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Several series of novel compounds have been prepared containing dicyanomethylidene groups including 1-alkyl-3-dicyanomethylideneindol-2-ones and 6,6-dicyanofulvenes. Their visible absorption properties are recorded and discussed.

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Malononitrile is a versatile compound of exceptional reactivity and its chemistry is of theoretical and synthetic interest. It has been used extensively as a reagent, particularly in condensation reactions to give a variety of addition products, which are often used as intermediates for the preparation of heterocycles [1]. This unique reactivity makes malononitrile an important chemical both in basic research and in applied medicinal and industrial chemistry. Polycyano compounds and especially the dicyanomethylidene derivatives are of particular interest [2,3]. For example, 7,7,8,8-tetracyanoquinodimethane (TCNQ), one of the few stable quinodimethanes, has received extensive study [4,5] because of its unusual stability and electrical properties. This compound and its analogs are particularly suited for the development of charge-transfer systems, of organic conductors, and of semiconductors, since tetracyanoquinodimethanes are efficient electron acceptors due to the two electron-withdrawing dicyanomethylidene groups [6,7].

Our recent studies in dyestuff chemistry, especially in mero-stabilized dyes [8], aroused our interest in dicyanomethylidene derivatives because the strong electron acceptor property of the dicyanomethylidene group confers chromophoric or highly efficient auxochromic character. Compounds containing a dicyano-methylidene group which is conjugated with another chromophore should be deeply colored. Although some colored dicyano- and tetracyanoquinodimethane derivatives have been reported [6,9], we believe that less attention than deserved has previously been given to this field.

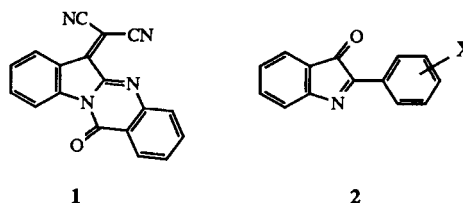
In the present paper, we report the detailed synthesis, characterization, and visible absorption properties of several series of novel compounds containing dicyanomethylidene groups derived from malononitrile.

1-Alkyl-3-dicyanomethylideneindol-2-ones.

A few dicyanomethylideneindoles are recorded. For example, the natural product Tryparthrin was converted into its dicyanomethylidene derivative **1** by reaction with malononitrile [10], and 3-dicyanomethylideneindol-2-one **5a** itself is known [11]. However, 2-arylidolenin-3-ones **2** were stated [12] not to react with malononitrile to form dicyanomethylidene compounds. We now report the synthe-

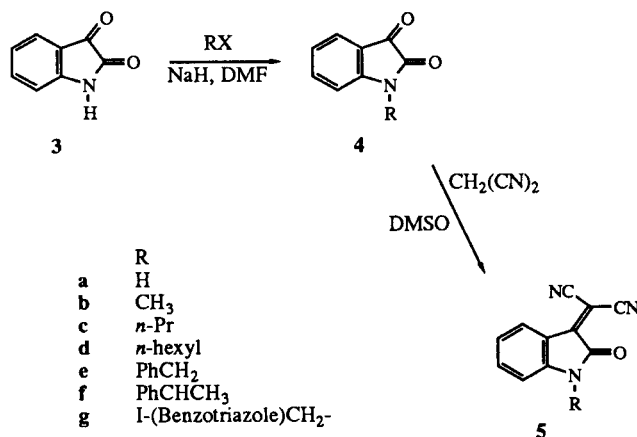
sis of a series of 1-alkyl-3-dicyanomethylideneindol-2-ones, and an examination of their visible absorption spectra.

