Synthesis of [2.2]Isoindolinophanes and Dihydro[c]furanophane and Their Charge-Transfer Complexes with π-Acceptors

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Reaction of 4,5,12,13-tetrakis(bromomethyl)[2.2]paracyclophane (6) with methane and *p*-toluenesulfonamide results in formation of dihydrobenzo[*c*]furanophane (4); however the desired isoindolophane 3 was not formed. Formation of 4 was supported by the interaction of 4,5,12,13-tetrakis(hydroxymethyl)[2.2]paracyclophane (2) with *p*-toluenesulfonic acid. On the other hand, interaction of 6 with some aromatic amines gave the corresponding [2.2]isoindolinophane derivatives 8a-f. Charge-transfer complexes of 8a-f (donors) with tetracyanoethylene (TCNE), chloranil (CHL), 2-dicyanomethylene-1,3-indanedione (CNIND), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as π-acceptors have been studied spectrophotometrically.

Until 1951 isoindole (1) was not prepared (*1*). Since that time there have been many reports of successful synthesis of isoindole and its derivatives. 1,2-Bis(bromomethyl)benzenes have served as important starting materials in the synthesis of isoindoles (*2*, *3*). Reaction of 1,2-bis[bromomethyl]-3,4,5,6-tetrachlorobenzene with methanesulfonamide followed by treatment with a base yields the tetrachloroisoindole(*2*). Also, *p*-toluenesulfonyl group can act as a leaving group instead of methanesulfonyl group in the synthesis of isoindole derivatives (*4*).

By analogy, in the present study, it was reasoned that treatment of 4,5,12,13-tetrabromomethyl[2.2]paracyclophane (**6**) (*5*) with methane and *p*-toluenesulfonamide might yield the corresponding methane- and *p*-toluenesulfonyl derivatives **5**, which apparently on treatment with a base bring about elimination reaction to the desired isoindolophane **3**. Actually, only a hitherto unknown reaction product, [2.2](4,7)-1*H*,3*H*-benzo[*c*]furanophane (**4**) was obtained (Figure 1), even though reaction conditions were varied over a wide range. Formation of **4** may be rationalized in terms of nucleophilic attack of the oxygen atom of the sulfonyl group on the carbon atom attached to the bromine atom. The structure of **4** was assigned on the basis of its analytical data and spectroscopic properties (see Experimental Method and Physical Measurements). A further evidence for the establishment of the structure of **4** was emphasized from its synthesis from the reaction of 4,5,12,13-tetrahydroxymethyl[2.2]paracyclophane (**2**) (*6*) with *p*-toluenesulfonic acid under reported conditions (*7*).

Reaction of **6** with different aromatic amines results in formation of the corresponding N-substituted isoindolinophanes **8a-f** (Figure 1) in relatively high yields (Table I). The physical data of isoindolinophanes **8a-f** are listed in Tables I-III.

In contrast, the reaction of **6** with two aliphatic amines (Figure 1) did not afford the expected heterocyclic products; rather open chain products were obtained. This behavior may be attributable to the high electron density of the aryl ring in the aromatic amines (6 π electrons) which in turn enhance the nucleophilic attack of the nitrogen atom on both methylene groups in **6**.

Formation of [2.2]isoindolinophanes **8b** via lithium aluminum hydride reduction of *N*,*N*′-diphenyl[2.2]paracyclophane-4,5,12,13-tetracarboxylic acid bisimide (**9**) (*8*) reinforces the proposed structure of isoindolinophanes **8a-f**.

Experimental Method and Physical Measurements

All melting points are uncorrected. IR spectra were recorded on a Shimadzu-408 spectrophotometer. ^{1}H NMR spectra were measured on Varian T-60 (60 MHz), Bruker 90 (80 MHz), and Varian XL 100 (100 MHz) spectrometers. ^{13}C NMR spectrum was measured on a Varian XL 100 (100 MHz) spectrometer. Mass spectra were made on a Varian MAT CH-7 and MAT 311A spectrometers. UV and visible spectra were made on a Beckman Model 26 and Perkin-Elmer 554 spectrophotometers.

