Synthesis and molecular and crystal structure of 1-allyl-4-[2-cyano-2-(indan-1,3-dione-2-ylidene)ethylidene]-1,4-dihydroquinoline

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The reaction of 1-allyl-4-methylquinolinium bromide with 2-dicyanomethyleneindan-1,3-dione in the presence of a two-fold excess of triethylamine affords 1-allyl-4-[2-cyano-2-(indan-1,3-dione-2-ylidene)ethylidene]-1,4-dihydroquinoline, a representative of a new class of merocyanines. The structure of this compound has been established by X-ray structural analysis. A substantial intramolecular charge transfer and a hydrogen bond between the vinyl hydrogen atom and the indandione oxygen atom have been found.

Key words: quinolinium salts; 2-dicyanomethyleneindan-1,3-dione; merocyanines, synthesis, X-ray structural analysis.

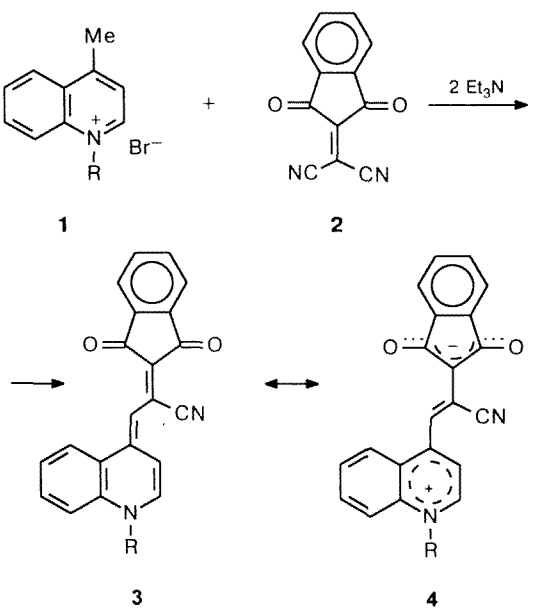
Previously,[1] we have studied the reaction of 1,4-dimethylquinolinium iodide with tetracyanoethylene, which affords merocyanine, 1-methyl-4-(2,2,3-tricyanoprop-2-ene-1-ylidene)-1,4-dihydroquinoline. It was of interest to obtain merocyanines based on another electron-deficient olefin, 2-dicyanomethyleneindan-1,3-dione. Abundant data on its reactions with different nucleophiles, which give colored products and dyes, are available in the literature[2–5]; however, reactions of this compound with quaternized salts of 2- and 4-methylquinolinium have not been studied.

We have studied the reaction of 1-allyl-4-methylquinolinium bromide **1** (as a representative of quinolinium salts with an active methylene group) with 2-dicyanomethyleneindan-1,3-dione (**2**) for the first time. When the synthesis was carried out in methanol at room temperature with the use of a two-fold excess of triethylamine, the first representative of a new class of merocyanines, 1-allyl-4-[2-cyano-2-(indan-1,3-dione-2-ylidene)ethylidene]-1,4-dihydroquinoline (**3**) was isolated (Scheme 1).

The results of ^{1}H NMR and IR spectroscopy allow the following conclusions.

First, the structure of the obtained compound is characterized by substantial intramolecular charge transfer, and as a result, the contribution of mesomeric form **4** is considerable. Thus, the lower absorption frequency of the carbonyl groups in the IR spectrum of the studied compound is close to the corresponding value of the absorption frequency of tropone (ν 1630 cm^{-1}),[6] for which a charge separation with a typical decrease of the degree of the double-bond character of the C=O group was well established. In the ^{1}H NMR spectrum, a shift of the signal of the C(2)H proton to a lower-field region