Block I



Reaction of isatin **3** and the appropriate alkyl halide in dimethylformide, with sodium hydride as a base, gave a variety of *N*-alkylisatins **4** in the form of orange crystals. These *N*-alkylisatins were readily converted into the corresponding 1-alkyl-3-dicyanomethylideneindol-2-ones **5**, in good yield, on stirring with malononitrile in dimethyl sulfoxide (Scheme 1). The products **5** were fully characterized analytically (Table I), and by their ir, ¹H (Table II) and ¹³C nmr spectra (Table III). The 3-dicyanomethylideneindol-2-one derivatives showed two absorption bands in their ir spectra at around 2200 cm⁻¹, characteristic of two non-equivalent cyano groups. Surprisingly, the amide carbonyl groups in the 3-dicyanomethylideneindol-2-ones absorb at above 1700 cm⁻¹, instead of around 1650 cm⁻¹ as normal. The ¹H and ¹³C nmr spectra are readily assigned (Tables II and III), and agree well with the assigned structures. In

Scheme I



the ^{13}C nmr spectra, the two cyano groups invariably show two different signals as expected.

The visible absorptions of the 1-alkyl-3-dicyanomethylideneindol-2-ones **5**, and of the corresponding 1-alkylisatins, were recorded in ethanol. As shown in Table I, the ex-

tinution coefficients, both of compound **4** and of **5**, are relatively small. However, introducing a dicyanomethylidene group into a 1-alkylisatin induces a dramatic bathochromic shift (80-100 nm red shift from **4** to **5**), together with a small hyperchromic effect.

Table I

Preparation and Visible Spectra of 1-Substituted Isatins **5** and Corresponding Dicyanomethylidene Derivatives **6**

No.	R	yield %	crystal form	UV/Vis λ (ϵ)	mp ($^{\circ}\text{C}$)	Calcd.			formula	Found		
						C	H	N		C	H	N
5a	H	92	red	492 (3400)	235-238	(lit [11] mp 235 $^{\circ}$)						
4b	CH_3	70	orange	422 (1200)	132-134 ^a	(lit [11] mp 135 $^{\circ}$)						
5b	"	85	violet	500 (2420)	220-223	68.90	3.32	20.29	$\text{C}_{12}\text{H}_7\text{N}_3\text{O}$	68.54	3.01	20.06
4c	<i>n</i> -Pr	54	orange	424 (1300)	62-63	69.84	5.72	7.41	$\text{C}_{11}\text{H}_{11}\text{NO}_2$	69.92	5.84	7.27
5c	"	73	violet	504 (2300)	143-145	70.89	4.64	17.72	$\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$	70.56	4.45	17.54
4d	<i>n</i> -hexyl	60	yellow	408 (1210)	39-40	72.73	7.36	6.06	$\text{C}_{14}\text{H}_{17}\text{NO}_2$	72.58	7.27	5.15
5d	"	76	red	496 (2510)	113-115	73.02	6.09	15.05	$\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}$	72.60	6.19	14.89
4e	PhCH_2	56	orange	418 (1100)	129-131	(lit [14] mp 130-131 $^{\circ}$)						
5e	"	66	red	497 (2480)	190-192	75.79	3.86	14.74	$\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}$	75.42	3.51	14.51
4f	PhCHCH_3	46	orange	416 (1050)	118-120	75.49	5.18	5.58	$\text{C}_{16}\text{H}_{13}\text{NO}_2$	76.21	5.32	5.29
5f	"	84	violet	500 (2150)	155-157	76.25	4.35	14.95	$\text{C}_{19}\text{N}_3\text{N}_3\text{O}$	76.04	4.28	14.27
4g	BtCH_2 [b]	49	yellow	400 (950)	177-180	64.65	3.60	20.14	$\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}_2$	64.26	3.32	20.34
5g	"	46	brown	475 (1800)	213-215	66.26	3.07	25.77	$\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_2$	66.35	2.77	25.46

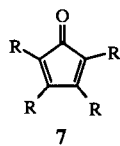
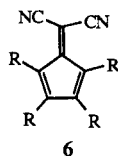
[a] lit [15] mp 233 $^{\circ}$. [b] Bt = benzotriazol-1-yl.

