compound 2[5] (1.50 g, 5.6 mmol) in 425 mL of acetone was photolyzed through Pyrex until GC indicated that no starting material remained (18 h). GC showed the formation of three new photoproducts (ratio 65:25:9), which were subsequently identified as the isomeric benzosemibullvalenes 4, 5, and 7, respectively. While compounds 5 and 7 were invariably eluted from the column together, the major product 4 could be isolated in pure form by flash column chromatography on 250 g of silica gel 60 (230–400 mesh) with petroleum ether (30–60 °C)–diethyl ether, 93:7 (v/v), as the eluting solvent. This afforded 0.96 g (64%) of a colorless oil, which was assigned the structure dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylate (4) on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1730 (C=O) cm^{-1}; MS m/e (relative intensity) 270 (M^+, 37), 238 (14), 210 (94), 183 (90), 152 (100); HRMS calcd for $C_{16}H_{14}O_4$ (M^+) 270.0892, found 270.0892; UV (CH_3CN) 278 nm, ϵ 1100.

Benzophenone-Sensitized Photolysis of Compound 2. A solution consisting of 50 mg (0.18 mmol) of 2 and 0.40 g (2.2 mmol) of benzophenone in 10 mL of acetone was photolyzed through a uranium glass filter sleeve for 3 h, at which time GC indicated no remaining starting material and the formation of a single volatile photoproduct corresponding in retention time to 4. The photoproduct was isolated in 78% yield by flash chromatography on silica gel; its spectra proved to be identical in every respect with those described above.

Photochemical Interconversion of Compounds 4 and 5. These photolyses could be conducted in either benzene (Corex filter) or acetone (Pyrex filter). The former method gives slightly better yields of 5 and was therefore used in a preparative run. A solution of 0.64 g (2.4 mmol) of compound 4 in 200 mL of benzene was irradiated for 13 h, at which time GC indicated the 4:5 ratio to be invariant at ca. 66:34. After removal of solvent the mixture was subjected to flash chromatography on silica gel with low-boiling petroleum ether–ethyl acetate 95:5 (v/v) as the eluting solvent. Compound 5 (59 mg, 9%) was eluted as a colorless oil followed closely by the starting material 4. Compound 5 was identified as dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene-1,6c(2a*H*)-dicarboxylate on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1719 (C=O) cm^{-1}; MS m/e (relative intensity) 270 (M^+, 55), 210 (62), 183 (47), 152 (100), 84 (42); HRMS calcd for $C_{16}H_{14}O_4$ (M^+) 270.0892, found 270.0885. The NMR spectrum of this material was identical with the spectrum of a sample of 5 (mixed with 7) isolated from photolysis of 2 in acetone.

The photostationary state nature of the reaction was established by a series of analytical-scale photolyses of mixtures of 4 and 5 of widely varying composition in both benzene (Corex) and acetone (Pyrex). The 4:5 GC ratios were (7 ± 1):(3 ± 1) in the former solvent and (8 ± 1):(2 ● 1) in the latter.

Acetone-Sensitized Photolysis of Compound 3. A solution of 100 mg (0.37 mmol) of benzocyclooctatetraene derivative 3 in 200 mL of acetone was irradiated through a Pyrex filter, and the course of the reaction was followed by GC. After 2 h, GC showed the complete disappearance of starting material and the formation of a single new photoproduct. The solution was evaporated to dryness, and the residue was subjected to flash chromatography with low-boiling petroleum ether–diethyl ether, 3:1 (v/v), as the eluting solvent. This afforded 71 mg (71%) of a colorless oil that was identified as dimethyl 2b,6b-dihydrobenzo[a]cyclopropa-[cd]pentalene-2,6c(2a*H*)-dicarboxylate (7) on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1718 (C=O) cm^{-1}; MS m/e (relative intensity) 270 (M^+, 34), 238 (19), 210 (92), 183 (58), 152 (78), 43 (100); HRMS calcd for $C_{16}H_{14}O_4$ 270.0892, found 270.0889. The NMR spectrum of this material was identical with the spectrum of a sample of 7 (mixed with 5) isolated from photolysis of 2 in acetone.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

Registry No. 2, 19981-73-8; 3, 19988-66-0; 4, 120172-73-8; 5, 120172-74-9; 7, 120172-71-6.

Syntheses and Electrochemical Properties of Tetracyano-*p*-quinodimethane Derivatives Containing Fused Aromatic Rings

Nazario Martín, Richard Behnisch, and Michael Hanack*

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, West Germany

Received November 7, 1988

Several fused aromatic tetracyano-*p*-quinodimethane (TCNQ) derivatives (11a–c, 5, and 12) have been synthesized by the reaction of the corresponding quinones and malononitrile. Syntheses of these derivatives by Diels–Alder reactions of *o*-quinodimethane and TCNQ have been attempted. In comparison with TCNQ, cyclic voltammetric data of these new compounds reveal a more negative value for the first and the second reduction potential.

