A Novel Reaction of (2,4,7-Trinito-9*H*-fluoren-9-ylidene)-propanedinitrile with *N*-Arylisoindolines

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N-Arylisoindolines **1a-c** reacted with (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**A**) in pyridine with admission of air *via* a net α-H-atom abstraction and formation of [3-(2-aryl-3-arylimino-2,3-dihydro-1*H*-isoindol-1-ylidene)-2-aryl-2,3-dihydro-1*H*-isoindol-1-ylidene]propanedinitriles **2a-c**, *N*-[2-aryl-3-(2-aryl-3-arylimino-2,3-dihydro-1*H*-isoindolyl-1-idene)-2,3-dihydro-1*H*-isoindol-1-ylidene]arenamines **3a,b**, *N,N'*-[2-aryl-1*H*-isoindole-1,3(2*H*)-diylidene]bisarenamines **4a,b** and *N*-arylphthalimides **5a-c** in moderate yields. 2,4,7-Trinitro-9-fluorenone as well as one reduction product each of the latter and of **A**, namely compounds **6** and **7**, respectively, are also found. The structure of **2b** has been unambiguously confirmed by an X-ray crystal structure analysis. A rationale for the conversions observed is presented. These involve dehydrogenation and oxidative couplings of **1a-c** as well as transfer of *N*-aryl fragment from **1a-c** to intermediate products.

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A particularly interesting fused *N*-heterocyclic system is 2*H*-isoindole [1] being accessible to electropholic attack at C1 and C3 as well as to addition of dienophiles across the C1-C7a-C3a-C3 unit [1-6]. It is also sensitive to polymerization. Since 2*H*-isoindoles may be formed by dehydrogenation of isoindolines [7], we undertook to investigate the reactions of several 2-aryl-2,3-dihydro1*H*-isoindoles (*N*-arylisoindolines) with various π-electron deficient reagents.

Recently we have demonstrated that *N*-arylisoindolines **1a-c** reacted with ethenetetracarbonitrile [8,9] under α-H-atom abstraction to give α-dicyanomethylene derivatives as well as α-oxygenated products. The latter type of products is also obtained from the interaction of 1,4-benzo- or 1,4-naphthoquinones with *N*-arylisoindolines [10,11]. The dicyanomethylene derivatives have recently been investigated electrochemically [12]. On the other hand, upon warming a mixture of each of the *N*-arylisoindolines **1a-c** with (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile in aerated pyridine, 2*H*-isoindoles bearing 3-cyano-1,4-naphthoquinon-2-yl groups at both C1 and C3 resulted [13], pointing to an electron transfer mediated isomerization of the acceptor [14].

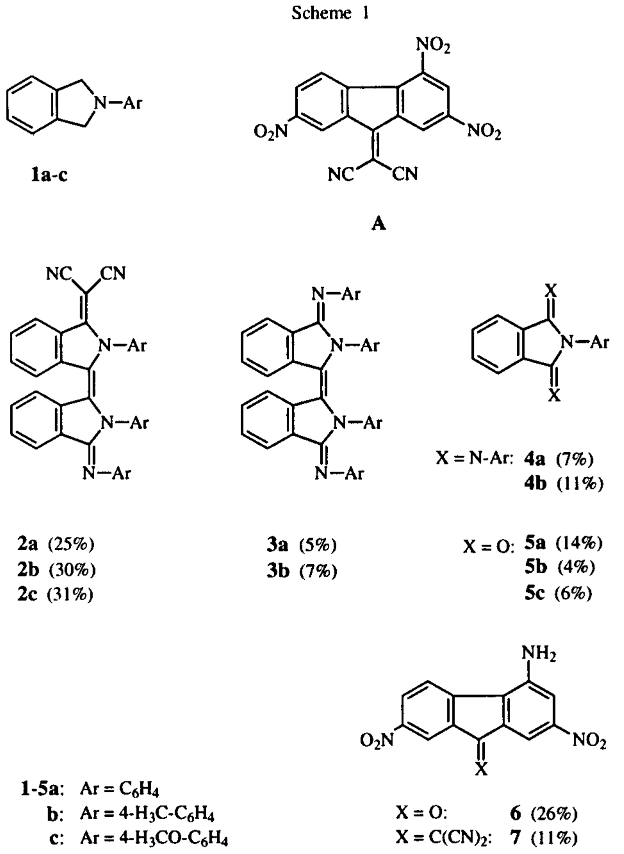
In this paper we describe the reaction of *N*-arylisoindolines **1a-c** with another π–acceptor **A**, namely (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (previously referred to as 9-dicyanomethylene-2,4,7-trinitrofluorene).

Pyridine solutions, 2.56 mmolar each in **A** and *N*-arylisoindoline **1a**, **1b** or **1c**, respectively, were kept at 100° for 5 hours with admission of air. Chromatographic separation of the residue obtained after concentration gave numerous colored zones, from which products **2a-c**, **3a,b**, **4a,b** and **5a-c** could be isolated (see Scheme 1). In addition, compounds **6** and **7** were found in small quantities in all cases.

Structural assignments of compounds **2-7** are based on spectral data, on combustion analyses and on chemical evidence. For **2b** the gross formula $C_{40}H_{29}N_5$ was confirmed by the mass spectrum which exhibited the molecular ion at m/z 579 (100%). The ir spectrum showed absorptions at 2205 (CN), 1645 (C=C), and 1591 cm^{-1} (aryl). The ^{1}H nmr (deuteriochloroform, 300 MHz) spectrum displayed two singlets at δ 2.35 (6H, 2 CH_3) and 2.39 (3H, CH_3) in addition to the aromatic protons.

