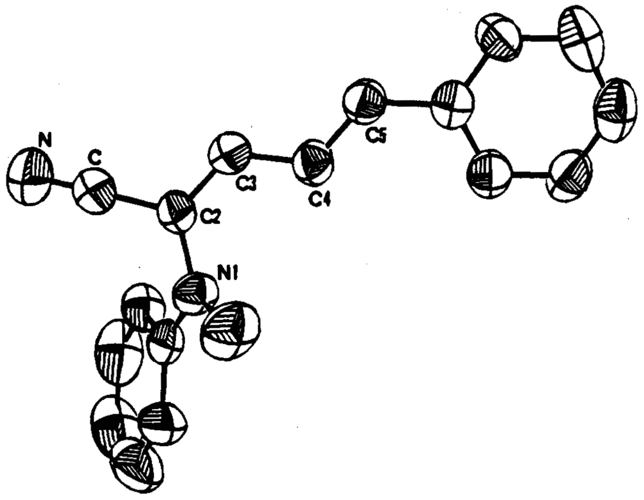

Figure 6. ORTEP drawing of **3b**.

Photochemistry was carried out in a Pyrex test tube placed 10 cm from a Conrad-Hanovia 7825 medium-pressure mercury lamp (450 W), which was placed in a water-cooled immersion well.

2-(*N*-Methylanilino)-5-phenyl-2,4-pentadienenitrile (3): 72% yield, **3a** (2*E*,4*E*)/**3b** (2*Z*,4*E*) = 1:1. **3a**: yellow crystal, mp 120−122 °C (from hexane); TLC (EtOAc/hexane, 5:95) R_f 0.20; IR (KBr) 2215 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.26 (3 H, s, NMe), 6.31 (1 H, d, J = 11.2 Hz, H-3), 6.62 (1 H, d, J = 15.4 Hz, H-5), 7.08−7.46 (11 H, m); ^{13}C NMR ($CDCl_3$, DEPT) δ 40.2 (q, NMe), 114.6 (s, CN), 121.1 (s), 122.4 (d), 123.8 (d), 124.2 (d), 124.3 (d), 126.4 (d), 127.9 (d), 128.6 (d), 129.3 (d), 133.6 (d), 136.8 (s), 145.7 (s, PhC−N); UV (hexane) λ_{max} (ϵ) 360 (35 400), 307 (18 850), 241 (16 100) nm; UV (CH_2Cl_2) 364 (42 400), 308 (10 500), 244 (10 250) nm; UV (CH_3CN) 360 (46 400), 271 (33 350) nm. **3b**: yellow crystal, mp 108−110 °C (from hexane); TLC (EtOAc/hexane, 5:95) R_f 0.26; IR (KBr) 2204 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.20 (3 H, s), 6.75 (1 H, dd, J = 9.8, 0.9 Hz), 6.86−6.96 (5 H, m), 7.25−7.40 (7 H, m); ^{13}C NMR ($CDCl_3$) δ 39.0 (q), 115.2 (d), 117.1 (s), 117.4 (d), 120.4 (d), 121.5 (d), 127.4 (s), 128.8 (d), 129.3 (d), 135.7 (s), 138.8 (d), 139.7 (d), 146.4 (s); UV (hexane) λ_{max} (ϵ) 363 (23 400), 305 (21 200), 240 (14 550) nm; UV (CH_2Cl_2) 369 (26 190), 308 (41 600), 243 (21 000) nm; UV (CH_3CN) 370 (10 650), 305 (28 400), 241 (15 450) nm; MS m/z (rel intensity) 260 (M$^+$, 80), 259 (100). Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.86; H, 6.22; N, 10.74.