Introduction

Many substituted TCNQ (tetracyano-*p*-quinodimethane) derivatives have been synthesized in order to obtain charge-transfer (CT) complexes.[1] In general, it has been found that substitution on the basic TCNQ skeleton results in CT complexes that are less conducting than those of TCNQ itself.[2] This behavior could be explained with the lower acceptor properties in some cases or to the complete charge transfer of stronger electron acceptors in other cases. Thus, TCNQ and tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$) react with hexamethylenetetraselenafulvalene (HMTSF) to form the corresponding organic salts. However, the complex HMTSF–TCNQ is one of the most highly conducting organic salts ever known. The reason for this behavior is due to the stronger electron-acceptor character in $TCNQF_4$ leading to a complete charge transfer in this complex. The result is a fully ionic Mott–Hubbard insulator.[2]

TCNQ analogues fused with aromatic rings have received less attention.[3] From theoretical studies it was

(1) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
(2) Bryce, M. R.; Murphy, L. C. *Nature* **1984**, *309*, 119.
(3) Gerson, F.; Heckendorn, R.; Cowan, D. O.; Kini, A. M.; Maxfield, M. *J. Am. Chem. Soc.* **1983**, *105*, 7017.

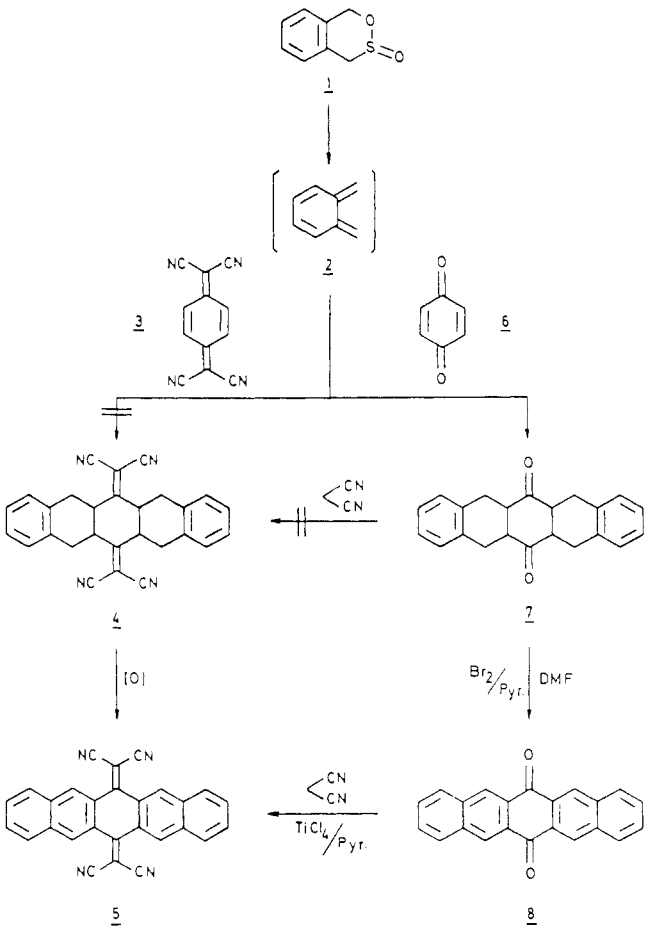
0022-3263/89/1954-2563$01.50/0

Table I. Preparation and Properties of Fused Aromatic TCNQ Derivatives

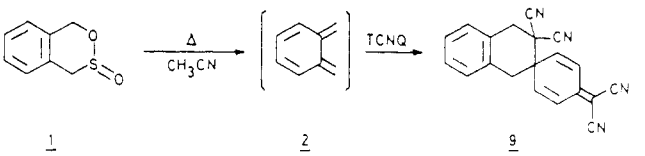
compd	conditions[a]	yield,[b] %	mp, °C	λ_{max},[c] nm	ν_{CN}, cm^{-1}
11a	110 °C/5 h	55	>320	425	2231
11b	110 °C/6 h	45	>320	440	2230
11c	110 °C/24 h	26	>320	505	2222
5	110 °C/15 h	54	>320	415	2228
12	reflux/3 h	42	237–238	370 (sh)	2218

[a] In pyridine (11a–c and 5); in chloroform (12). [b] Isolated compound. [c] In chloroform.

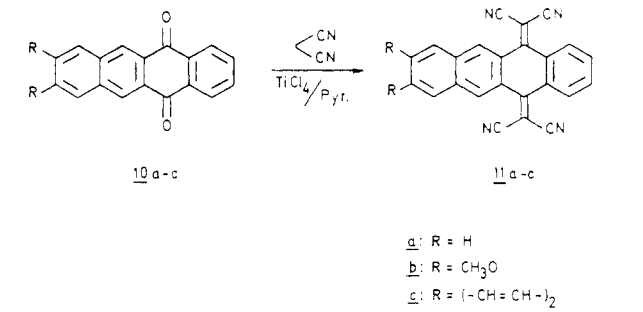
Scheme I



Scheme II



Scheme III



concluded that the π-system extension in such compounds results in a lowering of intramolecular Coulomb repulsion leading to highly conducting CT complexes.[4] However, in spite of the interest to synthesize such TCNQ derivatives, only a few examples of TCNQ molecules with an extended π-system are known.[5,6]

In a preliminary paper we reported[11] on the synthesis and electrochemistry of 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (TCPQ, 5). So far, this molecule presents the highest degree of conjugation in a TCNQ derivative. Now, we describe the synthesis of TCNQ analogues in which the extension of the π-system has been increased systematically. Cyclic voltammetric studies are performed on these new compounds to compare their reduction potentials with those of earlier reported more simple benzene-fused TCNQ derivatives.