Moreover, the structure of **2b** has been unambiguously established by an X-ray crystal structure analysis (see Figure 1 and Tables 1 and 2), which confirms a cisoid geometry with respect to the central C9-C 10 double bond (note that the crystallographic numbering does not correspond to IUPAC numbering rules). The sum of the C9-N1-C2, C9-N1-C32 and C2-N1-C32 angles is close to 360° as are the sums of the angles around C9 and C10 demonstrating planarity around N1, C9 and C10, whereas the sum of angles C10-N2-C25, C10-N2-C17 and C17-N2-C25 is 352.2°, revealing a slight pyramidalization at N2. The C9-C10 bond length of 1.372 Å is slightly longer than an unperturbed C=C double bond, and C3-C8 (1.408Å) is longer than its C11-C16 counterpart (1.397Å). The dihedral angle N1-C9-C10-N2 of +27.7° shows the

Scheme 1



considerable strain originating from the interaction of the *peri* hydrogen atoms at C7, C12 and from mutual repulsion of the two *N*-(*p*-tolyl) groups which avoid sandwiching.

It also seemed justified to assume analogous structures with *Z* geometry at the central double bonds for **2a** and **2c**. The spectral data (see Experimental) are in accord with this view.

Two compounds were isolated in low yield and from their ^1H nmr spectra were assigned to be symmetrical coupling products. The mass spectrum of **3b** exhibits a molecular ion at m/z 620 (100%). The ^1H nmr spectrum (deuteriochloroform, 300 MHz) clearly shows the presence of two singlets at δ 2.30 (6H, 2 CH_3) and 2.35 (6H, 2 CH_3) besides the signals of the aromatic protons. Again, a *Z* geometry is assigned by analogy with **2b** and the observations made earlier [9] on a related structure. By inspection of models one can clearly envisage that the "inner" *peri* hydrogen atoms can be accommodated in the *Z* configuration by twisting around the central double bond, but could not be accommodated while interfering with the *N*-aryl groups. If in an *E* configuration an "inner" *peri* hydrogen would reside over and close to the plane of the *N*-aryl group, a dramatic upfield shift for that proton in the ^1H nmr spectrum should result. The ^1H nmr spectra of all compounds in question, namely **2a-c** and **3a,b**, do not show such effects. The bis-imine **4b** has been assigned on the basis of elemental analysis supporting the gross formula $C_{29}H_{25}N_3$. This was confirmed by the mass spectrum which gave a correct molecular ion at m/z 415 (100%) and ^1H nmr as well as ir spectra (see Experimental part).

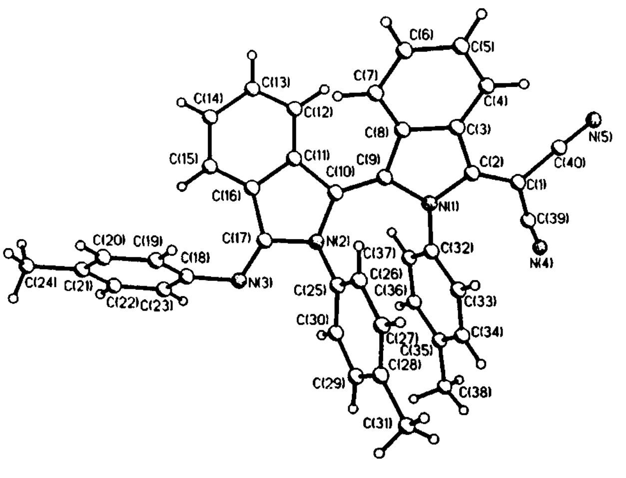


Figure 1. Molecular structure of crystalline compound **2b**. The crystallographic numbering does not represent the systematic numbering.

The identity of the phthalimides **5a-c** was demonstrated by comparison with authentic samples.

The isolation of reduction products **6** and **7** derived from **A** posed a special problem. The results of combustion analysis and spectral data suggested that one of the three nitro groups in both cases had been reduced, but it was difficult to decide on the basis of ir and ^1H nmr spectra which one of the three nitro groups had been replaced by an amino group. Acetylation of **6** gave a product showing a uv/vis spectrum very similar to that of 2,7-dinitrofluorenone (see Figure 2).

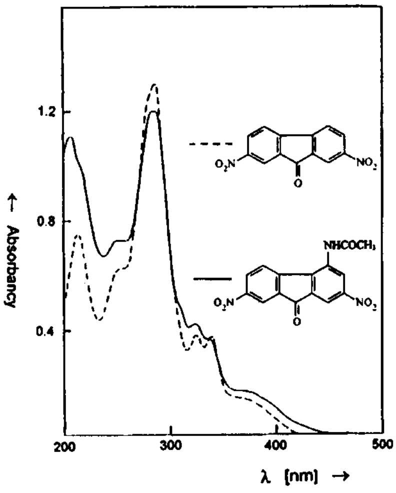


Figure 2. UV/Vis-spectra of 4.3 x 10^{-6} *M* solutions each of the acetyl derivative of compound **6** and 2,7-dinitro-9-fluorenone in acetonitrile, d = 1 cm.

On this basis it is suggested that compound **6** is 4-amino-2,7-dinitro-9-fluorenone. When the latter was treated with malononitrile in methanol in the presence of piperidine, a product identical in its mp, ir and ^{1}H nmr spectra with the sample of **7** as isolated before was obtained.

The formation of the unusual products **2**, **3** and **4** (see Scheme 1) is not easily rationalized. Since the *N*-arylimino groups must stem from the *N*-arylisoindolines **1a-c** used as starting materials, it becomes immediately clear that every *N*-arylimino group introduced requires the transformation of one extra molecule of starting material **1**. This in turn means that for their formation **2** and **4** require a total of three molecules of **1** and **3** would require the transformation of a total of four molecules of this starting material. This needs to be taken into account when determining and evaluating yields. Since the reactions occurring require a multitude of steps and are by necessity very complex, moderate yields as found (based throughout on the amount of starting material used, see Scheme 1) are acceptable, and it will not - except when unduly large efforts are made - be possible to clarify every detail.

