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Electrophilic Quinodimethanes
Synthesis and Polymerization of 7,8-Dialkoxycarbonyl-7,8-Dicyanoquinodimethanes

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Abstract

Two new electrophilic monomers, 7,8-di(alkoxycarbonyl)-7,8-dicyanoquinodimethanes, were prepared. These quinodimethanes exhibit moderate electron-acceptor abilities and are highly reactive toward spontaneous homopolymerization in solution as well as in the solid state. Quinodimethane homopolymers were also obtained from heterogeneous spontaneous solution polymerization in the presence of styrene, p-methoxystyrene and isobutyl vinyl ether.

Introduction

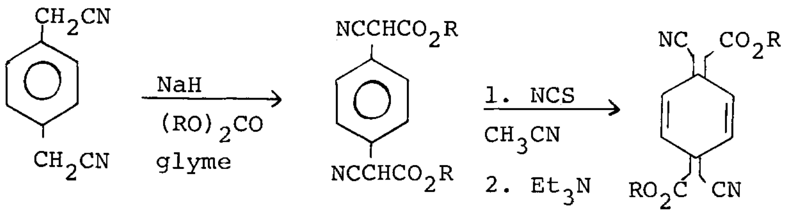
Quinodimethane has been known as a highly reactive and polymerizable compound for many years (ERREDE and SZWARC, 1958). In contrast tetracyanoquinodimethane (TCNQ) is easily isolated and does not polymerize (ACKER and HERTLER, 1962). Furthermore, chlorinated derivatives of quinodimethane have more recently been reported, the stability of which increases with increasing degree of chlorination (BALLESTER, CASTOVER and RIERA, 1966; IWATSUKI and KAMIYA, 1974: GILCH, 1966). Tetramethoxycarbonylquinodimethane (TMCQ), will thermally or radically polymerize to yield a high polymer and copolymerizes alternatingly with styrene, vinyl ethers, vinyl acetate and TCNQ (HALL and BENTLEY, 1980; IWATSUKI and ITOH, 1980).

Here we report the synthesis and polymerization along with the electron acceptor properties of 7,8-di-(methoxycarbonyl)-7,8-dicyanoquinodimethane, DMCQ (**3a**) and DECQ (**3b**).

Synthesis

p-Xylylenedicyanide (**1**) was treated with NaH and dimethyl carbonate in a modified Claisen condensation which gave the α,α'-bis(methoxycarbonyl)-p-xylylenedicyanide 2a (DEJONGH, DEJONGE, SINNEGE, MAGREE, MIJS, 1972). Oxidation to the quinodimethane was accomplished with N-chlorosuccinimide and triethyl amine, pyridine or collidine in acetonitrile. The product 3a precipitates from the reaction mixture as a yellow solid, 60-65% yield.

The less soluble trans-isomer was isolated and the structure assigned on the basis of the ^1H-NMR splitting pattern of the quinoid protons. Two sets of doublets with coupling (J ~ 2Hz) are seen at δ = 8.68, 8.50, 7.60 and 7.48 ppm. Two singlets with very small second order coupling are expected for the cis-isomer.



1

2 a $R=CH_3$
b $R=C_2H_5$

3 a $R=CH_3$
b $R=C_2H_5$

In essentially the same procedure, DECQ (3b) was prepared, 64% yield, mp 212-214°, ^1H-NMR: δ = 8.65 (d, 1H), 8.50 (d, 1H), 7.60 (d, 1H), 7.45 (d, 1H), 4.32 (q, 4H), 1.25 (t, 6H) ppm.

Electron Accepting Ability

DMCQ lies between TCNQ and TMCQ in its ability to accept an electron. This is indicated in Table I in which cyclic voltammetric reduction potentials (vs. Ag/Ag^+ in CH_3CN) are presented, TCNQ being most easily reduced, followed by DMCQ followed by TMCQ. This tendency is also manifested in reactions with the electron donors N,N,N',N'-tetramethyl-p-phenylene diamine (TMPD) and tetrathiafulvalene (TTF), Table I, in which it is seen that although TCNQ and DMCQ form a colored charge transfer complex with TTF, TMCQ does not. These results are in accord with the better ability of a cyano group to stabilize either a negative charge (Hammet σ^- values) or an unpaired electron (copolymerization Q values) relative to a carbonyl group.