Results and Discussion

Synthesis. Initially, the route followed for the synthesis of TCPQ (5) was a Diels–Alder reaction of TCNQ (3) with *o*-quinodimethane (2) generated in situ from 1,4-dihydro-2,3-benzoxathiin 3-oxide[12] (1) to form the bisadduct 4. Subsequent dehydrogenation of 4 would provide the tetracyanoquinodimethane (5) (Scheme I). However, contrary to previously reported results,[10] the generated *o*-quinodimethane reacted with the exocyclic double bond to give the spiro compound (9) (Scheme II). This result is in agreement with the reported reaction of 1-cyclopropylbutadiene with TCNQ to give the corresponding Diels–Alder adduct with the double bond bearing the cyano groups.[13]

5,5a,6a,7,12,12a,13a,14-Octahydro-6,13-pentacenedione (7) synthesized by reacting 1 with *p*-benzoquinone (6) in a one-step reaction[14] was then chosen as precursor for compound 4. However, under various conditions, the reaction of diketone 7 with malononitrile was met with futility. Probably, the high enolizability of diketone 7 and the steric hindrance of peri-hydrogens in 7 are responsible for this result (Scheme I).

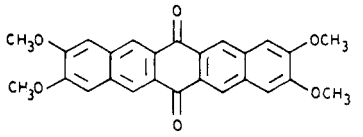
However, diketone 7 can be easily oxidized by bromine/pyridine in DMF to form the 6,13-pentacenedione 8.[16] In the presence of $TiCl_4$ as catalyst,[17] reaction of 8

(4) Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232.
(5) Chatterjee, S. *J. Chem. Soc. B* **1967**, 1170.
(6) The synthesis and electrochemical properties of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) has been published simultaneously by different authors (see ref 7–10).
(7) Yamaguchi, S.; Tatemitsu, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1983**, 1229.
(8) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618.
(9) Ong, B. S.; Keoshkerian, B. *J. Org. Chem.* **1984**, *49*, 5002.
(10) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.
(11) Martín, N.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1522.
(12) Harpp, D. N.; Steliov, K.; Chan, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 1222.
(13) Kataoka, F.; Nishida, S.; Tsuji, T.; Murakami, M. *J. Am. Chem. Soc.* **1981**, *103*, 6878.
(14) The reaction of 1 with *p*-benzoquinone gave rise to the mono Diels–Alder adduct,[15] which reacted with an excess of 1 to give the bisadduct 7. Compound 7 can also be obtained in a one-step reaction using an excess of the diene (see Experimental Section).
(15) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526.

with malononitrile using pyridine as solvent and base led to compound **5** in good yield.

Accordingly, we have carried out the syntheses of a variety of fused aromatic TCNQ derivatives (Table I) from the corresponding quinones (Scheme III). The quinones **10a–c** were reacted with malononitrile to form the corresponding tetracyano derivatives **11a–c**, which were isolated as stable yellow or red crystalline high-melting solids (Scheme III). The structures of **11a–c** were confirmed by its ^1H and ^{13}C NMR high-resolution spectra.

As expected, the starting quinones **8** and **10a–c** were poorly soluble in common organic solvents. However, reactions with malononitrile were successful in pyridine at high temperatures. Only 2,3,9,10-tetramethoxy-6,13-pentacenedione (**13**) did not react, probably, due to its even lower solubility. When the reaction of **13** with malononitrile was carried out in hot quinoline or nitrobenzene, only decomposition was observed.



13

Due to the low solubility of **13**, it was impossible to record a ^{13}C NMR spectrum in solution. However, this problem was overcome by using solid-state NMR spectroscopy. All the signals in the ^{13}C CP-MAS spectrum could be assigned easily on the basis of chemical shifts. The assignments were confirmed by using interrupted decoupling to suppress ^{13}C lines from carbons with attached protons (pulse sequence NQS).

Due to the better solubility of benz[*a*]anthracene-7,12-dione, the reaction with malononitrile was carried out in chloroform. However, only the monosubstituted quinone **12** was obtained. The presence of the peri-hydrogens so close to the carbonyl group prevent the second condensation. This result is in agreement with that obtained for 2,4-dimethylanthraquinone leading also to the monosubstituted quinone.[9]

The UV spectra of **5**, **11a–c**, and **12** suggest that these molecules are severely deformed from planarity as has been confirmed by X-ray data for the related compound TCAQ.[18] This fact is also supported in the IR spectra by the relatively high value for the stretching vibration of the conjugated cyano groups which appear at 2222–2231 cm^{-1} (Table I).

Electrochemistry. The half-wave redox potentials of **5**, **11a–c**, **12**, and some related compounds are summarized in Table II. The CV measurements of the new compounds have been carried out in acetonitrile at room temperature with tetrabutylammonium perchlorate as the supporting electrolyte.