Table II

Proton NMR and IR Spectral Data of 1-Substituted Isatins **4** and Dicyanomethylidene Analogs **5**

No.	R	^1H NMR (δ)	ν C=O	ν C ON	ν CN	ν CN	ν C=C
5a	H	7.0-7.4 (m), 7.6-8.1 (m), 11.5 (s, NH)					
4b	CH_3	7.70-7.95 (s, 2H), 7.00 (s, 2H), 3.40 (s, 3H, CH_3)	1740	1630			
5b	"	7.10-8.15 (m, 4H), 3.35 (s, 3H, CH_3)	---	1715	2220	2210	1600
4c	<i>n</i> -Pr	7.60-8.00 (m), 7.10-7.45 (m), 3.82 (t), 1.85 (m), 1.10 (t)	1730	1610			
5c	"	7.10-8.10 (m, 4H), 3.65 (t, 2H), 1.68 (m, 2H), 1.10 (t, 3H)	---	1715	2210	2200	1610
4d	<i>n</i> -hexyl	7.15-8.10 (m, 4H), 3.60 (t, 2H), 1.60 (m, 8H), 0.90 (t, 3H)	1730	1610			
5d	"	7.15-8.10 (m, 4H), 3.70 (t, 2H), 1.35 (m, 8H), 0.95 (t, 3H)	---	1715	2200	2180	1610
4e	PhCH_2	6.85-7.85 (m, 9H), 5.08 (s, 2H, CH_2)	1725	1630			
5e	"	8.20 (d, 1H), 7.10-7.85 (m, 8H), 5.12 (s, 2H, CH_2)	---	1710	2210	2200	1610
4f	PhCHCH_3	6.55-7.50 (m, 9H), 5.65 (q, 1H, CH), 1.90 (d, 3H, CH_3)	1740	1620			
5f	"	8.15 (d, 1H), 7.00-7.70 (m, 8H), 5.72 (q, 1H), 1.85 (d, 3H)	---	1710	2205	2200	1580
4g	BtCH_2	7.20-8.20 (m, 8H), 6.70 (s, 2H, CH_2)	1735	1610			1610
5g	BtCH_2	7.20-8.20 (m, 8H), 6.80 (s, 2H, CH_2)	---	1720	2210	2210	

Block 2



6,6-Dicyanofulvene Derivatives.

The 6,6-dicyanofulvene derivatives **6** may be regarded as the dicyanomethylene analogues of the well-known tetrasubstituted cyclopentadienones **7**. Tetraaryl cyclopentadienones **7** are well known to be deeply colored [16]. We reasoned that the replacement of the carbonyl group of cyclopentadienone **7** by a dicyanomethylidene group should result in a significant bathochromic shift, and compounds **6** should be highly colored. Indeed, 2,3,4,5-tetraaryl-

6,6-dicyanofulvene (**6**, R = Ph) has been reported to form green crystals [17], but the only known preparation (in 16% yield) was by the reaction of the organic molybdenum complex $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_6\text{H}_5$ with diphenylacetylene in boiling benzene. The ^{13}C nmr spectrum of **6** (R = Ph) has been studied [18]. In contrast with the difficult preparation published for the 6,6-dicyanofulvene **6**, the corresponding dicyanohepta- and dicyanotriafulvenes were reported to be rather easily synthesized from malononitrile with tropylium or with cyclopropenium systems, respectively [19,20]. Fluorenones substituted with a nitro group were also reported to condensed with malononitrile to give the expected dicyanomethylidene derivatives [21]. Unsubstituted 9-fluorenylidene malononitrile was prepared by the reaction of its tetrachlorocatechol ketal with malononitrile [22].