TABLE I

Electron Accepting Abilities of Quinodimethanes

			Reaction With	
	E_p^a(volts)	Ref.	TMPD	TTF
TCNQ	-0.20	Hall and Bentley	CT complex	CT complex
DMCQ	-0.65	(This work)	Deep blue complex	Purple complex
TMCQ	-0.83	Hall and Bentley	Deep blue complex	No Reaction

[a] In CH_3CN vs. Ag/Ag^+

Homopolymerization

DMCQ is considerably less soluble than DECQ (DMCQ: 50 mg/8mL $CHCl_3$, DECQ: 50 mg/3mL $CHCl_3$). Both monomers polymerize instantaneously upon dissolving in acetonitrile, DMSO, DMF and sulfolane and will polymerize within 1 hour in chloroform solution in the absence of an initiator and exposed to air.

The results of the homopolymerizations are shown in Table II. The polymerizations were performed in degassed sealed ampules ambient light at room temperature unless otherwise noted. High conversion to an insoluble polymer was obtained with DMCQ. The polymerizations of the diethyl ester gave soluble polymers of moderate molecular weight. These polymers form transparent, flexible films when cast from $CHCl_3$ solutions.

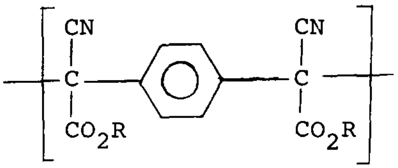
The structures of both DMCQ and DECQ polymers are represented as $\underset{\sim}{4}$ which is in accord with the UV, IR and ^1H-NMR spectra of the soluble DECQ polymer in which the quinoid protons of the monomer are no longer present and are replaced by benzene protons in the ^1H-NMR. In addition DECQ monomer has λ_{max} CH_3CN = 394, (ε = 900) and quinoid absorbance is absent in the polymer.

TABLE II

Results of Polymerization of DMCQ and DECQ

Monomer	Solvent (10 mL)	Temp.	Time	Yield	Inherent* Viscosity	Anal.	%C	%H	%N
DMCQ									
100 mg	$ClCH_2CH_2Cl$	r.t.	20 hr	98 mg	Insoluble	Calc:	62.2,	3.7,	10.3
						Found:	60.5,	3.7,	10.2
DECQ									
100 mg	$ClCH_2CH_2Cl$	r.t.	20 hr	72 mg	0.28	Calc:	64.4,	5.3,	9.3
						Found:	64.0,	4.8,	9.6
100 mg	CH_3CN	r.t.	20 hr	68 mg	0.17	Found:	64.0,	4.8,	9.3
200 mg	Benzene	AIBN/75°	20 hr	120 mg	0.43	Found:	64.2,	5.3,	9.3

*0.5 % con. in CH_3CN at 30°



4 a $R=CH_3$
b $R=CH_2CH_3$

It appears that the larger size of the ethyl groups compared to methyl causes the polymer chains to assume less ordered conformations and hence greater solubility. It might also be noted that there is a stereochemical aspect of the DECQ or DMCQ polymers, lacking in other quinodimethanes which have previously been prepared, namely that the adjacent $-C(CN)(CO_2R)$ groups may be meso- or racemic. As yet we have no information on this aspect of the structure.

Attempted Copolymerization

The reactivity of DMCQ towards nucleophilic olefins such as styrene, p-methoxystyrene and isobutyl vinyl ether differs in attempted spontaneous copolymerization from other substitued quinodimethanes reported (IWATSUKI and KAMIYA, 1974; IWATSUKI and ITOH, 1979; HALL and BENTLEY) in that the DMCQ reactions occur heterogeneously even in bulk yielding homopolymer of DMCQ. DECQ reacts with the above mentioned olefins under homogeneous conditions yielding a soluble product consisting only of homopolymer of DECQ.

Acknowledgements

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Experimental

^{1}H-NMR were obtained using a Varian T-60. Infrared spectra were determined on a Perkin-Elmer 332 grating IR-spectrophotometer. Elemental analysis were preformed by the University of Arizona Analytical Center, Tucson and Micro-Tech Analytical Laboratories, Skokie, Illinois. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

α,α'-Bis(methoxycarbonyl)-p-Xylylenedicyanide (2a). p-Xylylenedicyanide, 3.0 g (19 mmole), 7.0 ml (78 mmole) dimethyl carbonate, and 4.6 g (96 mmole) NaH (50% oil dispersion washed with hexane) in 100 ml dimethoxyethane (dried over calcium hydride) were stirred at room temperature under argon for 16 hr. The solvent was then removed under vacuum, and cold dilute aqueous acetic acid was added. Extraction with chloroform gave 4.5 g product, 82% yield, mp 133-135° after recrystallization from methanol.

