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Additivity Parameters for Anodic Peak Potentials in [2.2]Metacyclophanes and Tetrahydropyrene Formation[1)]

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Synopsis. The first anodic peak potentials $E_{pa}(O_1)$ for sixteen [2.2]metacyclophanes were surveyed in order to correlate the peak potential with the number and position of the alkyl groups. The analysis of the data gives the additivity parameters, which call for cathodic shifts of 0.14 and 0.035 V per methyl group for R_2 or R_5 (5- or 13-position) and for substitution at the rest of the positions respectively. The controlled-potential electrolysis of the representative metacyclophanes gave excellent yields of the corresponding tetrahydropyrenes.

The anodic oxidation of [2.2]metacyclophane and derivatives at the first anodic potential $E_{pa}(O_1)$ have previously been shown[2)] to be a highly efficient and selective reaction to give the corresponding 4,5,9,10-tetrahydropyrenes. The current efficiency reached almost 100% as a two-electron process, and the selectivity was far better than the alternative photolytic method.[3)] In this investigation, we surveyed the peak potentials, $E_{pa}(O_1)$, for a series of [2.2]metacyclophanes (**1a**—**1p**) to ascertain the effect of alkyl substitution on the one-electron transfer.

The preparation of **1** was carried out by the pyrolysis of disulfone, **3**, which had been obtained from disulfide, **2**. The cyclic voltammetry was determined in acetonitrile containing 0.1 mol dm^{-3} of Bu_4NClO_4(TBAP) at various scan rates. Of the three anodic peaks, the first peak was found to be sensitive to the impurity contained in acetonitrile. Accordingly, we carried out redeterminations for those compounds the data of which had been reported earlier.[2)]

The data determined at 250 mV/s are shown in Table 1. The inspection of the data revealed the following facts:

Table 1. Observed and calculated peak potentials E_{pa} (O_1) for compound **1**

	R_1	R_2	R_3	R_4	R_5	R_6	$E_{pa}(O_1)$/V	Calcd/V	ΔE_{pa}/V
1a[2a)]	H	H	H	H	H	H	1.37	—	
1b	H	Me	H	H	H	H	1.23	1.23	0
1c[2a)]	H	Me	H	H	Me	H	1.09	1.09	0
1d[2b)]	H	Et	H	H	Et	H	1.07	1.09	−0.02
1e[2b)]	H	*t*-Bu	H	H	*t*-Bu	H	1.08	1.09	−0.01
1f	Me	H	Me	H	H	H	1.32	1.30	+0.02
1g	Me	H	H	Me	H	H	1.33	1.30	+0.03
1h	Me	Me	Me	H	H	H	1.20	1.16	+0.04
1i	Me	H	Me	H	Me	H	1.18	1.16	+0.02
1j[2b)]	Me	H	Me	H	*t*-Bu	H	1.17	1.16	+0.01
1k	Me	Me	Me	H	Me	H	1.03	1.02	+0.01
1l	Me	H	Me	Me	H	Me	1.21	1.23	−0.02
1m	Et	H	Et	Et	H	Et	1.21	1.23	−0.02
1n	*i*-Pr	H	*i*-Pr	*i*-Pr	H	*i*-Pr	1.21	1.23	−0.02
1o	Me	Me	Me	Me	H	Me	1.09	1.09	0
1p	Me	Me	Me	Me	Me	Me	0.96	0.95	+0.01

Table 2. The scan-rate dependence of the peak potential shifts

Scan rate / mV/s	**1a**/V	**1c**/V	ΔE_{pa}/V	**1f**/V	ΔE_{pa}/V	**1i**/V	ΔE_{pa}/V
50	1.32	1.05	−0.27	1.26	−0.06	1.12	−0.20
100	1.34	1.07	−0.27	1.29	−0.05	1.16	−0.18
250	1.37	1.09	−0.28	1.33	−0.04	1.18	−0.19
500	1.40	1.11	−0.29	1.36	−0.04	1.20	−0.20

a) The introduction of a methyl group at the R_2 and/or R_5 positions causes a significant cathodic shift, amounting to −0.14 V per methyl group.

