Novel Non-benzenoid Electron Acceptors: Syntheses and Electron Acceptability of Tetracyanoazulenequinodimethanes and Dicyanoazulenequinonemethides

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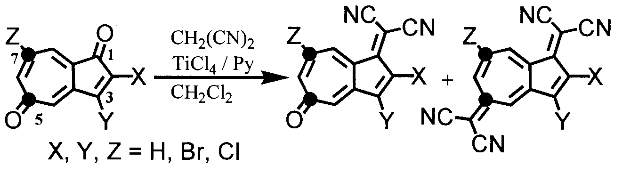
Tetracyanoazulenequinodimethanes and dicyanoazulenequinonemethides, a new family of azulene-based electron acceptors have been derived from mono-, di-, and tri-bromo- and -chloro-azulenequinones by reaction with titanium tetrachloride, malononitrile and pyridine. Their unique electron acceptability has been revealed by CV measurement.

Azulenequinones (AzQs) are novel and one of the most interesting classes of non-benzenoid quinones and their chemical and physical properties are of particular interest in connection with benzenoid quinones.[1–5] In 1980 and 1984 Scott and his co-workers reported the syntheses of mother 1,5- and 1,7-AzQs and predicted the stability of 16 possible AzQs' structures[2,4] and with regards to them a very strong electron acceptability of tetracyano-2,6-azulenequinodimethane was also anticipated. Although the high electrical conductivity found in TTF-TCNQ[6] complex in 1973 accelerated interest in organic conductors and many strong electron donors have been synthesized, far less new electron acceptors seem to have been developed except a considerable number of benzenoid TCNQ family. Recently, strong electron acceptors such as 4-oxo-2,6-bis(dicyanomethylene)-2,6-dihydrocyclopenta[2,1-*b*;3,4-*b*']-dithiophene,[7] the first molecular metal of heterophene-TCNQ, and 2,4,6,8-tetracyanoazulene[8] have been reported. In this context we have developed novel non-benzenoid TCNQ type compounds as a part of our study of AzQs.[9]

We present herein the syntheses of quinodimethanes (TCNAzQDMs) and dicyanoazulenequinonemethides (DCNAzQMs) from halo-1,5- and 1,7-AzQs **1**–**6**[9] and their physical properties centered on redox potentials.

Halo-AzQs **1**–**6** were treated with titanium tetrachloride in the presence of malononitrile and pyridine[10,11] to give DCNAzQMs **7**–**12**[11] as yellow to orange crystals and TCNAzQDMs **13**–**18**[11] as red to purple crystals (Scheme 1). The formers are the precursors to the latters, where not a heptafulvene but a fulvene structure was assigned to the formers because of disappearance of the characteristic IR absorption maximum of ca. 1720 cm^{-1} of the five-membered ring carbonyl group. Depending on molar ratio of the reagents the yields of products were changeable but their values were not high (1–48%) because of instability of the products. In **7**–**18** protons of peri-position to the dicyanomethylene groups of a five-membered ring showed a characteristic low field ^{1}H NMR chemical shift. The longest wave-maxima of UV–vis spectra of **7**–**12** appeared at ca. 450–550 nm in dichloromethane while those of **13**–**18** did at ca. 600–650 nm, indicating an increase in the length of the conjugated system in the latters.



1-6 **7-12** **13-18**

1a: 1,5-AzQ, X=H, Y=Br, Z=H
1b: 1,7-AzQ, X=H, Y=Br, Z=H
2a,b: X=H, Y=Cl, Z=H
3a,b: X=H, Y=Z=Br
4a,b: X=H, Y=Z=Cl
5a,b: X=Y=Z=Br
6a,b: X=Y=Z=Cl

7a,b, **13a,b**: X=H, Y=Br, Z=H
8a,b, **14a,b**: X=H, Y=Cl, Z=H
9a,b, **15a,b**: X=H, Y=Z=Br
10a,b, **16a,b**: X=H, Y=Z=Cl
11a,b, **17a,b**: X=Y=Z=Br
12a,b, **18a,b**: X=Y=Z=Cl

Scheme 1.

In order to survey the ability of AzQs, DCNAzQMs and TCNAzQDMs as an electron acceptor, their cyclic voltammetry (CV) was measured (Tables 1 and 2). The reversibility for AzQs and DCNAzQMs was poor but that for TCNAzQDMs was better and trichloro compounds, **6**, **12**, and **18** showed good reversibility.