Our attempts to convert 2,3,4,5-tetraaryl cyclopentadien-

Table III

Carbon NMR Spectral Data of 1-Substituted Isatins **4** and Dicyanomethylidene Analogs **5**

No.	C2	C3	C4	C5	C6	C7	C8	C9	C10	CN	CN	R					
5a	163.6	146.4	150.4	137.8	111.6	125.7	122.9	118.5	122.9	112.9	106.7						
4b	158.1	183.2	151.3	138.4	109.9	125.0	123.7	117.2				26.0					
5b	162.9	147.0	147.1	137.6	110.5	125.4	123.3	117.9	132.3	112.9	106.7	26.2					
4c	157.7	183.1	150.6	138.4	109.9	124.7	123.2	117.0				41.3	20.1	10.9			
5c	162.3	146.5	149.5	137.7	110.6	125.6	123.3	118.0	130.6	111.3	106.7	40.1	20.7	11.3			
4d	157.5	183.0	150.4	138.0	109.8	124.4	122.9	116.8				39.5	30.7	26.6	25.9	21.9	13.4
5d	162.4	146.6	149.6	137.8	110.7	125.7	123.4	118.1				39.8	30.9	25.7	25.9	22.0	13.9
4e	158.1	183.1	150.6	138.3	110.9	125.2	123.7	117.5	127.4			134.4	132.3	128.0	111.8	43.9	
5e	162.5	146.0	149.5	137.4	110.9	125.6	123.5	118.2		112.9	111.4	134.6	131.2	128.5	126.6	44.2	
4f	158.0	183.2	149.5	137.6	112.0	124.5	122.9		126.7			133.9	128.5	127.4	126.6	49.6	
5f	162.4	145.4	149.6	137.2	111.8	125.7	123.2	118.4		112.9	106.7	134.7	128.6	127.5	126.3	49.4	
4g	159.1	187.5	147.6	137.3	110.5	124.5	123.4	118.5	128.3			144.1	131.1	127.8	124.5	119.3	
5g	162.8	145.1	148.1	137.6	110.5	124.5	124.3	118.0		111.6	110.9	144.7	132.3	128.1	124.5	119.1	
												110.2	50.5				

Table IV

Preparation of Dicyanofulvene Derivatives

No.	heating time (h)	yield %	crystals (solvent)	mp (°C)	C	Calcd. H	N	Formula	C	Found H	N
9	6	61	violet (A)	118-120	66.82	2.78	6.50	$\text{C}_{24}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2$	66.45	3.11	6.60
10	7	55	red (A)	110-112	74.83	3.80	6.23	$\text{C}_{28}\text{H}_{15}\text{N}_2\text{OCl}$	74.62	4.14	6.39
11	24	57	green (B)	132-135	75.70	3.84	9.48	$\text{C}_{28}\text{H}_{15}\text{N}_3\text{O}_2$	75.28	4.08	9.09
12	5	59	red (A)	98-101	76.87	3.88	8.96	$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$	76.49	3.73	9.12
13	5	40	red (B)	102-105	73.41	3.29	6.59	$\text{C}_{26}\text{H}_{14}\text{N}_2\text{Cl}_2$	73.41	3.59	6.90

(A): ethanol, (B): acetone; * containing one mole of crystallization water.

ones **7** into the corresponding 6,6-dicyanofulvene derivatives **6**, by condensation directly with malononitrile, failed under various conditions. However, 2-dicyanomethylidene-1,3-diphenylpropane **8** was found to be a good precursor for the synthesis of just such 6,6-dicyanofulvene derivatives **6**. Condensation of 1,3-diphenylacetone with malononitrile catalyzed by ammonium acetate and acetic acid gave the required intermediate **8** in 65% yield. Reaction of 2-dicyanomethylidene-1,3-diphenylpropane **8** with tetrachloro-1,4-benzoquinone in dimethylformamide, in the presence of tributylamine as base, afforded the violet crystalline derivative **9** in 61% yield. Similarly, the reaction of **8** with 2,3-dichloro-1,4-naphthoquinone gave the tetrasubstituted 6,6-dicyanofulvene derivative **10**. The structure of this product is similar to that from the model reaction of 2,3-dichloro-1,4-naphthoquinone with 1,3-diphenylacetone (Scheme 2 compound **14**). The reaction of **8** with 3,4-dichloromaleimide afforded compound **11**.