Contrary to TCAQ which shows a single-wave, two-electron reduction to the dianion,[19] compounds **5**, **11a–c**, and **12** exhibit two reversible single-wave reductions to the corresponding radical anion and dianion. It has been demonstrated that the negative charges in the radical anion and dianion are located at the two $C(CN)_2$ groups.[3] This

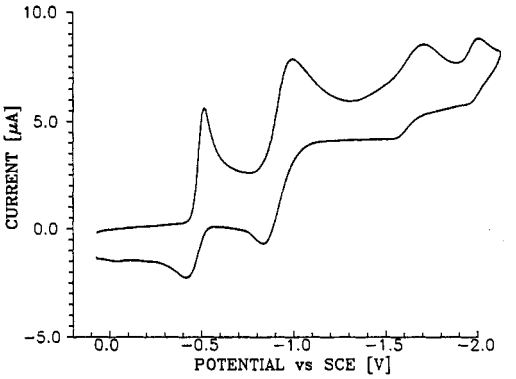


Figure 1. Cyclic voltammogram of **11b** at a scan rate of 20 mV/s.

charge distribution is not substantially altered by enlargement of the π-system. Thus, the $E_{1/2}{}^1$ and $E_{1/2}{}^2$ of compounds **5** and **11a–c** are more negative compared to benzo-TCNQ and TCAQ, probably due to the major influence of the molecular distortion of the fused benzene rings than to the electronic effect of increasing π-delocalization. In addition, compounds **5** and **11a–c** show a third reduction potential at −1.61, −1.85, −1.59 and −1.54 V, respectively. The formation of radical trianions in which the third electron is placed in the aromatic system has been observed by ESR in a previous work.[3] The facile access to these radical trianions is related to those of the corresponding dialkyl-substituted aromatic hydrocarbons. Thus, the third reduction potential decreases from benzo-TCNQ (−3.23 V),[3] TCAQ (−2.06 V),[10] **11a** (−1.85 V) to **5** (−1.61 V). These decreasing values with the extension of conjugation are comparable with the values found for the radical anions of aromatic hydrocarbons.[20]

Furthermore, a fourth single wave reduction at −1.96 V has been observed in **11b** that can be reasonably attributed to the formation of the corresponding tetraanion (Figure 1). Usually the fourth reduction potential of tetraanions is inaccessible by cyclic voltammetric studies, since the electrochemical available potential range is limited by the reduction of the solvent-supporting electrolyte system. On the other hand, substitution with methoxy or further benzo groups on the aromatic skeleton has almost no influence on the first and second reduction potentials (Table II). The effect of substitution is larger on the third reduction potential, which is in accordance with localization of the third electron on the aromatic skeleton.

It is worth mentioning that the cyclic voltammogramm of compound **11c** shows a very intense peak for the first reduction potential whereas the one corresponding to the second reduction potential is almost not visible. However, both peaks appear with comparable intensity in the presence of ferrocene, probably indicating a chemical reaction of the reduced species with ferrocene.

Cyclic voltammetry of compound **12** reveals two half-wave reduction potentials within a small potential range, which is in accordance with literature results on related systems.[24] The first redox potential is in the same range as that of **5** and **11**, which can be explained by the higher planarity in compound **12**. This observation is also supported by the stretching vibration of the cyano group in the IR spectra which is shifted to a lower value (Table I)

(16) 6,13-Pentacenedione can also be obtained from phthaldialdehyde and 1,4-cyclohexanedione as described by Ried, W.; Anthöfer, F. *Angew. Chem.* **1953**, *65*, 601.

(17) The use of $TiCl_4$ as catalyst in this kind of reactions have been recently described (see ref 8, 9).

(18) Schubert, U.; Hünig, S.; Aumüller, A. *Liebigs Ann. Chem.* **1985**, 1216.

(19) Two one-electron reduction waves at −0.46 and −0.65 V in acetonitrile have also been reported for TCAQ.[7]

(20) Gerson, F.; Ojya-Nishiguchi, H.; Wydler, C. *Angew. Chem.* **1976**, *88*, 617; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 552.

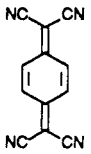
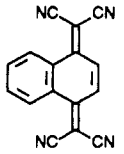
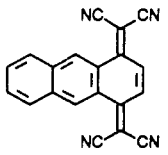
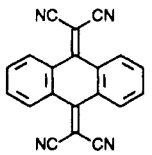
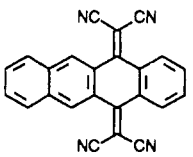
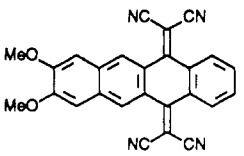
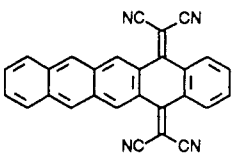
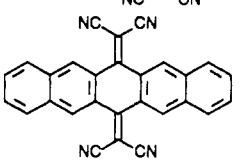
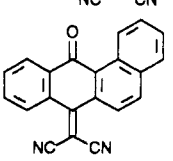
(21) Rifi, M. R.; Covitz, F. E. *Introduction to Organic Electrochemistry*; Marcel Dekker: New York, 1974.

(22) Serpaud, B.; Lepage, Y. *Bull. Soc. Chim. Fr.* **1977**, 539.

(23) Bhattacharjee, D.; Popp, F. D. *J. Heterocyclic Chem.* **1980**, *17*, 315.

(24) Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355.