Next, the question of the nature of the species ultimately providing the *N*-arylimino moiety needs to be addressed. In principle, an electrophilic species (as an arylnitrene) attacking an isoindole type intermediate or a nucleophilic species (an *N*-arylamine) attacking an electrophilic 1*H*-indolium intermediate, seem to be attractive possibilities. It is not possible yet on the basis of the results obtained so far to make a definite statement, in any case a process degrading starting material **1** in the proper way needs to be postulated. The nitrene pathway seems to be especially plausible since thermal nitrene release (probably in a [4+2] cheletropic process) from 7-azabicyclo[2.2.1]hepta-2,5-diene derivatives is known [15-17]. In this work a total of two arylnitrenes might be released from normal [4+4] or [4+2] cyclodimers of the isoindole **9a-c**. Another possibility is the direct acceptor-assisted cheletropic release of an arylnitrene from the isoindolines **1a-c** according to the following steps:

$$\mathrm{A} + 1 \rightarrow \overset{-}{\mathrm{A}^{\bullet}} + \overset{+}{1^{\bullet}}$$

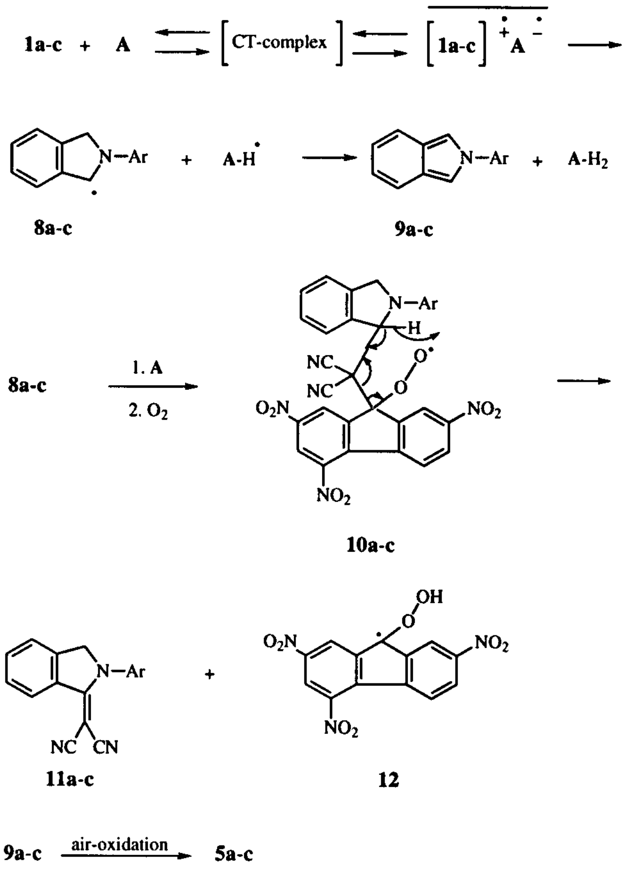
$$\overset{+}{1^{\bullet}} \rightarrow \text{Ar-}\overset{+}{\mathrm{N}^{\bullet}} + o\text{-quinodimethane}$$

$$\text{Ar-}\overset{+}{\mathrm{N}^{\bullet}} + \overset{-}{\mathrm{A}^{\bullet}} \rightarrow \text{Ar-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}} + \mathrm{A}$$

since various cases of aminylene fragmentation from 7-azabicyclo[2.2.1]hepta-2.5-dienes have been reported in which the aminylene moiety was converted into a more stable electrophilic species by attachment of an oxygen atom [18] or an electrophile [19-21] prior to spontaneous or thermally activated extrusion.

The reaction conditions provide an overall dehydrogenating and oxygenating environmment. The most likely introductory steps have been outlined in Scheme 2. Starting materials **1a-b** form, *via* a CT-complex followed by a radical ion pair and the radical pair [**8a-c**] / A-H $^{\bullet}$ as likely intermediates, the 2-aryl-2*H*-isoindoles **9a-c** and A-H$_2$. The radical **8a-c** may attack another molecule of **A** followed by pick up of oxygen to give **10a-c**, which in turn may break down to **11a-c** and **12**, being a precursor to 2,4,7-trinitro-9-fluorenone. Reduction product **7** may react similarly to generate **6**.