2-(*N*-Methyl-4-bromoanilino)-5-phenyl-2,4-pentadienenitrile (4): 53% yield; yellow crystal, mp 128−129 °C (from hexane); TLC (EtOAc/hexane, 10:90) R_f 0.30; IR (KBr) 2225 (CN); ^{1}H NMR ($CDCl_3$) δ 3.24 (3 H, s), 6.39 (1 H, d, J = 11.2 Hz), 6.67 (1 H, d, J = 15.4 Hz), 6.97 (2 H, dd, J = 6.8, 2.2 Hz), 7.17−7.41 (6 H, m), 7.45 (2 H, dd, J = 6.8, 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 40.1 (q), 114.5 (s), 116.8 (s), 120.4 (d), 123.3 (d), 123.8 (d), 126.3 (d), 126.6 (d), 128.3 (d), 128.7 (d), 132.4 (d), 134.9 (d), 136.6 (s), 144.9 (s); UV (hexane) λ_{max} (ϵ) 362 (43 050), 247 (22 500) nm; UV (CH_2Cl_2) 365 (42 900), 248 (18 500) nm; UV (CH_3CN) 365 (47 350), 246 (18 650) nm; MS m/z (rel intensity) 340 (99), 339 (86), 338 (100, M$^+$ [Br 79]). Anal. Calcd for $C_{18}H_{15}N_2Br$: C, 63.73; H, 4.46; N, 8.26. Found: C, 63.64; H, 4.46; N, 8.25.

2-(*N*-Methylanilino)-5-(2-methoxyphenyl)-2,4-pentadienenitrile (5): 71% yield, a mixture of (2*E*,4*E*)/(2*Z*,4*E*)-isomers (2:1); yellow oil; TLC (EtOAc/hexane, 10:90) R_f 0.29; IR (KBr) 2203 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.15/3.19 (s, NMe), 3.76/3.81 (s, OMe), 6.37 (d, J = 11.0 Hz, H-3), 6.70−7.34 (11.5 H, m), 7.51 (dd, J = 7.7, 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 38.4/39.6 (q, NMe), 54.9 (q, OMe), 110.4 (d), 110.6 (d), 114.4 (s), 114.6 (d), 116.0/116.7 (s), 119.6 (d), 119.8 (s), 120.2 (d), 120.3 (d), 121.4 (d), 121.5 (d), 123.4 (d), 124.1 (s), 124.2 (d), 125.2 (s), 125.5 (d), 126.2 (d), 126.9 (d), 128.5 (d), 128.6 (d), 128.8 (d), 130.1 (d), 134.5 (d), 139.4 (d), 145.4 (s), 145.9 (s), 156.4 (s), 157.1 (s); UV (hexane) λ_{max} (ϵ) 366 (55 750), 299 (25 200), 242 (26 700) nm; UV (CH_2Cl_2) 369 (52 470), 296 (34 445), 246 (32 531) nm; UV (CH_3CN) 365 (52 350), 298 (33 850), 245 (31 800) nm; MS m/z (rel intensity) 290 (100,

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(17) The author has deposited atomic coordinates for structures **3b**, **4**, **7−10**, **12**, and **13** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

M$^+$). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 77.54; H, 6.29; N, 9.43.

2-(*N*-Methyl-4-bromoanilino)-5-(2-methoxyphenyl)-2,4-pentadienenitrile (6): 58% yield; yellow oil; TLC (EtOAc /hexane, 10:90) R_f 0.28; IR (KBr) 2226 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.17 (3 H, s), 3.82 (3 H, s), 6.45 (1 H, d, J = 10.8 Hz), 6.83–7.29 (7 H, m), 7.39 (2 H, dd, J = 6.8, 2.1 Hz), 7.52 (1 H, dd, J = 7.7, 1.6 Hz); ^{13}C NMR (CDCl$_3$) δ 39.9 (q), 55.3 (q), 110.8 (d), 116.4 (s), 119.3 (s), 120.7 (d), 122.5 (d), 124.1 (d), 125.3 (s), 126.7 (d), 128.5 (d), 129.3 (d), 130.3 (d), 132.1 (d), 144.9 (s), 156.8 (s); UV (hexane) λ_{max} (ϵ) 371 (37 300), 250 (21 350) nm; UV (CH$_2$Cl$_2$) 374 (36 900), 252 (16 550) nm; UV (CH$_3$CN) 373 (38 100), 251 (14 700) nm; MS m/z (rel intensity) 370 (93), 368 (100, M$^+$ [Br 79]). Anal. Calcd for $C_{19}H_{17}N_2OBr$: C, 61.80; H, 4.64; N, 7.59. Found: C, 61.79; H, 4.71; N, 7.53.