Scheme 1



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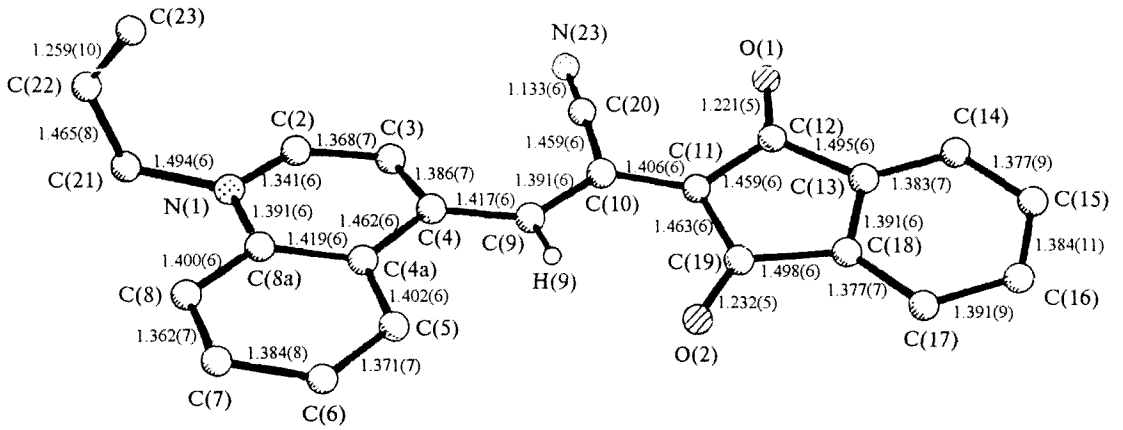

Fig. 1. Overall view of molecule **3** and bond lengths.

is consistent with a decrease in the electron density in the pyridine fragment.[7]

Second, in the studied compound, an intramolecular hydrogen bond, which is formed by the vinyl H atom and the nearest O atom, is observed. This is in agreement with a substantial low-field shift of the proton signal in the ^{1}H NMR spectrum (δ 9.10) compared to the corresponding proton signal (δ 6.78) in the spectrum of 1-methyl-4-(2,2,2-tricyanoprop-2-ene-1-ylidene)-1,4-dihydroquinoline,[1] as well as with a shift of the absorption band of the carbonyl group to a lower-frequency region (ν 1631 cm^{-1}) in the IR spectrum, which is also, as mentioned above, caused by a decrease in the degree of the double-bond character of the C=O group.

However, the spectral data give no way of describing unambiguously the structure of the synthesized compound (for example, the absorption band of the nitrile group is not observed in the IR spectrum). Therefore, with the aim of establishing the structure of compound **3**, we performed X-ray structural analysis of this compound. Figure 1 shows the overall view of the molecule **3** and bond lengths; bond angles are given in Table 1.

It has been found that the molecule of compound **3** is virtually planar, which is evidenced by small values of dihedral angles between the fragments of the molecule (the dihydroquinoline fragment (*A*, planar within ±0.030 Å), the C(4)=C(9)—C(10)=C(11) fragment (*B*, planar within ±0.005 Å), and the indandione fragment (*C*, the deviation of the atoms from the mean plane is ±0.021 Å)): *A*/*B*, *A*/*C*, and *B*/*C* are 6.7°, 13.2°, and 7.0°, respectively. The planar structure is determined by a substantial conjugation between two bicycles *A* and *C* through the atomic chain *B*. This is supported by a substantial elongation of the formally double bonds (C(4)=C(9) to 1.417(6) Å and C(10)=C(11) to 1.406(6) Å; the standard C(sp^2)=C(sp^2) bond length is 1.331 Å[8]) and a substantial shortening of the formally ordinary C(9)—C(10) bond to 1.391(6) Å (the standard C(sp^2)—C(sp^2) bond length is 1.478 Å[8]). A substantial redistribution of bond lengths that confirms the presence of conjugation, is observed in dihydroquinoline and indandione fragments (see Fig. 1). Therefore, the molecular structure may be described by mesomeric forms **3** and **4** with structure **4** being predominant. Previously, we have reported the same redistribution of bond lengths both in the dihydroquinoline and exocyclic fragments of the molecules in compounds with an intramolecular charge transfer.[1,9] As mentioned in Refs. 1 and 9, apparently, the nitrile group is involved in the conjugation chain to a lesser degree, which is evidenced by lengths of the C(10)—C(20) [1.459(6) Å] and C(20)≡N(23) [1.133(6) Å] bonds that are closer to the standard values[8] of C(sp^2)—C(sp) (1.427 Å) and C(sp)≡N (1.144 Å) bonds. Close values of the corresponding bond lengths [1.483(9) and 1.136(9) Å] were observed in the molecule of (*N*,*N*-dimethylaminophenyl)-(1,3-dioxo-2-indanylidene)acetonitrile, which contains such fragment.[10]