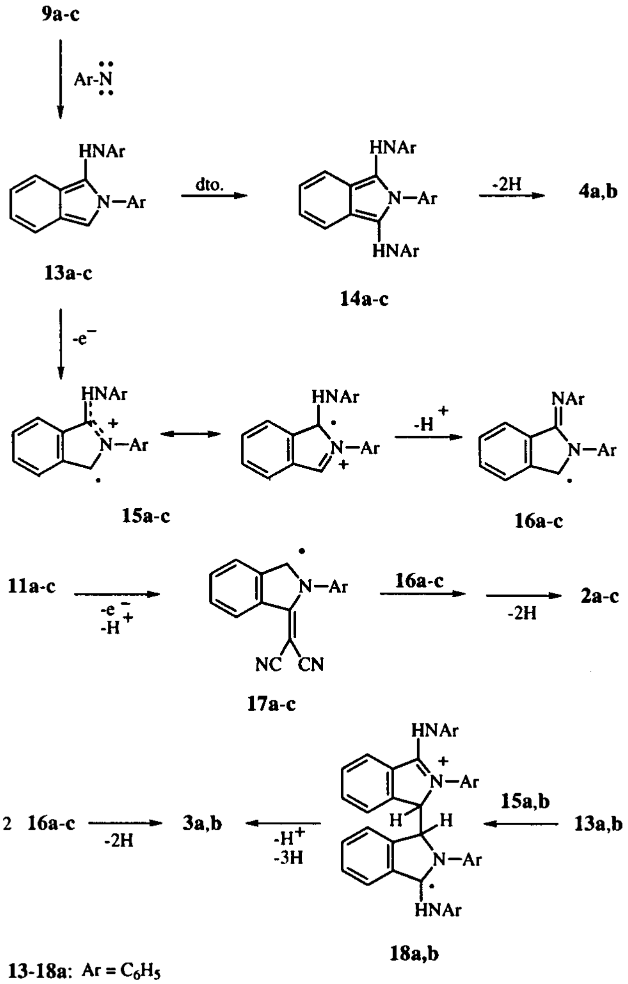
Scheme 2



8-11a: Ar = C_6H_5
b: Ar = 4-CH_3-C_6H_4
c: Ar = 4-CH_3O-C_6H_4

The phthalimides **5a-c** may well originate from **9a-c** by air oxidation [1b]. Oxidative couplings are also most likely involved in the formation of products **2a-c** and **3a,b**. Intermediates **9a-c** may - by attack of a suitable electrophile, see above - be transformed into **13a-c**. The latter as well as **11a-c** may, under the influence of unreacted **A**, undergo net hydrogen atom abstraction to yield radicals **16a-c** or **17a-c**, respectively. Symmetric coupling of two molecules of **16a,b** followed by dehydrogenation would lead to **3a,b**, and analogous coupling of one each of **17a-c** and **16a-c** would form products **2a-c**. It should be pointed out, though, that such couplings may also originate from direct attack of the radical cation of an isoindole (here **15a,b**) on the neutral isoindole [1a] (here **13a,b**) forming an intermediate dimer cation radical (as **18a,b**, see Scheme 3).

Scheme 3



13-18a: Ar = C_6H_5
b: Ar = 4-CH_3-C_6H_4
c: Ar = 4-CH_3O-C_6H_4

Introduction of a second arylamino group into **13a,b** would give rise to **14a,b**, dehydrogenation of the latter would form **4a,b**.

Compounds **6** and **7** were the only reduction products found originating from **A**. Whether the carbonyl group in **6** originates from an air oxidation of an aminodinitrofluorene anion or by another pathway has not been clarified yet.

Table 1

Compound **2b** ($C_{40}H_{29}N_5$). Coordinates and Coefficients of the Equivalent Isotropic Temperature Factors (without H atoms) [a]

Atom	x	y	z	U
N(1)	0.2416(3)	1.0836(2)	0.6998(3)	0.026(2)
N(2)	0.4691(3)	0.9626(2)	0.7656(3)	0.026(2)
N(3)	0.6472(3)	0.8869(3)	0.7939(3)	0.032(2)
N(4)	0.1362(3)	1.2761(3)	0.5104(3)	0.040(2)
N(5)	-0.1336(3)	1.2306(3)	0.6209(4)	0.050(2)
C(1)	0.0755(3)	1.1858(3)	0.6327(3)	0.030(2)
C(2)	0.1311(3)	1.1128(3)	0.6884(3)	0.027(2)
C(3)	0.0791(3)	1.0466(3)	0.7360(3)	0.028(2)
C(4)	-0.0180(3)	1.0558(3)	0.7670(3)	0.033(2)
C(5)	-0.0375(4)	0.9884(3)	0.8238(4)	0.039(2)
C(6)	0.0416(3)	0.9143(3)	0.8535(4)	0.037(2)
C(7)	0.1378(3)	0.9037(3)	0.8228(3)	0.031(2)
C(8)	0.1540(3)	0.9672(3)	0.7590(3)	0.026(2)
C(9)	0.2544(3)	0.9849(3)	0.7299(3)	0.027(2)
C(10)	0.3443(3)	0.9216(3)	0.7360(3)	0.025(2)
C(11)	0.3189(3)	0.7893(3)	0.6959(3)	0.027(2)
C(12)	0.2050(3)	0.6999(3)	0.6332(3)	0.031(2)
C(13)	0.2065(3)	0.5787(3)	0.5921(3)	0.032(2)
C(14)	0.3192(3)	0.5455(3)	0.6089(3)	0.030(2)
C(15)	0.4316(3)	0.6337(3)	0.6648(3)	0.027(2)
C(16)	0.4307(3)	0.7569(3)	0.7088(3)	0.025(2)
C(17)	0.5294(3)	0.8669(3)	0.7592(3)	0.026(2)
C(18)	0.7075(3)	0.7953(3)	0.8081(3)	0.029(2)
C(19)	0.7290(4)	0.7707(3)	0.9110(4)	0.038(2)
C(20)	0.7901(4)	0.6839(3)	0.9274(4)	0.041(2)
C(21)	0.8307(3)	0.6172(3)	0.8414(4)	0.043(2)
C(22)	0.8109(3)	0.6444(3)	0.7402(4)	0.039(2)
C(23)	0.7512(3)	0.7321(3)	0.7229(4)	0.034(2)
C(24)	0.8967(4)	0.5211(4)	0.8588(5)	0.068(3)
C(25)	0.5455(3)	1.0884(3)	0.8552(3)	0.025(2)
C(26)	0.5326(3)	1.1583(3)	0.9627(3)	0.029(2)
C(27)	0.6054(3)	1.2788(3)	1.0473(3)	0.033(2)
C(28)	0.6959(3)	1.3312(3)	1.0303(4)	0.035(2)
C(29)	0.7111(3)	1.2579(3)	0.9245(4)	0.035(2)
C(30)	0.6367(3)	1.1386(3)	0.8373(4)	0.030(2)
C(31)	0.7738(4)	1.4639(3)	1.1241(4)	0.056(3)
C(32)	0.3234(3)	1.1394(3)	0.6703(3)	0.026(2)
C(33)	0.3850(3)	1.2635(3)	0.7514(3)	0.027(2)
C(34)	0.4631(3)	1.3219(3)	0.7251(3)	0.030(2)
C(35)	0.4787(3)	1.2573(3)	0.6177(3)	0.030(2)
C(36)	0.4160(3)	1.1332(3)	0.5383(4)	0.035(2)
C(37)	0.3381(3)	1.0726(3)	0.5634(3)	0.030(2)
C(38)	0.5622(4)	1.3217(4)	0.5886(4)	0.046(2)
C(39)	0.1154(3)	1.2342(3)	0.5674(4)	0.030(2)
C(40)	-0.0398(4)	1.2094(3)	0.6276(4)	0.036(2)

