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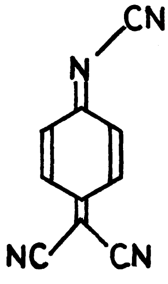
Preparation of Novel Electron-Accepting Quinone Methide Imines and Their Polymerizations

Shouji IWATSUKI,* Takahito ITOH, and Hiromu ITOH
Department of Chemical Research for Resources, Faculty of Engineering,
Mie University, Kamihama-cho, Tsu 514

N,7,7-Tricyanoquinone methide imine (1), N,11,11-tricyano-1,4-naphthoquinone methide imine (2), and N,15,15-tricyano-9,10-anthraquinone methide imine (3) were successfully prepared as novel electron-accepting quinone methide imine compounds. 1 is homopolymerizable with free radical and anionic initiators, while 2 and 3 are not.

Unsubstituted p-quinone methide imine (QMI) is so reactive to give polymeric material immediately at room temperature.1) Substitution of electron-donating groups such as phenyl, alkylthio, alkylamino etc. on its exocyclic carbon and nitrogen atoms makes QMI so less reactive to be obtained as crystalline material at room temperature.2-4) However, any substituted QMI with electron-accepting groups instead of electron-donating ones has not been prepared yet. It was expected that electron-accepting groups substituted QMIs should be so less reactive to be obtained as crystalline compounds and at the same time are polymerizable as highly conjugative and electron-accepting monomer, similarly to substituted quinodimethanes such as 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes (BCQ)5) and 7,8-diacyl-7,8-dicyanoquinodimethanes (ACQ).6)

In this letter are described preparation and polymerization of N,7,7-tricyanoquinone methide imine (1), N,11,11-tricyano-1,4-naphthoquinone methide imine (2), and N,15,15-tricyano-9,10-anthraquinone methide imine (3) as new QMI compounds with strongly electron-accepting cyano group at the exocyclic positions.



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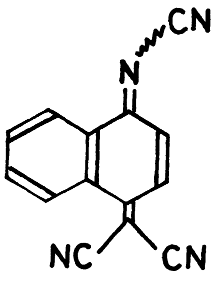

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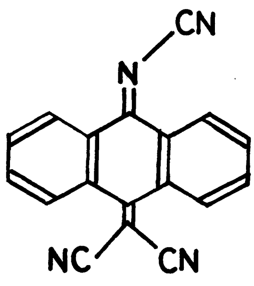

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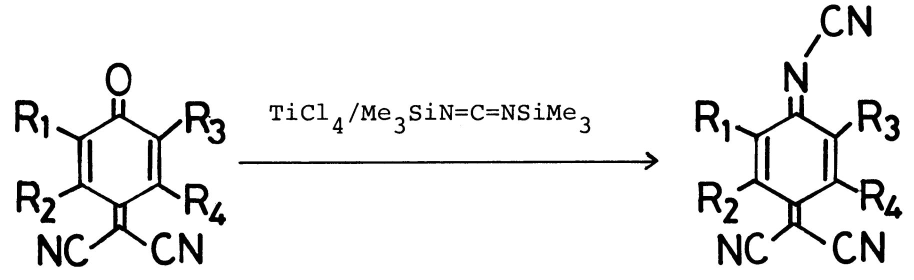
1, 2, and 3 were successfully prepared according to the procedure shown in Scheme 1:



	R_1	R_2	R_3	R_4
4 :	H	H	H	H
5 :	$\text{–(CH=CH)}_2\text{–}$		H	H
6 :	$\text{–(CH=CH)}_2\text{–}$		$\text{–(CH=CH)}_2\text{–}$	

	R_1	R_2	R_3	R_4
1 :	H	H	H	H
2 :	$\text{–(CH=CH)}_2\text{–}$		H	H
3 :	$\text{–(CH=CH)}_2\text{–}$		$\text{–(CH=CH)}_2\text{–}$	

Scheme 1.

