

Synthesis and semiempirical studies of quinodimethane derivatives as precursors for indigoid dyes

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Reaction of cyclohexan-1,4-dione with different active methylene heterocycles affords tetrahydroquinodimethane derivatives, in moderate to good yield. Semiempirical calculations indicate that introduction of double bonds in tetrahydroquinodimethane stabilizes the system due to the extended conjugation. All the synthesized products have been characterized by spectral techniques and their conformations ascertained by MO calculations.

Keywords: Indigo, quinodimethane, cyclohexan-1,4-dione, dye, chromophore

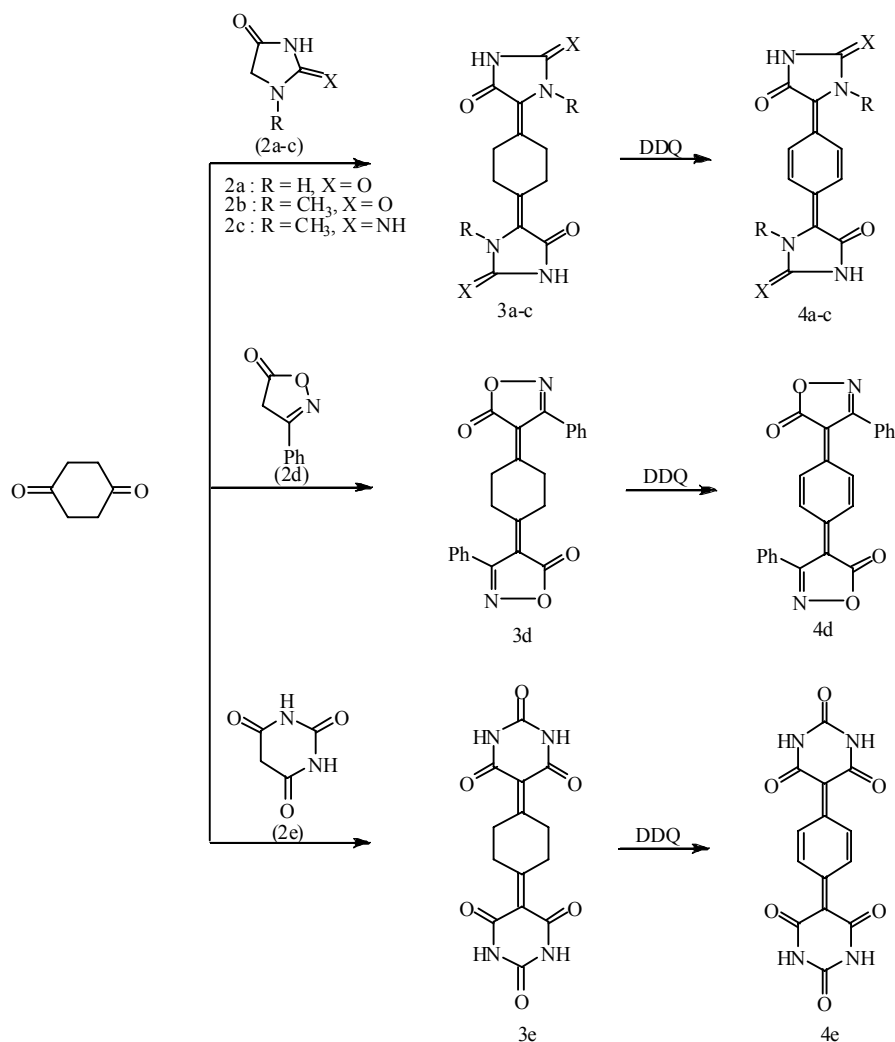
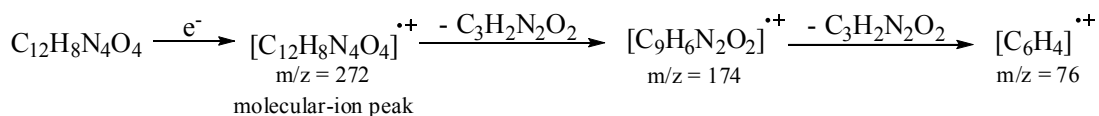
Indigo and indigoid dyes^{1,2} are important because of their applications in colouration in the textile dyeing. The indigoid compounds have UV absorption at very long wavelength which makes them attractive for optical materials³⁻⁶. The first *para*-quinodimethane derivative with donor-acceptor pattern of indigo chromophore was reported by Iwatsuki *et al.*⁷ The indigo chromophore and structurally related chromophores can be used to produce compounds with bathochromic shift. Besides, our attention was drawn to the compounds of this type because active methylene heterocycles of the type hydantoin, creatinine etc. have previously been used to synthesize indigo type dyes⁸. Hence in continuation to our work in the field of novel heterocycles of medicinal and industrial relevance⁹⁻¹⁴ and in order to produce analogues chromophores it appeared worthwhile to extend the studies to the synthesis of quinodimethane derivatives which may serve as useful precursors for indigoid dyes. Thus we have investigated the reaction of five membered active methylene heterocycles with cyclohexan-1,4-dione. The conformations of the products have been studied by semiempirical molecular orbital calculations and the results are presented below.