[a] The coefficients of the equivalent isotropic temperature factors are defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Related dehydrogenative couplings between two 2*H*-isoindole moieties have been reported for 1-phenyl-2*H*-isoindole [22] and 1-phenylimino-2-phenyl-2,3-dihydro-1*H*-isoindole [23]. Products structurally analogous to **2** and **3** may also be obtained from *o*-phthalaldehyde and 2,2'-diaminobiphenyls [24]. β-Isoindigoid structures related to **3** and 1,3-diimino-2,3-dihydro-1*H*-isoindolines analogous to **4** have been obtained from *N*-aryldithiophthalimides [25]. The connections of the transformations

Table 2

Compound **2b** ($C_{40}H_{29}N_5$). Interatomic Distances [Å] and Angles [°]

Distances:		Angles:	
C(1) - C(2)	1.397(6)	C(2) - C(1) - C(39)	127.0(4)
C(1) - C(39)	1.420(8)	C(2) - C(1) - C(40)	119.9(5)
C(1) - C(40)	1.425(7)	C(39) - C(1) - C(40)	112.9(4)
N(1) - C(2)	1.370(5)	C(2) - N(1) - C(9)	110.9(4)
N(1) - C(9)	1.421(6)	C(2) - N(1) - C(32)	122.4(4)
N(1) - C(32)	1.437(6)	C(9) - N(1) - C(32)	126.4(3)
C(2) - C(3)	1.458(7)	N(1) - C(2) - C(1)	125.7(5)
		N(1) - C(2) - C(3)	107.2(4)
		C(1) - C(2) - C(3)	127.0(4)
C(3) - C(4)	1.394(7)	C(2) - C(3) - C(4)	132.3(4)
C(3) - C(8)	1.408(6)	C(2) - C(3) - C(8)	107.0(4)
		C(4) - C(3) - C(8)	120.6(4)
C(4) - C(5)	1.379(8)	C(3) - C(4) - C(5)	119.0(4)
C(5) - C(6)	1.404(6)	C(4) - C(5) - C(6)	120.5(5)
C(6) - C(7)	1.381(7)	C(5) - C(6) - C(7)	121.2(5)
C(7) - C(8)	1.403(7)	C(6) - C(7) - C(8)	118.6(4)
C(8) - C(9)	1.449(7)	C(3) - C(8) - C(7)	119.9(4)
		C(3) - C(8) - C(9)	108.7(4)
		C(7) - C(8) - C(9)	130.4(4)
C(9) - C(10)	1.372(6)	N(1) - C(9) - C(8)	105.2(3)
		N(1) - C(9) - C(10)	128.4(4)
		C(8) - C(9) - C(10)	126.3(4)
C(10) - C(11)	1.473(5)	N(2) - C(10) - C(9)	128.4(4)
		N(2) - C(10) - C(11)	107.0(3)
		C(9) - C(10) - C(11)	124.2(3)
N(2) - C(10)	1.398(5)	C(10) - N(2) - C(17)	110.2(3)
N(2) - C(17)	1.420(5)	C(10) - N(2) - C(25)	122.9(3)
N(2) - C(25)	1.441(4)	C(17) - N(2) - C(25)	119.1(3)
C(11) - C(12)	1.389(5)	C(10) - C(11) - C(12)	130.6(4)
C(11) - C(16)	1.397(6)	C(10) - C(11) - C(16)	107.6(3)
		C(12) - C(11) - C(16)	120.8(3)
C(12) - C(13)	1.380(5)	C(11) - C(12) - C(13)	118.5(4)
C(13) - C(14)	1.402(6)	C(12) - C(13) - C(14)	121.1(3)
C(14) - C(15)	1.386(5)	C(13) - C(14) - C(15)	120.6(4)
C(15) - C(16)	1.399(5)	C(14) - C(15) - C(16)	118.4(4)
C(16) - C(17)	1.465(5)	C(11) - C(16) - C(15)	120.5(3)
		C(11) - C(16) - C(17)	108.7(3)
		C(15) - C(16) - C(17)	130.6(4)
C(17) - N(3)	1.274(5)	N(2) - C(17) - N(3)	121.0(3)
		N(2) - C(17) - C(16)	106.1(3)
		N(3) - C(17) - C(16)	132.9(4)
N(3) - C(18)	1.414(5)	C(17) - N(3) - C(18)	118.4(4)
C(18) - C(19)	1.389(7)	N(3) - C(18)- C(19)	120.3(4)
		N(3) - C(18) - C(23)	120.7(4)
		C(19) - C(18) - C(23)	119.0(4)
C(19) - C(20)	1.375(6)	C(18) - C(19) - C(20)	120.7(4)
C(20) - C(21)	1.384(7)	C(19) - C(20) - C(21)	121.3(5)
C(21) - C(22)	1.394(8)	C(20) - C(21) - C(22)	117.4(4)
C(21) - C(24)	1.508(7)	C(20) - C(21) - C(24)	121.2(5)
		C(22) - C(21) - C(24)	121.3(5)
C(22) - C(23)	1.376(6)	C(21) - C(22) - C(23)	122.3(4)
C(23) - C(18)	1.394(7)	C(18) - C(23) - C(22)	119.3(5)
C(25) - C(26)	1.382(6)	N(2) - C(25) - C(26)	120.4(4)
		N(2) - C(25) - C(30)	120.1(4)
		C(26) - C(25) - C(30)	119.4(3)
C(26) - C(27)	1.378(4)	C(25) - C(26) - C(27)	120.0(4)
C(27) - C(28)	1.384(7)	C(26) - C(27) - C(28)	121.4(4)
C(28) - C(29)	1.392(6)	C(27) - C(28) - C(29)	117.7(3)
C(28) - C(31)	1.512(5)	C(27) - C(28) - C(31)	120.3(4)
		C(29) - C(28) - C(31)	122.0(5)
C(29) - C(30)	1.374(4)	C(28) - C(29) - C(30)	121.5(5)
C(30) - C(25)	1.386(7)	C(25) - C(30) - C(29)	119.9(4)
C(32) - C(33)	1.382(4)	N(1) - C(32) - C(27)	121.5(3)
		N(1) - C(32) - C(33)	117.6(4)
		C(27) - C(32) - C(33)	120.9(4)
C(33) - C(34)	1.390(7)	C(32) - C(33) - C(34)	119.6(4)
C(34) - C(35)	1.386(6)	C(33) - C(34) - C(35)	120.7(3)
C(35) - C(36)	1.382(5)	C(34) - C(35) - C(36)	118.5(5)
C(35) - C(38)	1.510(8)	C(34) - C(35) - C(38)	120.4(3)
		C(36) - C(35) - C(38)	121.1(4)
C(36) - C(37)	1.393(7)	C(27) - C(36) - C(35)	121.8(4)
C(37) - C(32)	1.381(6)	C(32) - C(37) - C(36)	118.5(3)
C(39) - N(4)	1.148(7)	N(4) - C(39) - C(1)	173.2(4)
C(40) - N(5)	1.157(6)	N(5)- C(40) - C(1)	177.6(6)