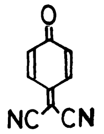
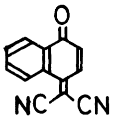
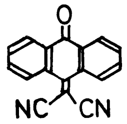
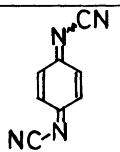
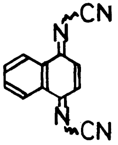
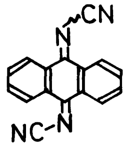
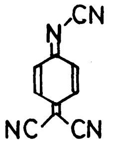
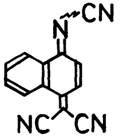
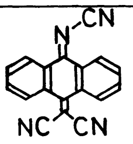
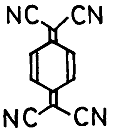
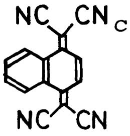
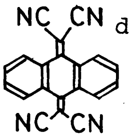
7,7-Dicyanoquinone methide7) (4) (0.33 g, 2.1 mmol) was dissolved in 50 mL of benzene at room temperature. Into the solution was added dropwise 1.12 mL (10.6 mmol) of titanium tetrachloride and then 1.97 g (10.6 mmol) of N,N'-bis-(trimethylsilyl)carbodiimide8) in 15 mL of benzene with stirring under nitrogen. After kept at room temperature with stirring for three days, the mixture was poured into 100 mL of water. The organic phase separated was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. Orange solid residue was chromatographed over silica gel with benzene to obtain an orange band which was placed under reduced pressure to leave orange crystalline compounds. It was recrystallized from a mixture of benzene and hexane to obtain orange plate of 1 in 47% yield (178 mg): mp 181 °C dec.; IR(KBr): 2240, 2180, 1550 cm^{-1}; ^{1}H NMR (60 MHz, CDCl$_3$): δ7.18 (d, J= 10.2 Hz, 1H), 7.51 (d, J= 10.2 Hz, 1H), 7.68 (d, J= 10.2 Hz, 2H); UV (toluene): 361 nm (ε= 2.9 x 10^4). Found: C, 66.57; H, 2.26; N, 30.63%. Calcd for C$_{10}$H$_4$N$_4$: C, 66.67; H, 2.22; N, 31.11%.

4-Dicyanomethylene-2,3,5,8,9,10-hexahydronaphthalene-1-one9) was oxidized by activated manganese dioxide in chloroform to give 11,11-dicyano-1,4-naphthoquinone methide (5) in 65% yield from which 2 was prepared in 62% yield in a process similar to that for 1 except for using dichloromethane instead of benzene. 2 was recrystallized from a mixture of dichloromethane and hexane to give yellow needles: mp 193 °C dec.; IR(KBr): 2230, 2180, 1550 cm^{-1}; ^{1}H NMR(CDCl$_3$): δ7.50 (d, J= 10 Hz, 1H), 7.85 (d, J= 3 Hz, 1H), 7.87 (d, J= 10 Hz, 1H), 7.95(d, J= 10 Hz 1H), 8.56 (m, 1H), 8.93 (m, 1H); UV(CH$_2$Cl$_2$): 367 (ε= 2.68 x 10^4), 355 (shoulder, ε= 2.60 x 10^4), 287 (ε= 9.5 x 10^3), 280 (ε= 1.08 x 10^4), 265 (shoulder, ε= 6.3 x 10^3)nm. Found: C, 72.66; H, 2.47; N, 23.77%. Calcd for C$_{14}$H$_6$N$_4$: C, 73.04; H, 2.43; N, 24.34%.

The compound 3 was prepared in 28% yield from 11,11-dicyano-9,10-anthraquinone methide10) (6) in a process similar to that for 2: mp 250.5-251.0 °C; IR(KBr): 2240, 2180, 1570 cm^{-1}; ^{1}H NMR(CDCl$_3$); δ7.80 (m, 4H), 8.34(m, 2H), 8.59 (m, 2H); UV(CH$_2$Cl$_2$): 344 (ε= 2.51 x 10^4), 282 (ε= 3.34 x 10^4)nm. Found: C, 77.43; H, 2.68; N, 19.35%. Calcd for $C_{18}H_8N_4$: C, 77.14; H, 2.86; N, 20.00%.