IR(KBr): 2275 (CN), 1750 (CO) cm^{-1}.
^{1}H-NMR ($CDCl_3$): $\delta = 7.60$ (s, 4H), 4.75 (s, 2H), 3.80 (s, 6H) ppm.

7,8-Di(methoxycarbonyl)-7,8-dicyanoquinodimethane (3a). The product 2a, 1.0 g (40 mmole) was dissolved in 15 ml acetonitrile along with 3 mg 3-tert-butyl-4-hydroxy-5-methylphenyl sulfide (BPS) radical inhibitor and chilled in an ice bath under argon. A cold solution of 1.0 g (80 mmole) N-chlorosuccimide in 10 ml acetonitrile was added and the solution was stirred for 5 min. In one portion 0.56 ml (7.6 mmole) triethyl amine was added and a yellow precipitate formed instantly. After filtration the precipitate was dissolved in chloroform and chilled to -25° and filtered while cold recovering 0.68 g, 64% yield, d. 268-270°.

IR(KBr): 2225 (CN), 1720 (CO) cm^{-1}.
^{1}H-NMR ($CDCl_3$): $\delta = 8.68$ (d, 1H), 8.50 (d, 1H), 7.60 (d, 1H), 7.48 (d, 1H), 3.96 (s, 6H) ppm.
Analysis calculated for $C_{14}H_{10}N_2O_4$: C, 62.2%; H, 3.7%, N, 10.3%. Found: C, 62.2%; H, 3.4%; N, 10.5%.

α,α'-Bis(ethoxycarbonyl)-p-xylylenedicyanide (2b). p-Xylylene dicyanide, 3.0 g (20 mmole), 9.0 ml (80 mmole) diethylcarbonate and 4.6 g NaH (95 mmole) in 35 ml glyme were heated 60° under argon with stirring for 4 hr. Aqueous acetic acid was added after removal of solvent. Chloroform extraction gave 4.6 g product, 80% yield, mp 63-65° after recrystallization from ligroin.

IR(KBr): 2250 (CN), 1750 (CO) cm^{-1}.
^{1}H-NMR ($CDCl_3$): $\delta = 7.5$ (s, 4H), 4.8 (s, 2H), 4.3 (q, 4H), 1.3 (t, 6H) ppm.
Analysis calculated for $C_{16}H_{16}N_2O_4$: C, 64.0, H, 5.3; N, 9.3. Found: C, 64.3; H, 5.6; N, 9.2

7,8-Di(ethoxycarbonyl)-7,8-dicyanoquinodimethane (3b). To 0.5 g (1.5 mmole) of α,α'-bis(ethoxycarbonyl)-

p-xylylenedicyanide in 10 ml acetonitrile and 3 mg BPS chilled in an ice bath under an argon atmosphere was added 0.4 g (3.0 mmole) N-chlorosuccinimide in 10 ml cold acetonitrile. After stirring for 5 min, 0.20 ml (1.4 mmole) Et_3N was added in one portion and a yellow precipitate formed instantly. After 5 min, the precipitate was filtered, dissolved in a minimum amount of $CHCl_3$ and chilled to -25°. The yellow product was filtered while cold, recovering 0.2 g, 44% yield, mp 214°.

IR(KBr): 2225 (CN), 1720 (CO) cm^{-1}.

^1H-NMR ($CDCl_3$): $\delta = 8.65$ (d, 1H), 8.50 (d, 1H), 7.60 (d, 1H), 7.45 (d, 1H), 4.32 (q, 4H), 1.25 (t, 6H) ppm.

Analysis calculated for $C_{16}H_{14}N_2O_4$: C, 64.4; H, 5.3; N, 9.3. Found: C, 64.0; H, 4.6; N, 8.9.

Electrochemical Measurements

Spectrograde acetonitrile was used directly without purification. Sample preparation and electrochemical measurements were carried out under nitrogen atmosphere. A three compartment electrochemical cell with a main compartment of 100 ml capacity was used for voltammetric studies. The side arms contained a reference electrode (0.1 M $AgNO_3$ in CH_3CN and a Ag wire) and a counter platinum electrode, respectively. The Pt working electrode was a 1.16 cm flag and was cleaned in nitric acid, over dried and heated in a flame to incandescence prior to each run. Lithium perchlorate was used as a supporting electrolyte. A PAR Model 173 potentiostat and Hewlett-Packard Model 7001A x-y recorder was used for electrochemical measurements.

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