reported in this study to the rich chemistry of isoindoline based pigments should be noted [26].

In conclusion, the reactions and products presented here provide an insight into the spontaneous reactions between the electron donating isoindolines **1a-c** and a suitable electron acceptor, here **A**, which go far beyond the mere formation of charge transfer complexes.

EXPERIMENTAL

The uncorrected melting points were determined with a Reichert Thermovar hot stage microscope. The ir spectra were recorded on a Perkin-Elmer 983 spectrophotometer using potassium bromide pellets. The 300 MHz ^{1}H nmr spectra were recorded on a Bruker WM 300 instrument with tetramethylsilane as internal reference, s = singlet, m = multiplet. The mass spectra (70 eV, electron impact mode) were obtained on an AMD 604 instrument. The uv/vis spectra were recorded on a Perkin-Elmer 554 spectrophotometer. Combustion analyses were carried out with a Carlo Erba Model 1106 CHN analyses. Preparative layer chromatography used air dried 1.0 mm thick layers of slurry applied silica gel Merck PF_{254} on 48 cm wide and 20 cm high glass plates. Zones were detected by their color or by quenching of indicator fluorescence upon exposure to 254 nm light.

Starting Materials.

2-Aryl-2,3-dihydro-1*H*-isoindoles **1a-c** were prepared according to the literature [7,13,27] as were also 2-phenyl-2,3-dihydro-1*H*-isoindole (**1a**), mp 170-171°, ref [7] 172-173°, 2-(4-methylphenyl)-2,3-dihydro-1*H*-isoindole, (**1b**), mp 190-192°, ref [7] 193°, 2-(4-methoxyphenyl)-2,3-dihydro-1*H*-isoindole (**1c**), mp 218-220°, ref [7] 219°. (2,4,7-Trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**A**) was prepared from 2,4,7-trinitro-9-fluorenone and malononitrile according to Mukherjee [28].

Reaction of *N*-Arylisoindolines **1a-c** with **A**.

To 2.56 mmoles of *N*-arylisoindoline **1a-c** in dry pyridine (10 ml) equimolar amounts of **A** in 20 ml of dry pyridine were added with stirring. The mixture was heated gently without increasing the temperature above 100° for 5 hours. The solvent was removed by concentration and the residue was washed several times with ethanol to remove residual pyridine. The residue was dissolved in acetone and separated by preparative layer chromatography using cyclohexane-ethyl acetate (5:1) as eluent into numerous zones, five of which were extracted. The fastest migrating zone contained 2,4,7-trinitro-9-fluorenone, the second zone which was characterized by its red color contained compound **3**; the third and fourth zones which quenched all indicator fluorescence upon exposure to 254 nm uv-light contained compounds **4** and **5**. The fifth zone, which is always characterized by a blue color, contained compound **2**. The material confined to the start was rechromatographed using cyclohexane/ethyl acetate (2:1) to give another two zones; the faster migrating one of which contained 4-amino-2,7dinitro-9-fluorenone (**6**) whereas the second zone (deep blue color) contained (4-amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**7**). Extraction of the zones with acetone gave a residue which was rechromatographed with the same eluent to enhance separation. Recrystallization from suitable solvents afforded the samples of 2,4,7-trinitro-9-fluorenone and compounds **2-7**.