b) On the other hand, a methyl group at other positions (R_1, R_3, R_4, and R_6) causes less of a cathodic shift. The extent of the cathodic shift is normal for alkylated aromatics.[4)] The shift is approximately one-fourth as large as that of R_2 or R_5, namely, −0.07 V for two methyl groups or −0.14 V for four methyl groups. The situation is similar for inner methyl derivatives, **4**, of which C-8, 16 methyl groups show cathodic shifts similar in magnitude to the above.

c) The cathodic shift is essentially similar for ethyl, isopropyl, and *t*-butyl derivatives, as with the corresponding methyl compound.

The predicted E_{pa} values for **1a**—**1p** are shown in Table 1. These were calculated by assuming incremental cathodic-shift changes caused by alkylation on **1a**. Such calculation at the scan of 250 mV/s is derived by means of:

$$E_{pa}(O_1) = 1.37 + m(-0.14) + n(-0.035)$$

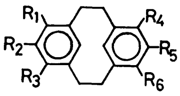
where

m = the number of R_2 and R_5 alkyl groups

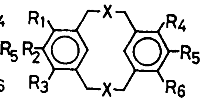
n = the number of alkyl groups other than R_2 and R_5.

For example, the effect of R_2 and R_5 methyl groups in compounds **1b**—**1e** is shown by a large cathodic shift, either by −0.14 or −0.28 V. By contrast, the cathodic shifts for **1f** and **1g** are smaller (−0.07 V). Compounds **1h** and **1i** are isomeric and contain both types of substitution, criterion a) and b), thus resulting in the potential shift of −0.21 V.

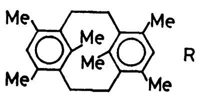
The anomalously large stabilization effect caused by R_2 and R_5 alkyl groups is taken as an indication that the O_1 peak corresponds to the formation of the transannular cation radical, **5**, proposed earlier.[2)]



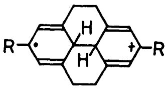
1



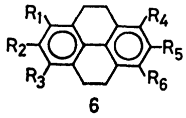
2 X=S
3 X=SO2



4 Epa(O1):1.17 V
250 mV/s



5



6

The peak potentials vary with the scanning rates. Incremental changes caused by alkyl substitution were, however, found to be constant within the usual scan

Table 3. Anodic oxidation of **1** and analytical and melting-point data for **6**

Compound	Oxdn. potential V	Electricity F/mol	Product,a) (%)	Mp °C	Formula	Calcd (%)		Found(%)	
						C	H	C	H
1g	1.34	2.0	**6g**(96)	oil	$C_{18}H_{18}$	92.26	7.74	92.27	7.76
1j	1.21	2.0	**6j** (91)	147—148	$C_{22}H_{26}$	90.98	9.02	91.35	8.97
1k	1.15	2.0	**6k**(92)	118—120	$C_{20}H_{22}$	91.55	8.45	91.88	8.40
1l	1.24	2.0	**6l**b) (85)						
1o	1.24	2.0	**6o**(100)	173—174	$C_{21}H_{24}$	91.25	8.75	91.22	8.76
1p	1.11	2.0	**6p**b)(100)						

a) For substitution pattern see Table 1. b) See Ref. 7.