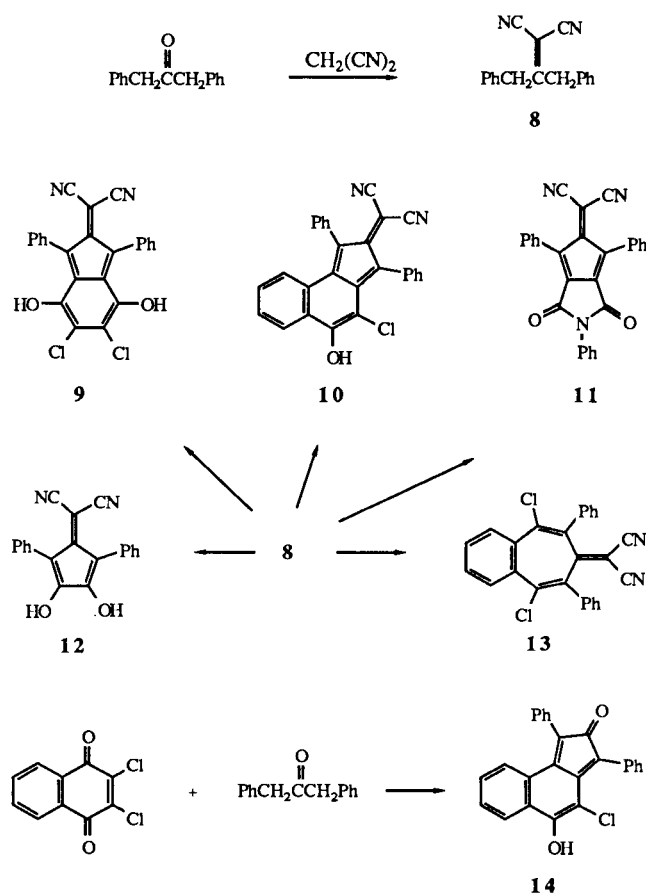
The regiochemistry of the reactions of **8** to form **9-11** deserves comment. We believe that, in each case, the initial reaction involves chloride displacement by the anion of **8**: the ring is then closed to give **9** and **11** by the displacement of a second chloride. However in the formation of **10**, the ring closes by attack at the carbonyl group, probably because this gives the angular (rather than the linear) tricyclic system. The ^{13}C nmr spectra would have allowed confirmation of these conclusions due to the symmetry of **9** and **11**; unfortunately, none of these products was sufficiently soluble to enable this.

Compound **8** also reacted with bis-acyl chlorides, thus 2,5-diphenyl-3,4-dihydroxyl-6,6-dicyanofulvene **12** was obtained from the reaction with oxalyl chloride, and the heptafulvene derivative with two chlorine atoms **13** was produced by condensation with phthaloyl chloride. The attempted condensation of **8** with α -diketones was unsuccessful. Structures were assigned on the basis of the analytical data. A compound of type **12** with chlorine in place of hydroxyl is a possible precursor to **12**. These chlorine atoms are expected to be more easily hydrolysed than those in **13** which possess an aromatic seven-membered ring.

Table V
Spectral Data of Dicyanofulvene Derivatives

No.	visible λ (ϵ)	^1H NMR (dimethyl sulfoxide- d_6 , TMS, δ)	ν CN	ν C=C	ν C=C
9	536 (21900)	7.50-7.30 (m)	2180	1630	1590
10	522 (8800)	7.65-7.30 (m)	2190	1580	
11	609 (9500)	7.20-7.50 (m)	2180	1630	1590
12	508 (4000)	7.30 (m, 10H), 3.70 (s, 2H)	2190	1650	1620
13	526 (6600)	8.00-7.50 (m, 14H), 2.70 (s, 2H)	2200	1630	1590

Scheme 2



The properties and the elemental analyses of the new dicyanofulvene derivatives **9-13** are summarized in Table IV, and characteristic features of their spectra are given in Table 5. The presence of cyano groups in the products was clearly indicated by the absorption at 2180-2200 cm^{-1} in their infrared spectra. The visible spectra of these dicyanofulvene derivatives **9-13** were measured in ethanol; they form red solutions (absorption maxima around 520 nm), except for **11** which absorbs at 609 nm. However, the extinction coefficients are not very intense.