First and second reduction potential values, E_1 and E_2, of 1, 2, and 3 were measured by cyclic voltammetry using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as solvent and Ag/AgCl as reference electrode, as listed in Table 1 together with those of related compounds, cyano-substituted quinodimethanes, quinone diimines, and quinone methides. It is obvious that their E_1 and E_2 values increase with the number of cyano group and decrease with the number of fused benzene rings and that 1, 2, and 3 are just intermediate in electron-accepting character between fully cyano-substituted compounds of quinodimethane and quinone diimine as expected from their chemical structures.

Table 1. First and Second Reduction Potential[a)] of Hetero-p-quinones

	Benzoquinones			Naphthoquinones			Anthraquinones		
		E_1/V	E_2/V		E_1/V	E_2/V		E_1/V	E_2/V
Quinone methides		-0.12	-0.57		-0.29	-0.78		-0.75	-1.01
Quinone dimines[b)]		-0.03	-0.53		-0.06	-0.56		-0.62	-0.92
Quinone methide imines		+0.17	-0.44		+0.01	-0.47		-0.49	-0.69
Quinodi- methanes		+0.19	-0.39	 c)	+0.02	-0.38	 d)	-0.43	-0.63

a) Solvent: dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); Reference electrode: Ag/AgCl; Relative error: ±0.01 V.

b) Prepared according to the method of Aumüller and Hünig.[11)]

c) Prepared according to the method of Chatterjee.[9)]

d) Prepared according to the method of Ong and Keoshkerian.[12)]

When 1 was dissolved in a solvent such as benzene, toluene, dichloromethane, tetrahydrofuran (THF), acetonitrile, and acetone, orange color of 1 remained almost unchanged in the former three solvents for two days and changed slowly from orange to yellow in the latter three solvents for one day. After kept standing for a day, the solutions were subjected to gel permeation chromatography (GPC) to determine the molecular weight of the reaction products. The benzene, toluene, and dichloromethane solutions showed only monomer peaks and the THF, acetonitrile, and acetone solutions showed both the monomer and oligomer peaks, the latter of which corresponds to the molecular weight of 400 to 1000, suggesting that 1 is polymerizable in aprotic polar solvents such as THF, acetonitrile, and acetone, similarly to BCQ5) and ACQ6) etc. 2 and 3 in these solvents remained almost unchanged in their yellow color for a week and their GPC charts showed only the monomer peak, indicating that 2 and 3 are not polymerizable in these solvents. It is concluded therefore that 1 is polymerizable in polar solvents but 2 and 3 are not.

Polymerizations of 1, 2, and 3 were attempted with various initiators such as 2,2'-azobis(isobutyronitrile)(AIBN), butyllithium, triethylamine, and triphenylphosphine as summarized in Table 2. It was found that 1 is polymerizable with all these initiators but 2 and 3 are not, similarly to their above-mentioned polymerization behavior in polar solvents. The polymer of 1 was obtained as white powder, which is soluble in THF, dimethyl sulfoxide, and N,N-dimethylformamide and insoluble in methanol and hexane.

Table 2. Homopolymerization of 1 with Various Initiators

Run no.	1 mg	Initiator	10^{-3}mmol	[1]/[Initiator]	Solvent mL	Time /h	Temp /°C	Conv. /%	$10^{-3}\overline{\mathrm{Mn}}$ a)
1	40.3	AIBN	8.1	28	Benzene, 4	164	60	3.2	2.5
2	31.2	BuLi	17	10	Toluene, 5	18	0	34	1.1
3	31.4	Et_3N	6.4	27	Toluene, 7	48	0	17.9	2.5
4	29.9	Ph_3P	6.7	25	Toluene, 7	5	0	14.2	2.5

a) Determined by GPC. THF was the eluent.

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