2-(*N*-Methylanilino)-5-(4-nitrophenyl)-2,4-pentadienenitrile (7): 67% yield; red crystal, mp 151–152 °C (from hexane); TLC (EtOAc/hexane, 20:80) R_f 0.31; IR (KBr) 2219 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.32 (3 H, s), 6.18 (1 H, d, J = 11.3 Hz), 6.58 (1 H, d, J = 15.3 Hz), 7.16–7.52 (8 H, m), 8.15 (2 H, dd, J = 7.0, 1.8 Hz); ^{13}C NMR (CDCl$_3$) δ 40.6 (q), 114.0 (s), 118.7 (d), 123.9 (s), 124.1 (d), 125.8 (d), 126.4 (d), 129.1 (d), 129.5 (d), 129.7 (d), 143.6 (s), 145.2 (s), 146.4 (s); UV (hexane) λ_{max} (ϵ) 408 (16 500), 308 (13 600), 241 (11 450) nm; UV (CH$_2$Cl$_2$) 425 (19 300), 331 (16 100), 274 (25 750) nm; UV (CH$_3$CN) 421 (26 550), 265 (14 350) nm; MS m/z (rel intensity) 305 (74, M$^+$), 304 (100). Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76. Found: C, 70.14; H, 4.95; N, 13.27. After solid-state photoreaction, the recovered starting material **7** contained some (2*Z*,4*E*)-isomer: orange-red powder, mp 80–82 °C (from hexane); TLC (EtOAc/hexane, 10:90) R_f 0.20; IR (KBr) 2207 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.25 (3 H, s), 6.68–6.97 (5 H, m), 7.28–7.52 (6 H, m), 7.95 (1 H, dd, J = 7.9, 1.5 Hz); ^{13}C NMR (CDCl$_3$) δ 39.4 (q), 116.1 (d), 116.6 (s), 119.8 (s), 121.1 (d), 124.9 (d), 126.3 (d), 128.3 (d), 129.2 (d), 129.4 (d), 131.5 (s), 133.2 (d), 135.7 (d), 146.3 (s), 148.0 (s); UV (CH$_2$Cl$_2$) λ_{max} (ϵ) 248 (28 224), 288 (30 133), 403 (11 635) nm; MS m/z (rel intensity) 305 (100, M$^+$).

2-(*N*-Methyl-4-bromoanilino)-5-(4-nitrophenyl)-2,4-pentadienenitrile (8): 65% yield, red crystal, mp 185–186 °C (from EtOAc/hexane, 20:80); TLC (EtOAc /hexane, 20:80) R_f 0.25; IR (KBr) 2226 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.31 (3 H, s), 6.24 (1 H, d, J = 11.2 Hz), 6.63 (1 H, d, J = 15.4 Hz), 7.05 (2 H, dd, J = 6.9, 2.0 Hz), 7.27 (1 H, dd, J = 15.3, 11.2 Hz), 7.47–7.56 (4 H, m), 8.17 (2 H, dd, J = 7.0, 1.9 Hz); ^{13}C NMR (CDCl$_3$) δ 40.4 (q), 113.8 (s), 118.7 (s), 120.4 (d), 123.2 (s), 124.1 (d), 125.2 (d), 126.6 (d), 128.7 (d), 130.2 (d), 132.6 (d), 143.3 (s), 144.2 (s), 146.6 (s); UV (hexane) λ_{max} (ϵ) 402 (14 700), 332 (10 900), 286 (13 500) nm; UV (CH$_2$Cl$_2$) 425 (25 050), 322 (12 800), 253 (11 800) nm; UV (CH$_3$CN) 419 (27 950), 321 (10 050), 256 (12 250) nm; MS m/z (rel intensity) 385 (93), 383 (100, M$^+$ [Br 79]). Anal. Calcd for $C_{18}H_{14}N_3O_2Br$: C, 56.27; H, 3.67; N, 10.94. Found: C, 56.27; H, 3.75; N, 10.66. After solid-state photoreaction, the starting material **8** contained some (2*Z*,4*E*)-isomer: red oil; TLC (EtOAc/hexane, 10:90) R_f 0.17; IR (KBr) 2207 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.21 (3 H, s), 6.73–6.90 (3 H, m), 7.34–7.55 (7 H, m), 7.95 (1 H, dd, J = 8.1, 1.3 Hz); ^{13}C NMR (CDCl$_3$) δ 39.2 (q), 113.1 (s), 116.2 (s), 117.1 (s), 118.9 (s), 124.8 (d), 125.6 (d), 128.2 (d), 129.4 (d), 131.1 (d), 132.1 (d), 133.2 (d), 134.2 (d), 137.1 (d), 145.2 (s), 147.8 (s).