EXPERIMENTAL

Melting points of the products were measured by a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 283 B. The ^1H nmr spectra were obtained with a Varian EM 360 L using tetramethylsilane as an internal standard, and ^{13}C nmr with JEOL JNM FX 100 spectrometer. Visible spectra were measured on a Perkin-Elmer 330 spectrophotometer. Elemental analyses were carried out under the supervision of Dr. R. King of this Department. 1-(Chloromethyl)benzotriazole is prepared by the literature method [23], mp 134-136° (lit [23] mp 136°).

1-Alkylisatins, General Procedure.

Sodium hydride (25 mmoles) was added to isatin (20 mmoles) in

dimethylformamide with stirring, the solution turned dark violet and the stirring was continued for 30 minutes. Then the appropriate alkyl halide (20 mmoles) was added and the reaction mixture was stirred at 25° for 10-20 hours until the color changed to orange. The whole was poured into cool water and extracted with chloroform (in a few cases, separated by filtration), and the extract was dried with magnesium sulfate. Evaporation of solvent gave the crude product, which was recrystallized from ethanol to give orange 1-alkylisatins (for details see Table I).

1-Alkyl-3-dicyanomethyleneindol-2-ones, General Procedure.

The 1-alkylisatin (10 mmoles) was dissolved in 20 ml of dimethyl sulfoxide and malononitrile (0.66 g, 10 mmoles) was added with stirring. The reaction mixture was stirred at 60° for 2 to 10 hours. After cooling, the reaction solution was poured into ice-water, the resulting solid was collected by filtration and recrystallized from ethanol to give the red or purple products (for details see Table I).

2-Dicyanomethylidene-1,3-diphenylpropane **8**.

A mixture of 1,3-diphenylacetone (5.25 g, 25 mmoles), malononitrile (2.00 g, 30 mmoles), glacial acetic acid (30 ml) and ammonium acetate (5 g) in benzene (200 ml) was refluxed for 2 days, the water formed during the reaction was removed azeotropically by means of a Dean-Stark trap. Then the mixture was washed with water, extracted with ether. Evaporation of the solvent gave the crude product which was purified by column chromatography (silica gel/chloroform-cyclohexane 2:3) (65%), mp 49-51°; ¹H nmr (deuteriated chloroform): 7.0-7.5 (m, 10H, Ph-H), and 3.80 (s, 4H, CH₂); ¹³C nmr: 180.6, 134.2, 128.9, 128.0, 112.0, 86.6, and 40.3; ir (bromoform): 2210 (CN), and 1590 (C=C) cm⁻¹.

Anal. Calcd. for C₁₈H₁₄N₂: C, 83.71; H, 5.43; N, 10.85. Found: C, 83.31; H, 5.44; N, 10.61.

6,6-Dicyanofulvene Derivatives, General Procedure.

The reaction mixture of 5 mmoles of **8**, 5 mmoles (2.5 mmoles for tetrachlorobenzoquinone) of corresponding substrates with active chlorine and 10 mmoles of tributylamine in dimethylformide (20 ml) was stirred at 50° for 4-10 hours. Addition of ether and filtration afforded a deep colored solid which on recrystallization from ethanol gave the 6,6-dicyanofulvenes (for details see Table IV).

2H-1,3-Diphenyl-4-chloro-5-hydroxy-6,7-benzoinde-2-one **14**.

Prepared as above, mp 175-177°; ¹H nmr (dimethyl sulfoxide-d₆): 7.60-7.25 (m); ir (bromoform): 1680 (CO), 1630 (C=C) cm⁻¹.

Anal. Calcd. for C₂₅H₁₅ClO₂: C, 78.43; H, 3.93. Found: C, 78.32; H, 4.30.

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