Results and Discussion

Reaction of cyclohexan-1,4-dione **1** with different active methylene heterocycles **2a-e** was carried out in the molar ratio of 1:2 in refluxing ethanol in the

presence of hot saturated solution of NH₄Cl at 80°C for 2 hr (**Scheme I**), whereby it afforded tetrahydroquinodimethane derivatives **3a-e** in 54-85% yield. Dehydrogenation of **3a-e** to *p*-quinodimethane derivatives **4a-e** was accomplished with an excess of DDQ in refluxing chlorobenzene in 50% yield. It may be mentioned here that Gompper *et al.*¹⁵ have reported similar indigoid dyes with rhodanine. The UV-Vis absorption of **4a-e**, $\lambda_{\max} = 400$ nm has a wavelength about 150 nm greater than **3a-e**, $\lambda_{\max} = 250$ nm. Clearly insertion of quinodimethane system causes a bathochromic shift, which is typical of indigoid systems.

The structure of the compounds **3a-e** and **4a-e** has been ascertained from their spectral data. In the IR spectrum of **3a** characteristic absorption band was observed at 3230-3440 cm⁻¹ for NH group at 1700 cm⁻¹ for carbonyl stretching. The UV-Vis absorption of previously reported¹⁶ **4a** in ethanol showed λ_{\max} at 400 nm which has a wavelength of about 150 nm greater than **3a**. The ¹H NMR spectrum of **3a** showed signals corresponding to CH₂ protons as a singlet at δ 3.90 and imino protons as a singlet at δ 7.74 and 10.66 respectively. In the ¹H NMR spectrum of **4a**, CH protons appeared as doublet at δ 7.45 ($J = 10$ Hz) and δ 7.7 ($J = 10$ Hz), NH protons appeared as a singlet at δ 10.64. In the ¹³C NMR of **3a** peaks appeared δ 173.9 (C=O), 158.4 (C=O), 95.46 and 92.8 (C=C) and 47.35, 47.25, 43.01, 42.21 (CH₂) whereas in the ¹³C NMR of **4a** peaks appeared at δ 179.4 (C=O), 176.2 (C=O), and 115.20, 113.20, 95.00



Scheme I

(C=C) respectively. Mass spectrum of **4a** gave molecular ion peak at m/z 272. The daughter peaks observed at m/z 174 and 76 were due to loss of one and two hydantoin moieties respectively.

The spectral data of **3a-e** and **4a-e**^{17,18} are presented in **Table I**.

The conformation of the product was established by molecular modeling using AM1 Hamiltonian on MOPAC6 programme. The ΔH_f values of **3a-e** and **4a-e** are summarized in **Table II**.

From **Table II** it may be concluded that quinodimethane products **4a-c** are thermodynamically more

stable than corresponding tetrahydroquinodimethane derivatives **3a-c**. This indicated that introduction of double bonds stabilizes the system due to the extended conjugation through lone pair electrons of nitrogen atom, besides stabilization of **4b** is greater than **4a** because of +I effect of methyl group present at nitrogen atom. However, ΔH_f of **4d** is greater than **3d** because no such extended conjugation is possible. The conformation of product **3a-d** and **4a-d** appeared to be *anti* because of less steric hindrance (**Figure 1**). Compounds **3e** and **4e** do not appear in *syn/anti* conformation due to symmetry of molecules.

Table I — Spectral data of tetrahydroquinodimethane **3a-e** and quinodimethane **4a-e** derivatives