The electron acceptability increases in the order of AzQs, DCNAzQMs and TCNAzQDMs in which the compounds of

Table 1. The Redox Potentials[a] and IR data (seven- and five-membered ring CO) of AzQs **1** - **6**

Compound	$E^1_{1/2}$ / V	$E^2_{1/2}$ / V	ν /cm^{-1}
1a	-0.72	-	1587, 1705
1b	-0.68	-	1583, 1704
2a	-0.79	-	1593, 1709
2b	-0.80	-	1579, 1708
3a	-0.47	-	1589, 1710
3b	-0.59	-	1584, 1718
4a	-0.54	-	1599, 1716
4b	-0.56	-	1587, 1724
5a	-0.43	-	1582, 1710
5b	-0.46	-	1590, 1716
6a	-0.48	-1.13	1587, 1717
6b	-0.48	-1.08	1597, 1716
1,4-NQ	-0.62	-1.16	
p-BQ	-0.43	-0.98	

[a]Concentration of the compounds, 10^{-3} M; solvent, CH_3CN; electrolyte, 0.1 M Et_4NClO_4; scan rate, 100 mV/s; electrode, Pt vs SCE.

Table 2. The Redox Potentials[a] and IR data (CO or CN[b]) of DCNAzQMs **7 - 12** and TCNAzQDMs **13 - 18**

Compound	$E^1_{1/2}$ / V	$E^2_{1/2}$ / V	ν /cm^{-1}
7a	-0.23	-	1579, 2228
7b	-0.23	-	1589, 2226
8a	-0.31	-	1587, 2227
8b	-0.22	-	1589, 2226
9a	-0.12	-	1599, 2228
9b	-0.21	-	1589, 2224
10a	-0.13	-	1593, 2231
10b	-0.13	-	1589, 2226
11a	0.00	-	1584, 2234
11b	-0.07	-	—
12a	-0.03	-0.65	1597, 2222
12b	-0.04	-0.64	1589, 2226
13a	-0.01	-0.39	2222
13b	-0.11	-0.47	2220
14a	-0.11	-0.50	2225
14b	-0.19	-0.51	2224
15a	0.08	-0.26	2212
15b	0.04	-0.30	2215
16a	-0.01	-0.38	2222
16b	-0.04	-0.38	2217
17a	0.13	-0.19	—
17b	0.13	-0.13	2214
18a	0.06	-0.27	2215
18b	0.04	-0.25	2215
TCNQ	0.25	-0.28	

[a] Concentration of the compounds, 10^{-3} M; solvent, CH_3CN; electrolyte, 0.1 M Et_4NClO_4; scan rate, 100 mV/s;electrode, Pt vs SCE. [b] Single absorption maximum was observed.

1,5-series are equal to or stronger than those of 1,7-series. The most strong electron acceptors were tribromo-1,5- and -1,7-TCNAzQDMs **17a,b** ($E^1_{1/2}$ 0.13 V). The more the number of substitution by bromine or chlorine increases the higher the reduction potential becomes throughout those series, which seems to be explained by inductive effects of halogens. Unexpectedly, however, chloro-series were inferior to bromo-series (**14** vs **13**, **16** vs **15,** and **18** vs **17**) in spite of the weaker electronegativity of bromine. The bond orders calculated by PM3[12] between carbon and bromine are 1.0435 (five-membered ring) and 1.0169 (seven-membered ring) in **15a** and those between carbon and chlorine are 0.9789 (five-membered ring) and 0.9677 (seven-membered ring) in **16a**. The optimized geometry of **17a** and **17b** are almost planar. Thus the balance sheet of electron-withdrawing inductive effects and electrondonating resonance effects from halogens might be reflected in the results; Hammett σ_m values for Cl (0.37) and Br (0.39) could be another choice for the explanation.

In summary, we have first prepared halo-TCNAzQDMs and halo-DCNAzQMs, a new family of azulene-based electron acceptors, from halo-AzQs and measured their redox potentials by cyclic voltammetry.

References and Notes

‡ Deceased in October 1, 1998.

‡‡ Deceased in April 4, 1996.

1 a) T. A. Turney, in “The Chemistry of Quinonoid Compounds,” ed. by S. Patai, John Wiley & Sons, NewYork (1974), Vol. 2, Chap.16, p 857. b) H. N. Wong, T. L. Chan; and T. Y. Luh, in “The Chemistry of Quinonoid Compounds,” ed. by S. Patai and Z. Pappoport, John Wiley & Sons, London (1988), Vol. 2, Chap. 26, p 1501.