2-(*N*-Methylanilino)-5-(2-nitrophenyl)-2,4-pentadienenitrile (9): 61% yield; orange crystal, mp 104–105 °C (from EtOAc/hexane, 20:80); TLC (EtOAc/hexane, 10:90) R_f 0.28; IR (KBr) 2223 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.32 (3 H, s), 6.24 (1 H, d, J = 9.8 Hz), 7.05–7.44 (8 H, m), 7.56 (1 H, t, J = 7.4 Hz), 7.76 (1 H, d, J = 7.9 Hz), 7.91 (1 H, d, J = 8.1 Hz); ^{13}C NMR (CDCl$_3$) δ 40.6 (q), 114.1 (s), 119.5 (d), 123.6 (s), 124.0 (d), 124.8 (d), 125.7 (d), 125.9 (d), 127.5 (d), 127.7 (d), 129.5 (d), 129.7 (d), 132.4 (s), 133.0 (d), 145.3 (s), 147.5 (s); UV (hexane) λ_{max} (ϵ) 381.5 (15 400), 346 (15 150), 242 (12 150) nm; UV (CH$_2$Cl$_2$) 379 (25 225), 351 (28 108), 250 (15 901) nm; UV (CH$_3$CN) 377 (25 150), 344 (28 100), 240 (23 550) nm. Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76. Found: C, 70.65; H, 5.04; N, 13.79.

2-(*N*-Methyl-4-bromoanilino)-5-(2-nitrophenyl)-2,4-pentadienenitrile (10): 64% yield, red crystal, mp 148–150 °C (from EtOAc/hexane, 20:80); TLC (EtOAc/hexane, 10:90) R_f 0.27; IR (KBr) 2220 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.29 (3 H, s), 6.30 (1 H, dd, J = 6.8, 3.6 Hz), 7.02 (2 H, dd, J = 6.8, 2.1 Hz), 7.15–7.18 (2 H, m), 7.41–7.58 (4 H, m), 7.76 (1 H, dd, J = 8.1, 1.3 Hz), 7.93 (1 H, dd, J = 8.1, 1.3 Hz); ^{13}C NMR (CDCl$_3$) δ 40.5 (q), 114.0 (s), 118.6 (s), 121.3 (d), 122.9 (s), 124.9 (d), 125.2 (d), 127.1 (d), 127.7 (d), 128.0 (d), 129.3 (d), 132.2 (s), 132.6 (d), 133.1 (d), 144.4 (s); UV (hexane) λ_{max} (ϵ) 378.5 (13 300), 348 (12 400), 246 (8450) nm; UV (CH$_2$Cl$_2$) 372 (17 164), 344 (18 124), 248 (10 341) nm; UV (CH$_3$CN) 376 (24 900), 351 (25 300), 251 (16 050) nm; MS m/z (rel intensity) 385 (33), 383 (30, M$^+$ [Br 79]), 185 (100). Anal. Calcd for $C_{18}H_{14}N_3O_2Br$: C, 56.27; H, 3.67; N, 10.94; Found: C, 56.21; H, 3.72; N, 10.86. After solid-state photoreaction, the starting material **10** contained some (2*Z*,4*E*)-isomer: TLC (EtOAc/hexane, 20:80) R_f 0.30; IR (KBr) 2201 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.24 (3 H, s), 6.70–6.94 (5 H, m), 7.39–7.53 (4 H, m), 8.16 (2 H, dd, J = 7.0, 1.8 Hz); ^{13}C NMR (CDCl$_3$) δ 39.6 (q), 113.7 (s), 116.3 (s), 117.5 (d), 119.4 (s), 124.2 (d), 125.2 (d), 127.8 (d), 132.3 (d), 136.4 (d), 136.7 (d), 141.8 (s), 145.3 (s), 147.7 (s).