Compd	Physical State	Yield (%)	m.p. (°C)	¹ H NMR (δ)	¹³ C NMR (δ)	HRMS (m/z)
3a	Black Solid	69	203-205	2.56 (s, 2 × CH ₂), 3.90 (s, 2 × CH ₂), 7.74, 10.66 (s, NH)	173.9, 158.4 (C=O), 95.46, 92.8 (C=C), 47.35, 47.25, 43.01, 42.21 (CH ₂)	276.1956
3b	Brown Crystals	84	222	2.59 (s, NCH ₃), 3.89 (s, 2 × CH ₂), 10.7 (s, NH)	178.2, 160.3 (C=O), 100.0, 98.2 (C=C), 52.5 (CH ₃), 50.8, 49.5, 44.6, 42.1 (CH ₂)	304.2269
3c	Violet Crystals	54	262	2.95 (s, NCH ₃), 3.4 (s, 2 × CH ₂), 3.9 (s, CH ₃), 9.2 (s, NH)	175.2 (C=O), 170.5 (C=NH), 99.6, 95.2 (C=C), 55.4 (N-CH ₃), 47.8, 46.5, 44.3, 43.1 (CH ₂)	-
3d	Brown Yellow Solid	50	285	3.4 (d, CH), 4.3 (d, CH), 9.2 (s, NH), 7.25-7.4 (m, ArH)	-	-
3e	Coffee Brown Crystals	85	233	2.5 (s, 2 × CH ₂), 3.83 (s, 2 × CH ₂), 9.85 (s, NH), 11.5 (s, NH)	178.3 (C=O), 169.1 (C=NH), 110.0, 109.0, 100.5, 98.5, 90.8, 92.2 (C=C), 56.8 (N-CH ₃)	332.1854
4a	Brown Crystals	50	230	7.45 (d, <i>J</i> = 10Hz, 2 × CH), 7.7 (d, <i>J</i> = 10Hz, 2 × ArH), 10.46 (s, NH)	179.4, 176.2 (C=O), 115.20, 113.20, 95.0 (C=C)	272.1643
4b	Violet Crystals	54	229	2.50 (s, NCH ₃), 7.0 (d, <i>J</i> = 10Hz, 2 × CH), 7.3 (d, <i>J</i> = 10Hz, 2 × CH), 10.68 (s, 4 × NH)	178.5, 170.8 (C=O), 120.0, 118.5, 98.4 (C=C), 48.3 (CH ₃)	300.1956
4c	Black Crystals	35	306(dec.)	2.64 (s, NCH ₃), 6.4 (d, 2 × CH), 6.8 (d, 2 × CH), 9.8 (s, NH)	176.6, 173.3, 172.4 (C=O), 92.5, 91.8, 87.8, 88.92 (C=C), 40.8, 50.1 (CH ₂)	-
4d	Greenish Black Crystals	30	321(dec.)	6.4 (d, 2 × CH), 6.6 (d, 2 × CH), 7.1-7.6 (m, ArH)	-	-
4e	Brown Crystals	53	212	7.2 (d, <i>J</i> = 10Hz, 2 × CH), 7.4 (d, <i>J</i> = 10Hz, 2 × CH), 8.9, 11.2 (s, 4 × NH)	175.2, 174.5, 171.2 (C=O), 105.0, 94.3 (C=C)	328.1541

Table II — Heat of formation of **3a-e** and **4a-e** on AM1 Hamiltonian

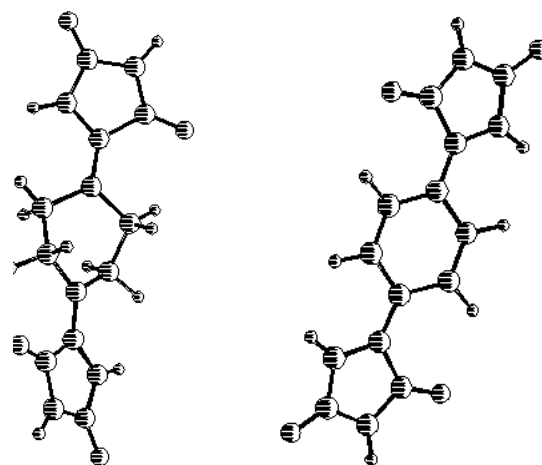
Compd	ΔH_f	ΔH_f	Compd	ΔH_f	ΔH_f
	(<i>syn</i>) (eV)	(<i>anti</i>) (eV)		(<i>syn</i>) (eV)	(<i>anti</i>) (eV)
3a	-52.25	-53.36	4a	-36.93	-36.43
3b	-71.73	-73.56	4b	-22.34	-23.58
3c	47.29	45.41	4c	-	36.51
3d	60.10	58.51	4d	111.60	111.23
3e	-	-182.78	4e	-	-124.13

Experimental Section

All the operations were carried out as reported elsewhere¹².

Representative method for synthesis of quinodimethane derivatives is described below:

A mixture of imidazolidine-2,4-dione **2a** (1.78 g, 17.8 mmol) and cyclohexan-1,4-dione **1** (1.0 g, 8.9 mmol) in the molar ratio 2:1 was refluxed under



Optimized structure of **3a** Optimized structure of **4a**
Figure 1

nitrogen atmosphere for 2 hr in absolute ethanol (10 mL). Subsequently to the cooled reaction-mixture was added first 3.5 mL of concentrated ammonia solution and then hot solution of 3.5 g of ammonium chloride

in 6.0 mL water. The resultant precipitate was filtered off and from the residual filtrate tetrahydroquinodimethane derivative of imidazolidine-2,4-dione **3a** was crystallized from dichloromethane as black solid in 69% yield (1.92 g).

A reaction-mixture of tetrahydroquinodimethane **3a** (0.36 g, 1.3 mmole) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.06 g, 9.1 mmoles) in the molar ratio of 1:7 was refluxed under N₂ atmosphere for 2 hr in chlorobenzene (30 mL). After completion of the reaction as monitored by TLC the solvent was removed azeotropically with benzene (2 × 5 mL) whereby brownish crystals **4a** were obtained. These were further purified by crystallization from toluene in 50% yield (1.18 g).

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