Table II. Cyclic Voltammetric Data for TCNQ and Fused Aromatic Ring Derivatives (in volts vs SCE)

compound	formula	solvent	$E_{1/2}^1$	$E_{1/2}^2$	$\lvert E_{1/2}^2 - E_{1/2}^1 \rvert$	$E_{1/2}^3$	ref
TCNQ		CH_3CN	0.08	−0.48	0.56		8
		BuCN	−0.09	−0.75	0.66		10
		DMF	−0.12	−0.72	0.59		10
benzo-TCNQ		CH_3CN	−0.04	−0.41	0.37		7
		BuCN	−0.26	−0.74	0.48		10
		DMF	−0.30	−0.73	0.43		10
naphtho-TCNQ		CH_3CN	−0.18	−0.48	0.30		7
TCAQ		CH_3CN		−0.285		−2.06	10
		BuCN		−0.71			10
		DMF		−0.705			10
11a		CH_3CN	−0.44	−0.93	0.49	−1.85	this work
11b		CH_3CN	−0.44	−0.89	0.45	−1.59	this work
11c		CH_3CN	−0.50	−0.92[a]	0.42	−1.54	this work
5		CH_3CN	−0.57	−0.91	0.34	−1.61	this work
12		CH_3CN	−0.49	−0.57	0.08		this work

[a] Measured in the presence of ferrocene.

compared to TCAQ or compounds **11** and **5**.

Attempts to form charge-transfer complexes from compounds **5** or **11a–c** and tetrathiofulvalene (TTF) were carried out in DMF. However, no evidence of complexation was observed, probably as a consequence of the high negative value for the first reduction potential exhibited by these compounds.

Experimental Section

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 398 spectrometer and FIR spectra on a Bruker IFS 114c spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 5 instrument. ^1H and ^{13}C NMR spectra were determined with a Bruker WM 400 or a Bruker WH 90 spectrometer. ^{13}C CP-MAS were obtained on a Varian MAT 711 instrument and elemental analyses were performed on a Carlo Erba Elemental Analyses 1104 apparatus.

Cyclovoltammetric measurements were performed on a PAR 273 Potentiostat/Galvanostat interfaced with a IBM PC/XT-type microcomputer data station. A standard three-electrode cell configuration was employed using a glassy carbon disk working electrode, a Pt wire auxillary electrode, and a Ag wire as a Ag/Ag^+ quasireference electrode. The reference electrode was calibrated at the completion of each measurement to a saturated calomel electrode (SCE). As internal reference redox system we used the ferrocene/ferricenium couple whose redox potential was measured to 0.39 V (vs SCE).

Solvent and supporting electrolyte for electrochemistry were purified according to literature procedures.[21] 5,12-Naphthacenedione (**10a**) and benz[*a*]anthracene-7,12-dione were

purchased from Aldrich and were crystallized before using.

5,5a,6a,7,12,12a,13a,14-Octahydro-6,13-pentacenedione (7). To a solution of 1,4-dihydro-2,3-benzoxathiin 3-oxide (1) (3.02 g, 18 mmol) in dry benzene (15 mL) was added *p*-benzoquinone (0.79 g, 7.3 mmol). The resulting yellow solution was refluxed for 2.5 h. A precipitated solid was filtered off and washed with a small quantity of benzene to give 530 mg of a white solid. Further purification was accomplished by recrystallization from DMF or THF in 23% yield: mp 233–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.08 (m, 8 H, arom), 3.15–3.09 (m, 8 H), 2.92–2.90 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.87, 133.74, 128.60, 126.56, 45.49, 28.87; IR (KBr) 1705, 1500, 1170, 965, 790, 755, 750 cm^{-1}; MS *m/e* (%) 316 (M^+, 16), 298 (6), 280 (6), 157 (7), 142 (100), 129 (40), 115 (12). Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.54; H, 6.32. Found: C, 83.08; H, 6.31.

2,2-Dicyano-1,2,3,4-tetrahydronaphthalene-3-spiro-1′-[4′-(dicyanomethylene)-2′,5′-cyclohexadiene] (9). TCNQ (3) (0.61 g, 3 mmol) was added to a solution of 1,4-dihydro-2,3-benzoxathiin 3-oxide (1) (1.11 g, 6.6 mmol) in 30 mL of dry acetonitrile. After 22 h of refluxing under nitrogen atmosphere, the hot solution was filtered, and a crystalline solid was formed in the mother liquors. The solid obtained was crystallized from acetonitrile in 40% yield: mp 213–215 °C dec; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ 7.32–7.20 (m, 4 H, arom), 7.17 (d, 2 H, =CH, *J* = 10 Hz), 6.93 (d, 2 H, =CH, *J* = 10 Hz), 3.88 (s, 2 H, CH_2) 3.18 (s, 2 H, CH_2); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ 153.6, 143.6, 129.3, 129.2, 128.9, 127.7, 127.5, 127.3, 126.0, 113.6, 112.2, 80.2, 45.1, 39.2, 34.6, 33.7; IR (KBr) 2232, 2222, 1657, 1645, 1542, 1496, 1455, 1433, 836, 816, 749 cm^{-1}; MS *m/e* (%) 308 (M^+, 100), 281 (M^+ – HCN, 82), 254 (M^+ – 2HCN, 12), 243 (92), 216 (32), 178 (34). Anal. Calcd for $C_{20}H_{12}N_4$: C, 77.92; H, 3.89; N, 18.12. Found: C, 77.86; H, 4.04; N, 18.29.

Syntheses of Quinones. 5,14-Pentacenedione (**10c**) was obtained according to the reported procedure.[22] 6,13-Pentacenedione[16] (**8**) was synthesized by a new procedure.