[3-(2-Phenyl-3-phenylimino-2,3-dihydro-1*H*-isoidol-1-ylidene)-2-phenyl-2,3-dihydro-1*H*-isoindol-1-ylidene]propanedinitrile (**2a**).

This compound was obtained as blue crystals (acetonitrile), mp 306-308°, (113 mg, 25%); ir: ν 2202 (CN), 1631 (C=C), 1591 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 6.55-6.95 (m, 5H, aryl), 7.10-7.40 (m, 10H, aryl), 7.45-7.65 and 7.80-8.05 (two m, 6H, aryl), 8.35-8.45 (m, 1H, aryl), 8.65-8.75 (m, 1H, aryl); ms: m/z (%) 537 (M$^+$, 67), 489 (17), 460 (11), 445 (17), 414 (24), 372 (16), 322 (44), 297 (90), 271 (45), 245 (18), 205 (44), 179 (46), 77 (100).

Anal. Calcd. for $C_{37}H_{23}N_5$: C, 82.66; H, 4.31; N, 13.03. Found: C, 82.49; H, 4.12; N, 12.88.

{3-[2-(4-Methylphenyl)-3-(4-methylphenylimino)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(4-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (**2b**).

This compound was obtained as blue crystals (acetonitrile), mp 318-320°, (148 mg, 30%); ir: ν 2205 (CN), 1645 (C=C), 1591 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.35 (s, 6H, 2 CH_3), 2.39 (s, 3H, CH_3), 6.40-7.00 (m, 4H, aryl), 7.10-7.70 (m, 14H, aryl), 8.25-8.40 (m, 1H, aryl) 8.65-8.80 (m, 1H, aryl); ms: m/z (%) 579 (M$^+$, 100), 514 (7), 488 (8), 473 (15), 415 (10), 324 (6), 311 (32), 289 (27), 214 (52), 91 (71), 65 (44).

Anal. Calcd. for $C_{40}H_{29}N_5$: C, 82.88; H, 5.04; N, 12.08. Found: C, 82.69; H, 5.22; N, 11.89.

{3-[2-(4-Methoxyphenyl)-3-(4-methoxyphenylimino)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(4-methoxyphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (**2c**).

This compound was obtained as blue crystals (acetonitrile), mp 297-299°, (166 mg, 31%); ir: ν 2210 (CN), 1640 (C=C), 1600 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.82 (s, 6H, 2 OCH_3), 3.85 (s, 3H, OCH_3), 6.50-7.20 (m, 16H, aryl), 7.40-7.80 (m, 2H, aryl), 8.30 (m, 1H, aryl), 8.80 (m, 1H, aryl); ms: m/z (%) 627 (M$^+$, 100), 612 (19), 520 (13), 505 (20), 358 (40), 343 (32), 301(61), 235 (48), 130 (32), 92 (28), 77 (46).

Anal. Calcd. for $C_{40}H_{29}N_5O_3$: C, 76.54; H, 4.66; N, 11.16. Found: C, 76.65; H, 4.43; N, 11.29.

N-[2-Phenyl-3-(2-phenyl-3-phenylimino-2,3-dihydro-1*H*-isoindol-1-ylidene)-2,3-dihydro-1*H*-isoindol-1-ylidene]benzenamine (**3a**).

This compound was obtained as red crystals (cyclohexane), mp 328-330°, (17 mg, 5%); ir: ν 1634 (C=C), 1588 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 6.65-6.75 and 6.85-7.00 (two m, 8H, aryl), 7.05-7.40 (m, 12H, aryl), 7.50-7.70 (m, 6H, aryl), 7.90-8.45 (m, 2H, aryl); ms: m/z (%) 564 (M$^+$, 100), 472 (37), 394 (18), 282 (22), 205 (19), 77 (38).

Anal. Calcd. for $C_{40}H_{28}N_4$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.92; H, 4.86; N, 9.76.

N-{2-(4-Methylphenyl)-3-[2-(4-methylphenyl)-3-(4-methylphenylimino)]-2,3-dihydro-1*H*-isoindol-1-ylidene}(4-methylbenzenamine) (**3b**).

This compound was obtained as red crystals (*n*-hexane), mp 293-295°, (29 mg, 7%); ir: ν 2920, 2840 (CH_3), 1615 (C=C), 1600 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.30 (s, 6H, 2 CH_3), 2.35 (s, 6H, 2 CH_3), 6.60 (m, 2H, aryl), 6.75-6.90 (m, 8H, aryl), 7.05-7.15 (m, 4H, aryl), 7.20-7.40 and 7.50-8.20 (m, 8H, aryl), 8.40 (m, 2H, aryl); ms: m/z (%) 620 (M$^+$, 100), 514 (41), 422 (10), 311 (52), 219 (14), 91 (25).

Anal. Calcd. for $C_{44}H_{36}N_4$: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.31; H, 5.85; N, 8.91.

N,N'-[2-Phenyl-1*H*-isoindole-1,3(2*H*)-diylidene]bisbenzenamine (**4a**).

This compound was obtained as pale yellow crystals (cyclohexane), mp 222-224°, (23 mg, 7%); ir: ν 1646 (C=C), 1587 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 6.60-6.74 (m, 2H, aryl), 6.90-7.00 (m, 3H, aryl), 7.10-7.18 (m, 3H, aryl), 7.28-7.40 (m, 4H, aryl), 7.47-7.65 (m, 7H, aryl); ms: m/z (%) 373 (M$^+$, 100), 296 (62), 269 (9), 205 (5), 186 (10), 167 (8), 77 (43).