2 L. T. Scott, M. D. Rozeboom, K. N. Houk, T. Fukunaga, T. Lindner, and K. Hafner, *J. Am. Chem. Soc.*, **102**, 5169 (1980).

3 L. T. Scott, in “The Chemistry of Quinonoid Compounds,” ed. by S. Patai and Z. Rappoport, John Wiley & Sons, London (1988), Vol. 2, Chap. 24, p 1385.

4 L. T. Scott and C. M. Adams, *J. Am. Chem. Soc.*, **106**, 4857 (1984).

5 T. Nozoe and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **69**, 1149 (1996).

6 L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1123 (1973).

7 K. Takahashi and S. Tarutani, *Chem. Commun.*, **1998**, 1233.

8 S. Schmitt, M. Baurngarten, J. Simon, and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, **37**, 1078 (1998).

9 O. Sato, N. Matsuda, S. Yoshioka, A. Takahashi, Y. Sekiguchi, J. Tsunetsugu, and T. Nozoe, *J. Chem. Res. (M)*, **1998**, 635, O. Sato, N. Matsuda, S. Yoshioka, A. Takahashi, Y. Sekiguchi, J. Tsunetsugu, and T. Nozoe, *J Chem. Res. (S)*, **1998**, 108.

10 W. Lehnert, *Tetrahedron Lett.*, **11**, 4723 (1970), W. Lehnert, *Synthesis*, **1974**, 667.

11 The typical procedures are as follows: To an ice-cooled solution of **6a** (15 mg, 0.057 mmol) in 1.0 mL of dry CH_2Cl_2 was added dropwise a solution of titanium tetrachloride (165 mg, 0.87 mmol) in 0.87 mL of CH_2Cl_2 during a 10 min period under N_2. To this solution a solution of 7.6×10^{-3} mL of malononitrile (0.11 mmol) and 1.0 mL of dry CH_2Cl_2 was added during 5 min period, and after the solution was stirred for 10 min, a mixture of 4.5×10^{-2} mL of pyridine (0.86 mmol) and 1.0 mL of dry CH_2Cl_2 was added during 10 min. The reaction mixture was stirred for 0.3 h and then poured into cold water. The aqueous layer was extracted with CH_2Cl_2, the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by neutral silica gel (CH_2Cl_2) column chromatography to yield 1.4 mg of **18a** (6.8 %) and 7.0 mg of **12a** (39%). **18a**: reddish violet crystals; mp 145 °C (dec); ^1H NMR (300 MHz, δ , $CDCl_3$) 7.51 (1H, *J* = 2.2 Hz), 7.61 (1H, dd, *J* = 2.2, 1.8Hz), 8.34 (1H, d, *J* = 1.8 Hz); IR (KBr, cm^{-1}) 2215; UV–vis (CH_2Cl_2, λ_{max} nm, log ε) 257 (4.1), 286 (4.0), 338 (3.6), 375 (3.8), 412 (3.9), 441 (4.0), 499 (3.8), 528 (3.8), 570 (3.7), 622 (3.3); MS (EI, 70 eV, *m/z*, %) 356 (M^+, 100), 358 (M^+ + 2, 100), 360 (M^+ + 4, 36), 362 (M^+ + 6, 5); HRMS (EI) (Calcd for $C_{16}H_3N_4{}^{35}Cl_3$: 355.9423, Found: 355.9404. **12a**: yellow plates; mp 152 °C (dec); ^1H NMR (300M Hz , δ , $CDCl_3$) 7.10 (1H, d, *J* = 2.4 Hz), 7.28 (lH, dd, *J* = 2.4, 1.5Hz), 8.43 (1H, d, *J* = 1.5 Hz); IR (KBr, cm^{-1}) 2222, 1597; UV–vis (CH_2Cl_2, λ_{max} nm, log ε) 234 (3.9), 284 (4.2), 296 (4.1), 315 (4.2), 328 (4.1), 347 (4.0), 367 (4.0), 409 (4.1), 432 (4.l) 455 (3.9); MS (EI, 70 eV, *m/z*, %) 308 (M^+, 20), 3 10 (M^+ + 2, 18), 312 (M^+ + 4, 10), 314 (M^+ + 6, 2).

12 MOPAC Ver.6: J. J. Stewart, *QCPE Bull.*,**9**, 10 (1989).