Table 1. Bond angles (ω) in molecule **3**

Angle	ω/deg	Angle	ω/deg
C(2)—N(1)—C(8a)	119.6(4)	C(2)—N(1)—C(21)	117.6(4)
C(8a)—N(1)—C(21)	122.7(4)	N(1)—C(2)—C(3)	122.6(5)
C(2)—C(3)—C(4)	122.5(4)	C(3)—C(4)—C(4a)	115.5(4)
C(3)—C(4)—C(9)	125.3(4)	C(4a)—C(4)—C(9)	119.2(4)
C(4)—C(4a)—C(5)	122.6(4)	C(4)—C(4a)—C(8a)	119.9(4)
C(5)—C(4a)—C(8a)	117.5(4)	C(4a)—C(5)—C(6)	121.3(4)
C(5)—C(6)—C(7)	120.1(5)	C(6)—C(7)—C(8)	120.8(5)
C(7)—C(8)—C(8a)	120.0(5)	N(1)—C(8a)—C(4a)	119.6(4)
N(1)—C(8a)—C(8)	120.2(4)	C(4a)—C(8a)—C(8)	120.1(4)
C(4)—C(9)—C(10)	130.4(4)	C(9)—C(10)—C(11)	123.2(4)
C(9)—C(10)—C(20)	120.8(4)	C(11)—C(10)—C(20)	116.0(3)
C(10)—C(11)—C(12)	125.5(4)	C(10)—C(11)—C(19)	126.4(4)
C(12)—C(11)—C(19)	108.1(4)	O(1)—C(12)—C(11)	128.6(4)
O(1)—C(12)—C(13)	124.4(4)	C(11)—C(12)—C(13)	107.0(4)
C(12)—C(13)—C(14)	129.7(4)	C(12)—C(13)—C(18)	109.0(4)
C(14)—C(13)—C(18)	121.2(4)	C(13)—C(14)—C(15)	117.8(5)
C(14)—C(15)—C(16)	121.0(6)	C(15)—C(16)—C(17)	121.6(6)
C(16)—C(17)—C(18)	117.1(6)	C(13)—C(18)—C(17)	121.3(4)
C(13)—C(18)—C(19)	108.9(4)	C(17)—C(18)—C(19)	129.7(4)
O(2)—C(19)—C(11)	128.6(4)	O(2)—C(19)—C(18)	124.6(4)
C(11)—C(19)—C(18)	106.8(4)	N(23)—C(20)—C(10)	177.5(4)
N(1)—C(21)—C(22)	113.0(4)	C(21)—C(22)—C(23)	128.1(6)

The planar structure of molecule **3** determines the occurrence of a shortened nonbonded O(2)...C(9) contact (2.978(5) Å; the sum of van der Waals radii of the atoms is 3.22 Å[11]), which is, according to the data in the literature,[12] is attributable to the presence of an intramolecular C—H...O hydrogen bond with the parameters C(9)—H(9) 0.98(4) Å and H(9)...O(2) 2.24(4) Å (the C(9)—H(9)...O(2) angle is 132(3)°), which hinders the rotation of the indandione fragment about the C(10)—C(11) bond (the C(9)—C(10)—C(11)—C(19) torsion angle is 6.1°).

The allyl substituent is perpendicular to the plane of the 1,4-dihydroquinoline fragment (the C(2)—N(1)—C(21)—C(22) and N(1)—C(21)—C(22)—C(23) torsion angles are −95.7° and 4.4°, respectively). Note that the conformation of molecule **3** is affected by forced shortened nonbonded contacts O(1)...C(20) [2.772(6) Å], C(20)...H(3) [2.39(4) Å], H(2)...H(21b) [2.11(4) Å], H(5)...H(9) [1.98(4) Å], and H(8)...H(21a) [2.09(4) Å] (the sums of van der Waals radii[11] of O and C and of C and H are 3.22 and 2.90 Å, respectively; the double radius of the H atom is 2.40 Å).[11] The analysis of the crystal packing demonstrated that only one shortened intermolecular contact C(2)...C(18) ($1-x$, $1-y$, $1-z$) [3.325(6) Å] occurs (double the van der Waals radius of the C atom is 3.40 Å).[11]

Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer; electronic spectra were obtained on a Specord M-40 spectrophotometer (because of the low solubility of the product, the recorded spectra were of low quality). ^{1}H NMR spectra were recorded on a Bruker WP-100 SY instrument (100 MHz); GLC was performed on Silufol UV-254 plates in a 1 : 3 acetone—benzene system.