6,13-Pentacenedione (8). To a suspension of the diketone **7** (0.158 g, 0.5 mmol) in 10 mL of dry dimethylformamide was added a solution of bromine (4.5 mmol) in 2 mL of dry dimethylformamide. The reaction mixture was slowly heated, and a solution of 1.0 g of dry pyridine in 2 mL of dry dimethylformamide was added dropwise. Stirring was continued at 100–110 °C for 18 h, cold water (10 mL) was added subsequently, and stirring of the mixture was continued for an additional 2 h. The crude product (0.12 g, 78%) was filtered, washed with water, and dried: mp >320 °C (lit.[16] mp 394 °C). The IR spectrum (C=O, 1675 cm^{-1}) was identical with a sample prepared as described.[16]

2,3,9,10-Tetramethoxy-6,13-pentacenedione (13). To a mixture of 4,5-dimethoxyphthaldialdehyde (3.88 g, 20 mmol) and 1,4-cyclohexanedione (1.12 g, 10 mmol) in 300 mL of ethanol was added a 5% aqueous KOH solution (5 mL). After refluxing for 3 h, the reaction mixture was cooled, and the precipitated solid was filtered off and crystallized from nitrobenzene in 43% yield: mp >320 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 4 H), 7.33 (s, 4 H), 4.06 (s, 12 H); ^{13}C NMR (solid state) δ 183.0 (C=O), 150.5 (=$COCH_3$), 128.2 (2 C, =C), 107.7 (2 C, =CH), 55.2 (CH_3O); IR (KBr) 1670, 1620, 1590, 1510, 1480, 1435, 1390, 1250, 1210, 1160 cm^{-1}; MS *m/e* (%) 428 (M^+, 100), 385 (14), 357 (10), 214 (12), 200 (10). Anal. Calcd for $C_{26}H_{20}O_6$: C, 72.90; H, 4.67. Found: C, 73.34; H, 4.84.

8,9-Dimethoxy-5,12-naphthacenedione (10b). A mixture of 4,5-dimethoxyphthaldialdehyde[23] (1.94 g, 10 mmol) and 1,4-dihydroxynaphthalene was dissolved in 50 mL of dry pyridine, and the solution was refluxed overnight under nitrogen atmosphere. A separated yellow solid was obtained in 45% yield: mp >320 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 4.06 (s, 6 H), 7.33 (s, 2 H), 7.83 (m, 2 H), 8.40 (m, 2 H), 8.66 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.09, 152.32, 134.49, 133.91, 131.79, 128.62, 127.38, 127.30, 107.87, 56.18; IR (KBr) 1665, 1615, 1590, 1575, 1515, 1480, 1440, 1290, 1260, 1160, 1015, 970, 715 cm^{-1}; MS *m/e* (%) 318 (M^+, 100), 275 (30), 247 (16), 204 (18), 176 (10), 145 (10). Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.47; H, 4.40. Found: C, 75.27; H, 4.32.

Condensation of Quinones with Malononitrile. General Procedure. To a suspension of 5 mmol of the corresponding quinone in 150 mL of dry pyridine was added 10 mmol of $TiCl_4$, and the reaction mixture was heated under nitrogen atmosphere. To the warmed yellow suspension was added a solution of 60–100 mmol of malononitrile in 20 mL of dry pyridine, and the reaction mixture was refluxed for a variable time (5–24 h). The dark solution was concentrated to the half of its volume, and after cooling a solid precipitated. The solid product was filtered off, washed several times with water, and dried. Further purification was accomplished by recrystallization from an appropriate solvent.

13,13,14,14-Tetracyano-5,12-naphthacenequinodimethane (11a). After 5 h of refluxing, **11a** was obtained from **10a** with malononitrile in 1:12 ratio and recrystallized from DMF in 55% yield: mp >320 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 2 H), 8.25–8.23 (m, 2 H), 8.03–8.01 (m, 2 H), 7.75–7.72 (m, 4 H); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ 160.65, 132.39, 132.25, 130.48, 130.14, 129.07, 128.40, 127.24, 126.19, 114.13, 82.50; IR (KBr) 2231, 1590, 1556, 1495, 1393, 1319, 915, 782, 755 cm^{-1}; UV max ($CHCl_3$) 262, 302, 326, 425 nm; MS *m/e* (%) 354 (M^+, 100), 327 (M^+ – HCN, 19), 300 (M^+ – 2HCN, 10), 273 (M^+ – 3HCN, 6), 150 (13), 137 (12), 79 (14). Anal. Calcd for $C_{24}H_{10}N_4$: C, 81.35; H, 2.82; N, 15.82. Found: C, 81.26; H, 2.98; N, 15.76.

8,9-Dimethoxy-13,13,14,14-tetracyano-5,12-naphthacenequinodimethane (11b). After 6 h of refluxing, **11b** was obtained from **10b** with malononitrile in 1:12 ratio and recrystallized from DMF in 45% yield: mp >320 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2 H), 8.25, 8.22 (m, 2 H), 7.72–7.69 (m, 2 H), 7.24 (s, 2 H), 4.05 (s, 6 H, 2 CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19, 153.20, 132.33, 130.93, 129.94, 127.52, 127.07, 124.35, 113.75, 113.50, 107.40, 81.26, 56.41; IR (KBr) 2230, 1615, 1540, 1510, 1470, 1430, 1390, 1275, 1215, 1165, 1010, 770, 695 cm^{-1}; UV max ($CHCl_3$) 240 (sh), 305, 360, 440 nm; MS *m/e* (%) 414 (M^+, 100), 371 (18), 343 (12), 328 (14), 301 (8), 207 (8). Anal. Calcd for $C_{26}H_{14}N_4O_2$: C, 75.36; H, 3.38; N, 13.52. Found: C, 75.08; H, 3.44; N, 13.45.