Table 4. Melting points and analytical data for compounds **1** and **2**

Compound	Mp/°C	Yield/%	Formula	Calcd(%)		Found (%)	
				C	H	C	H
1b	64.5—66	85.0	$C_{17}H_{18}$	91.84	8.16	91.85	8.08
1h	101—101.5	72.5	$C_{19}H_{22}$	91.14	8.86	91.24	8.84
1i	62—63.5	34.5	$C_{19}H_{22}$	91.14	8.86	91.18	8.84
1k	113.5—114.5	64.0	$C_{20}H_{24}$	90.85	9.15	90.71	9.13
1o	197—198	73.0	$C_{21}H_{26}$	90.59	9.41	90.54	9.09
2b	107—108	50.2	$C_{17}H_{18}S_2$	71.28	6.33	71.38	6.37
2h	198—199.5	38.5	$C_{19}H_{22}S_2$	72.56	7.05	72.52	6.91
2i	110.5—112	53.6	$C_{19}H_{22}S_2$	72.56	7.05	72.66	7.04
2k	123—124	63.5	$C_{20}H_{24}S_2$	73.12	7.36	72.86	7.27
2o	195—196	85.5	$C_{21}H_{26}S_2$	73.63	7.65	73.90	7.62

rates. Table 2 shows the scan-rate dependence on $E_{pa}(O_1)$ and the shift differences.

When electrolyzed anodically at the potential of O_1, these [2.2]metacyclophanes gave the corresponding 4,5,9,10-tetrahydropyrenes in high yields (Table 3).

Experimental

The following compounds were prepared as previously reported: **1a**,[2a] **1c**,[2a] **1d**,[2b] **1f**,[5] **1g**,[6] **1j**,[2b] **1l**,[7] **1m**,[7] **1n**,[7] and **1p**.[7] The unsymmetrical [2.2]metacyclophanes, **1b**, **1h**, **1i**, **1k**, and **1o**, were prepared by the pyrolysis of disulfone (**3**), which had been obtained from disulfide (**2**). The physical properties and analytical data of these are summarized in Table 4. As a typical example, the preparation of 4,5,6,12,-14-pentamethyl[2.2]metacyclophane (**1o**) will be described.

5,6,7,14,16-Pentamethyl-2,11-dithia[3.3]metacyclophane (2o). A solution of 1,3-bis(chloromethyl)-4,5,6-trimethylbenzene (3.0 g, 13.8 mmol) in 200 ml of benzene and a solution of 1,3-bis(mercaptomethyl)-4,6-dimethylbenzene (2.74 g, 13.8 mmol) in 200 ml of benzene were added simultaneously and at the same rate to boiling ethanol (1 1) containing sodium hydroxide (1.1 g, 28.3 mmol) under good stirring over the course of 27 h. After a usual work-up,[2c] compound **2o** (4.0 g, 85.5%) was obtained as colorless needles; mp 195—196 °C (from benzene-hexane); ^{1}H NMR ($CDCl_3$) δ 2.10s (3H), 2.19s (6H), 2.24s (6H), 3.80s (8H), 6.62s (1H), and 6.77m (2H).

4,5,6,12,14-Pentamethyl[2.2]metacyclophane (1o) Disulfide **2o** (1.27 g) was oxidized to disulfone **3o** (mp>300 °C), using 30% hydrogen peroxide in acetic acid-benzene. The pyrolysis of **3o** used a vacuum pyrolysis furnace similar to that described by Staab *et al.*[8] at 500 °C. The purification of the sublimate gave **1o** (0.75 g, 73%) as colorless plates; mp 197—198 °C; ^{1}H NMR δ 1.77d (4H), 2.31s (15H), 3.32q (4H), 4.22s (1H), 4.28s (1H), and 7.00s (1H).

The controlled potential electrolysis of (**1**) was carried out as has been described before.[2] A typical run is as follows.

Controlled Potential Electrolysis of 1o. A solution of **1o** (55.7 mg, 0.20 mmol) in acetonitrile (60 ml) containing TBAP (0.1 mol dm^{-3}) was electrolyzed at the O_1 potential supplied from a potentiostat until 38.6 C (2.0 F mol^{-1}) had been consumed. A usual work-up and chromatography (silica gel) gave **6o** (55.0 mg, 99.5%) (mp 168.5—170 °C), which was further purified and recrystallized from hexane, thus yielding analytical samples as colorless needles; mp 173—174 °C; ^{1}H NMR δ 2.29s (15H), 2.78s (8H), and 6.90s (1H).

The physical properties and analytical data of the newly prepared tetrahydropyrenes are listed in Table 3.

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