Anal. Calcd. for $C_{26}H_{19}N_3$: C, 83.62; H, 5.13; N, 11.25. Found: C, 83.79; H, 5.22; N, 11.12.

N,N'-[2-(4-Methylphenyl)-1*H*-isoindole-1,3(2*H*)-diylidene]bis-(4-methylbenzenamine) (**4b**).

This compound (38 mg, 11%) was obtained as pale yellow crystals (cyclohexane), mp 211-213°, ref [29] 187°; ir: ν 2860 (CH_3), 1645 (C=C), 1605 (aryl) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.30 (s, 6H, 2 CH_3), 2.35 (s, 3H, CH_3), 6.70-6.75 (m, 2H, aryl), 6.80 (m, 2H, aryl), 7.10-7.30 (m, 8H, aryl), 7.35 (m, 2H, aryl), 7.45 (m, 2H, aryl); ms: m/z (%) 415 (M$^+$, 100), 324 (61), 309 (46), 208 (21), 91 (24).

Anal. Calcd. for $C_{29}H_{25}N_3$: C, 83.82; H, 6.06; N, 10.11. Found: C, 83.69; H, 6.04; N, 10.03.

N-Phenylphthalimide (**5a**).

This compound had mp 209-210°, ref [30] 212°, 20 mg (4%).

N-(4-Methylphenyl)phthalimide (**5b**).

This compound had mp 204-206° ref [31] 205°, 26 mg (4%).

N-(4-Methoxyphenyl)phthalimide (**5c**).

This compound had mp 165-167° ref [30] 164°, 40 mg (6%).

4-Amino-2,7-dinitro-9-fluorenone (**6**).

This compound was obtained as orange crystals (dimethylformamide), mp 310-312°, (192 mg, 26%); ir: ν 3400 (NH_2), 1710 (CO), 1630, 1600 (aryl) cm^{-1} and was insoluble in all common organic solvents; ms: m/z (%) 285 (M^+, 100), 239 (31), 193 (32), 181 (10), 164 (33), 153 (9), 138 (28).

Anal. Calcd. for $C_{13}H_7N_3O_5$: C, 54.75; H, 2.47; N, 14.73. Found: C, 54.54; H, 2.63; N, 14.49.

Treatment of **6** with acetic anhydride and one drop of pyridine at 70° for 2 hours gave an acetyl derivative, mp 244-246°.

(4-Amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**7**).

This compound was obtained as blue crystals (acetonitrile), mp 340-342°, (96 mg, 11%); ir: ν 3500, 3380 (NH_2), 2220 (CN), 1645 (C=C), 1600 (aryl) cm^{-1}; ^1H nmr (perdeuteriotetrahydrofuran): δ 6.20 (s, 2H, NH_2), 7.80-8.60, 9.25 (two m, 5H, aryl); ms: m/z (%) 333 (M^+, 100), 317 (2), 303 (7), 287 (20), 275 (15), 257 (10), 241 (48), 229 (12), 213 (46), 202 (11), 187 (14).

Anal. Calcd. for $C_{16}H_7N_5O_4$: C, 57.67; H, 2.12; N, 21.01. Found: C, 57.52; H, 2.31; N, 20.87.

To a suspension of 142.5 mg (0.5 mmole) of **6** in 15 ml of boiling methanol, 99 mg (1.5 mmoles) of malononitrile and one drop of piperidine were added. After 10 minutes the mixture was allowed to cool to room temperature. The precipitate was filtered, washed with methanol and recrystallized from acetonitrile to give 100 mg (60%) of **7**, mp 340-342°; the ir is identical with that of the sample reported above.

X-ray Crystal Structure Determination of Compound **2b**.

A crystal suitable for X-ray diffraction (*ca.* 0.38 x 0.22 x 0.17 mm) was mounted at the top of a glass capillary. The orientation matrix and the unit cell parameters were obtained by a least-squares fit of the setting angles of 18 centered reflections in the range $20° < 2\theta < 40°$.

Crystallographic Details.

Empirical formula is $C_{40}H_{29}N_5$, molecular mass 579.68, triclinic, space group P1, a = 12.389(9), b = 12.134(9), c = 12.806(9) Å, $\alpha = 115.73(6)$, $\beta = 113.83(6)$, $\gamma = 93.18(6)°$, V = 1522.99 $Å^3$, Z = 2, $\mu(MoK_a) = 0.08\ mm^{-1}$, $D_x = 1.264\ gcm^{-3}$.

Data Collection.

Siemens P4RA four-circle diffractometer, rotating anode generator, LT-2 low temperature device, MoK_α radiation (μ = 0.71073 Å), graphite monochromator, scintillation counter, ω scan, empirical absorption correction (ψ scan, transmission range 0.962 - 0.917) was used.

Structure Solution and Refinement.

All calculations including data reduction (Lorentz and polarization corrections) and empirical absorption corrections were done by using the SHELXTL PLUS program package [32] on an MS-DOS personal computer equipped with an INTEL 80486 microprocessor. The structure was solved by direct methods and refined to $R = (\Sigma \| F_o | - | F_c \|) / \Sigma | F_o | = 0.0577$ and $R_w = [\Sigma w (| F_o | - | F_c |)^2 / \Sigma w F_o^2]^{1/2} = 0.0714$ (hydrogen atoms at idealized positions, non-hydrogen atoms anisotropic, full-matrix least-squares, 408 variables, 4782 unique reflections of which 3237 were considered observed ($I > 2\sigma(I)$), one isotropic extinction parameter, one scaling factor). Atomic scattering factors were taken from standard sources [33]. Both the f' and f" components of the anomalous dispersion were included for all non-hydrogen atoms. The atomic coordinates of the non-hydrogen atoms are listed in Table 1, a selection of interatomic distances and angles is given in Table 2.

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