15,15,16,16-Tetracyano-5,14-pentacenequinodimethane (11c). After 24 h of refluxing, **11c** was obtained from **10c** with malononitrile in 1:20 ratio and recrystallized from DMF in 26% yield: mp >320 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 2 H), 8.63 (s, 2 H), 8.27–8.25 (m, 2 H), 8.12–8.07 (m, 2 H), 7.75–7.73 (m, 2 H), 7.64–7.62 (m, 2 H); IR (KBr) 2222, 1579, 1534, 1527, 1445, 1413, 1319, 1286, 1267, 926, 768, 760, 691 cm^{-1}; UV max ($CHCl_3$) 250, 288, 332, 365, 505 nm; MS *m/e* (%) 404 (M^+, 100), 377 (M^+ – HCN, 10), 350 (M^+ – 2HCN, 6), 323 (M^+ – 3HCN, 3), 175 (10), 161 (6). Anal. Calcd for $C_{28}H_{12}N_4$: C, 83.16; H, 2.97; N, 13.86. Found: C, 82.80; H, 3.22; N, 14.14.

15,15,16,16-Tetracyano-6,13-pentacenequinodimethane (5). After 15 h of refluxing, **5** was obtained from **8** by using malononitrile in 1:20 ratio and recrystallized from DMF in 54% yield: mp >320 °C; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ 8.86 (s, 4 H), 8.23–8.21 (m, 4 H), 7.84–7.81 (m, 4 H); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ 161.56, 132.62, 130.18, 129.13, 128.35, 126.70, 114.29, 82.11; IR (KBr) 2228, 2222, 1575, 1559, 1552, 1506, 1490, 1447, 1394, 1290, 917, 785, 753 cm^{-1}; UV max ($CHCl_3$) 249, 322, 415 nm; MS *m/e* (%) 404 (M^+, 100), 377 (M^+ – HCN, 18), 350 (M^+ – 2HCN, 8), 323 (M^+ – 3HCN, 5), 175 (12), 161 (10). Anal. Calcd for $C_{28}H_{12}N_4$: C, 83.16; H, 2.97; N, 13.86. Found: C, 82.97; H, 3.12; N, 13.97.

10-(Dicyanomethylene)benz[*a*]anthrone (12). To a solution of the benz[*a*]anthracene-7,12-dione (5.16 mg, 2 mmol) in 50 mL of dry $CHCl_3$ was added $TiCl_4$ (1.52 g, 8 mmol). To the yellow suspension was added dropwise a solution of malononitrile (2.64 g, 40 mmol) and dry pyridine (6.36 mL, 80 mmol) in 40 mL of $CHCl_3$. The reaction mixture was refluxed for 3 h. After cooling, the brown-yellow suspension was poured into 300 mL of crushed ice. The organic phase was separated, washed several times with water, and dried over sodium sulfate. After the solvent was removed, a yellow solid was obtained. Further purification was accomplished by recrystallization from acetonitrile in 42% yield: mp 237–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, 1 H), 8.25–8.11 (m, 4 H), 7.92 (d, 1 H), 7.76–7.64 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.04, 162.42, 135.67, 135.05, 134.30, 134.20, 133.28, 132.93, 132.31, 132.12, 130.33, 128.92, 128.74, 127.85, 127.82, 127.31, 126.04, 122.59, 113.75, 113.70, 83.84; IR (KBr) 2218, 1668, 1586, 1523, 1456, 1429, 1374, 1366, 1331, 1283, 1230, 829, 772, 740, 700 cm^{-1}; UV max ($CHCl_3$) 255, 285, 320, 370 (sh), 430 (sh); MS *m/e* (%) 306 (M^+, 100), 278 (32), 251 (12), 224 (5), 153 (16), 125 (12), 112 (18). Anal. Calcd for $C_{21}H_{10}N_2O$: C, 82.35; H, 3.26; N, 9.15. Found: C, 82.23; H, 3.22; N, 9.15.

Acknowledgment. This work was financially sup-

ported by Bundesministerium für Forschung und Technologie (BMFT) under the research project 03 M 4013A.

Registry No. 1, 51439-46-4; 3, 1518-16-7; 5, 120086-27-3; 6, 106-51-4; 7, 120086-22-8; 8, 3029-32-1; 9, 120086-23-9; **10a**, 1090-13-7; **10b**, 43073-49-0; **10c**, 6006-83-3; **11a**, 120086-24-0; **11b**, 120086-25-1; **11c**, 120086-26-2; **12**, 120086-28-4; **13**, 120086-29-5; 4,5-dimethoxyphthaldialdehyde, 43073-12-7; 1,4-cyclohexanedione, 637-88-7; 1,4-dihydroxynaphthalene, 571-60-8; malononitrile, 109-77-3; benz[*a*]anthracene-7,12-dione, 2498-66-0.