***N*-Methyl-*N*-phenylcyanoformamide (11).** A solution of the diene **3** (10 mg) in benzene (5 mL) was placed in a Pyrex test tube, purged with O$_2$, and irradiated with a medium-pressure mercury lamp for 6 h. Benzene was removed, and the residue was chromatographed on a silica gel column by elution with EtOAc/hexane (3:97) to give cinnamaldehyde (5.1 mg, 95%) and **11** (6.2 mg, 95%). **11**: colorless crystal, mp 51–52 °C (from hexane); IR (KBr) 2230 (CN), 1698 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.37 (3 H, s), 7.20–7.46 (5 H, m); MS (rel intensity) m/z 160 (100, M$^+$); HRMS calcd for $C_9H_8N_2O$ requires 160.0637, found 160.0642.

1,3-Bis(*N*-methylanilino)-2,4-bis(2-phenylethenyl)cyclobutane-1,3-dicarbonitrile (12). In a Pyrex test tube was placed a MeOH solution (2 mL) of the diene **3** (10 mg). The solvent was removed in vacuo and the residual solid deposited on the surface of the test tube. After irradiation with a medium-pressure mercury lamp for 6 h, the mixture containing [2 + 2] cycloadduct **12** and the starting material was treated with MeOH (3 mL). The white solids (**12**, 2.1 mg) were collected by filtration and **3** (7.9 mg) was recovered from the filtrate. More cycloadduct **12** (up to 99%) was obtained by repeated irradiation of the recovered material **3**. **12**: colorless crystal, mp 196–197 °C; IR (KBr) 2216 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.80 (3 H, s), 3.57 (1 H, d, J = 10 Hz), 6.24 (1 H, d, J = 16 Hz), 6.48 (1 H, dd, J = 16, 5.8 Hz), 7.11–7.34 (10 H, m); ^{13}C NMR (CDCl$_3$) δ 41.5 (q), 53.2 (d), 62.7 (s), 117.6 (s), 121.5 (d), 124.8 (d), 125.5 (d), 126.8 (d), 128.4 (d), 128.6 (d), 129.3 (d), 136.1 (s), 136.9 (d), 147.8 (s); MS m/z (rel intensity) 493 (19, M$^+$ − HCN), 416 (14), 387 (6), 260 (100). Anal. Calcd for $C_{36}H_{32}N_4$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.66; H, 6.24; N, 10.78.

1,3-Bis(*N*-methyl-4-bromoanilino)-2,4-bis(2-phenylethenyl)cyclobutane-1,3-dicarbonitrile (13). The solid-state photochemistry of **4** was similarly carried out to give **13**: colorless crystal, mp 190–191 °C; IR (KBr) 2217 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.78 (3 H, s), 3.53 (1 H, d, J = 9 Hz), 6.24–6.47 (2 H, m), 7.08 (2 H, dd, J = 6.7, 2.2 Hz), 7.29–7.43 (7 H, m); ^{13}C NMR (CDCl$_3$) δ 41.4 (q), 53.2 (d), 62.5 (s), 117.3 (s), 118.8 (d), 120.9 (d), 126.3 (d), 126.8 (d), 128.7 (d), 132.4 (d), 135.7 (d), 137.4 (d), 146.8 (s); MS m/z (rel intensity) 651 (20), 649 (12), 338 (100). Anal. Calcd for $C_{36}H_{30}N_4Br_2$: C, 63.73; H, 4.46; N, 8.26. Found: C, 63.86; H, 4.56; N, 8.05.

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