1-Allyl-4-[2-cyano-2-(indan-1,3-dione-2-ylidene)ethylidene]-1,4-dihydroquinoline (3). Triethylamine (0.56 mL, 4 mmol) was added to a solution of salt **1** (0.53 g, 2 mmol) and compound **2** (0.42 g, 2 mmol) in 5 mL of methanol. The reaction mass was stirred for 5 h and allowed to stand overnight. The residue was filtered off and washed with methanol. Dihydroquinoline **3**, m.p. 462—463 °C (from a MeCN—DMF mixture), was obtained in 45 % (0.33 g) yield. Found (%): C, 79.23; H, 4.51; N, 7.55. $C_{24}H_{16}N_2O_2$. Calculated (%): C, 79.11; H, 4.43; N, 7.69. IR (KBr), ν/cm^{-1}: 1612 (C=C); 1631 (C=O). UV (MeOH), λ_{max}/nm: 600. ^{1}H NMR (DMSO-d_6), δ: 5.05—5.57 (m, 4 H, N—CH_2, =CH_2); 5.78—6.46 (m, 1 H, CH=); 7.36—7.74 (m, 4 H, C_6H_4); 7.80—8.55 (m, 5 H, C(3)H, C(5)H, C(6)H, C(7)H, C(8)H); 8.87 (d, 1 H, C(2)H); 9.10 (s, 1 H, C(4)=CH).

X-ray structural analysis of compound 3. Crystals of **3** are monoclinic, at 20 °C a = 7.683(2) Å, b = 16.140(3) Å, c = 14.777(4) Å, β = 98.92(2)°, V = 1810(1) Å^3, d_{calc} = 1.343 g cm^{-3}, Z = 4, space group $P2_1/c$. The unit-cell parameters and intensities of 3942 independent reflections were measured on a automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ_{max}= 28°). The structure was solved by the direct method, which makes it possible to reveal all non-hydrogen atoms; the structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms using 2942 reflections with $I > 3\sigma(I)$. All hydrogen atoms were located from difference electron density syntheses and were included in the refinement with isotropic thermal parameters. The final value of R factor was R = 0.068 (R_w = 0.068). All calculations were performed using the SHELXTL PLUS program[13] (the PC version). Atomic coordinates are given in Table 2 (thermal parameters are available from the authors).

Table 2. Atomic coordinates (×10^4; ×10^3 for H) in molecule **3**

Atom	x	y	z
O(1)	2306(5)	6337(2)	8404(2)
O(2)	3052(4)	6534(2)	5294(2)
N(1)	693(5)	2368(2)	5110(2)
N(23)	720(7)	4577(3)	8016(3)
C(2)	292(7)	2690(3)	5889(3)
C(3)	658(7)	3494(3)	6144(3)
C(4)	1448(6)	4042(3)	5610(3)
C(4a)	1769(5)	3718(3)	4727(3)
C(5)	2417(6)	4213(3)	4073(3)
C(6)	2700(7)	3893(3)	3249(3)
C(7)	2404(7)	3061(3)	3059(3)
C(8)	1757(6)	2556(3)	3666(3)
C(8a)	1414(6)	2874(3)	4502(3)
C(9)	1929(6)	4869(3)	5852(3)
C(10)	1909(5)	5296(3)	6668(2)
C(11)	2462(5)	6124(3)	6800(3)
C(12)	2609(6)	6579(3)	7661(3)
C(13)	3215(6)	7435(3)	7480(3)
C(14)	3635(7)	8089(3)	8078(4)
C(15)	4214(8)	8813(4)	7730(5)
C(16)	4354(8)	8884(4)	6811(5)
C(17)	3946(7)	8227(4)	6206(4)
C(18)	3383(6)	7502(3)	6559(3)
C(19)	2971(6)	6681(3)	6104(3)
C(20)	1258(6)	4903(3)	7439(3)
C(21)	395(7)	1461(3)	4951(4)
C(22)	1983(8)	965(4)	5231(4)
C(23)	3470(12)	1206(5)	5620(5)
H(2)	−33(5)	233(3)	624(3)
H(3)	30(5)	364(3)	668(3)
H(5)	270(5)	479(3)	417(3)
H(6)	322(5)	424(3)	285(3)
H(7)	272(6)	285(3)	254(3)
H(8)	149(5)	204(3)	352(3)
H(9)	253(5)	518(2)	542(2)
H(14)	358(6)	805(3)	872(3)
H(15)	443(7)	929(3)	813(3)
H(16)	489(6)	935(3)	660(3)
H(17)	412(6)	825(3)	560(3)
H(21a)	−16(6)	136(3)	424(3)
H(21b)	−58(6)	132(3)	532(3)
H(22)	257(7)	39(3)	507(3)
H(23a)	378(7)	177(4)	572(4)
H(23b)	449(9)	69(4)	569(4)

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