A Theoretical Study of Substituent Effects. Analysis of Steric Repulsion by Means of Paired Interacting Orbitals

Hiroshi Fujimoto,* Yoshitaka Mizutani, Jun Endo, and Yasuhisa Jinbu

Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan

Received April 19, 1988

The steric effect of substituent groups is studied by taking a simple model of the acid-catalyzed esterification of acetic acid. By replacing the hydrogens of the acetyl group by methyl groups, the changes in activation barriers for the nucleophilic attack are examined by means of MO calculations. The possible origin of steric repulsion is investigated by applying the transformation of MO's into paired interacting orbitals. The transition-state structures are located for some simple reaction models. The Cram and anti-Cram selectivities in the nucleophilic additions to chiral C=O systems are also discussed.

Introduction

Among the factors that govern rates and selectivities of chemical reactions, the polar effect and steric effect of substituents have been investigated most extensively.[1] With respect to the polar effects, there exists a very useful and practical way of generalization, i.e., electron-withdrawing and electron-releasing groups. This view has been represented in a concise equation by Hammett[2] and has been applied widely throughout the vast field of chemistry. The usefulness of the equation and the parameters involved in it have also been discussed from theoretical viewpoints.[3,4]

An attempt to represent quantitatively steric effects of substituent groups was made by Taft[5] by measuring the rates of some model reactions suggested by Ingold.[6] The steric parameters E_s were determined from average values of log (k/k_0) for four types of related reactions, e.g., acid-catalyzed ester hydrolysis and esterification of carboxylic acids at 25 °C, where k_0 stands for the reaction rate for the reference group CH_3 and k for other substituent groups. Since then, several papers appeared to criticize and/or attempt to improve the Taft E_s scale.[7-9] Dubois and his collaborators proposed a revised version of steric parameters and called them E_s'.[10] To eliminate possible errors originating from averaging the reaction rates for different reactions in the Taft E_s values, they have reevaluated the steric constant of groups for the rates of acid-catalyzed esterification of carboxylic acids in methanol at 40 °C. These steric parameters, however, do not seem to indicate a complete separation of steric and polar effects.

When we carry out molecular orbital (MO) calculations, both the steric and polar effects are included. For instance, we may partition the energy of interaction between two fragment species into several energy terms, e.g., the Coulombic, delocalization, polarization, and exchange energies.[11-13] The delocalization interaction brings about formation of new bonds between the reagent and reactant, as well as transfer of an electronic charge from one fragment to the other fragment.[14] This interaction, as well as the Coulombic interaction, is closely related to the polar effect of the substituent groups. The exchange interaction arises from the interaction between the occupied MO's of two fragments.[15] A bulkier group possesses a greater number of occupied MO's having large amplitude in the space spanned by that group and, hence, brings about a stronger closed-shell repulsion with the occupied MO's of an attacking reagent. The understanding of steric effects is clearly of profound significance in organic syntheses. Thus, we made an attempt to elucidate the steric effects of substituents by means of theoretical calculations.

Method of Calculation

In order to discuss steric effects theoretically, we set up first a simplified reaction model as sketched in Figure 1.[16] A methoxy anion attacks a carboxylic acid molecule in the presence of a proton as an acid catalyst. Acetic acid is the reference system in the present study. One may start a discussion of reactivities and selectivities from a comparison of the magnitudes of activation energy by calculating the transition-state structures for each reacting system and for each path.[17] In this work, we try to in-

(1) See for example: (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: New York, 1969. (b) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt: New York, 1959; pp 199-249.
(2) (a) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940; pp 184-199. (b) McGary, C. W.; Okamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 3037.
(3) Henri-Rousseau, O.; Texier, F. *J. Chem. Educ.* **1978**, *55*, 437.
(4) Fujimoto, H.; Mizutani, Y.; Iwase, K. *J. Phys. Chem.* **1986**, *90*, 2768.
(5) Taft, R. W. *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 556-675.
(6) Ingold, C. K. *J. Chem. Soc.* **1932**, 1032.
(7) Shorter, J. *Advances in Linear Free Energy Relationships*; Chapmann, N. B., Shorter, J., Eds.; Plenum: London, 1972.
(8) Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552.
(9) Hancock, C. K.; Meyers, E. A.; Yager, B. Y. *J. Am. Chem. Soc.* **1961**, *83*, 4211.
(10) (a) MacPhee, J. A.; Panaye, A.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 3553. (b) Panaye, A.; MacPhee, J. A.; Dubois, J. E. *Ibid.* **1980**, *36*, 759. (c) Dubois, J. E.; MacPhee, J. A.; Panaye, A. *Ibid.* **1980**, *36*, 919. (d) MacPhee, J. A.; Panaye, A.; Dubois, J. E. *J. Org. Chem.* **1980**, *45*, 1164.
(11) Murrell, J. N.; Randić, M.; Williams, D. R. *Proc. R. Soc.* **1965**, *A284*, 566.
(12) Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1989.
(13) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.
(14) Fujimoto, H.; Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 2670.
(15) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841. (b) Fujimoto, H.; Osamura, Y.; Minato, T. *J. Am. Chem. Soc.* **1978**, *100*, 2954 and the references cited therein.
(16) We assumed here tentatively that the anion attacks at the right angle to the C=O bond (cf. Ann, N. T. *Fortschr. Chem. Forsch.* **1980**, *88*, 145). The O-C bond was taken to be 1.5 Å and the standard values were taken for other bonds and bond angles.

0022-3263/89/1954-2568$01.50/0