1. Reaction of 4,5,12,13-Tetrakis(bromomethyl)[2.2]paracyclophane (6) with p-Toluenesulfonamide. A mixture of 0.2 g (0.345 mmol) of **6** and 0.118 g (0.69 mmol) of *p*-toluenesulfonamide in 10 mL of dimethylformamide was heated under reflux for 4 h. The reaction mixture was concentrated and allowed to cool at room temperature. The precipitated product was collected and recrystallized from dimethylformamide to yield 0.043 g (43%) of [2.2](4,7)-1*H*,3*H*-benzo[*c*]furanophane (**4**), mp 286-8 °C, as colorless crystals. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 81.75; H, 7.22. IR(KBr, cm^{-1}): 2900-2745 (CH_2); 3040, 1482, 910, 787 (Ar-H7; 1057 (CH_2-O-CH_2). ^{1}H NMR($CDCl_3$, Me_4Si, δ): 2.87 (s, 8 H, 2-CH_2-CH_2); 4.92 (s, 8 H, 4-CH_2); 6.65 (s, 4 H, Ar-H). ^{13}C NMR($CDCl_3$, Me_4Si, δ): C_1(74.37); C_2(132.80); C_3(139.86); C_4(128.28); C_5(30.81). MS (70 eV, *m/e*, rel intensity): 293 (15, M^+ + H), 292 (56, M^+), 277 (23, M^+ - O + H), 264 (28, M^+ -CH_2CH_2), 146 (100, $M^+/2$).

2. Reaction of 6 with Methanesulfonamide. The reaction was carried out as in subsection 1; 0.2 g (0.345 mmol) of **6** and 0.066 g (0.69 mmol) of methanesulfonamide gave 0.038 g (38%) of **4**, mp 286-8 °C. The structure was proved by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample prepared in experiment 3.

3. Reaction of 4,5,12,13-Tetrakis(hydroxymethyl)[2.2]paracyclophane (2) with p-Toluenesulfonic Acid; Formation of 4. To a solution of 0.1 g (0.3 mmol) of **2** in 10 mL of 1,2-dichloroethane was added 10 mL of saturated solution of *p*-toluenesulfonic acid in the same solvent. The mixture was heated at 40-50 °C for 3 h, and then washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent and crystallization of the solid product from dimethylformamide yields 0.03 g (34%) of **4**. The structure of **4** was proved by comparison of its IR and ^{1}H NMR spectra with those of the product of experiment 1.

4. Lithium Aluminum Hydride Reduction of N,N′-Diphenyl[2.2]paracyclophane-4,5,12,13-tetracarboxylic Acid Bisimide (9). A suspension of 0.2 g (0.4 mmol) of **9** and 0.02 g (0.5 mmol) $LiAlH_4$ in 30 mL of absolute tetrahydrofuran was heated under reflux for 6 h. The reaction mixture was cooled to -10 °C and hydrolyzed with dilute hydrochloric acid (2 *N*). The solid product was filtered and washed with water and dried. Recrystallization from dimethylformamide gave 0.085 g (48 %) of *N*,*N*′-diphenyl[2.2](4,7)-isoindolinophane (**8b**). The identity of **8b** was established by mixture melting point and IR deter-

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Table I. Melting Points and Yields of 7a,b and 8a-f

compd[a]	7a	7b	8a	8b	8c	8d	8e	8f
mp, °C	>300	>300	>300	>300	215–216	225–226	>300	>300
yield, %	44	40	71	68	69	57	60	64

[a] All compounds gave satisfactory analytical data.

Table II. ^{1}H NMR and IR Spectra of [2.2]Isoindolinophanes 8a-f

	^{1}H NMR(Me_2SO-d_6, Me_4Si) δ				IR(KBr), cm^{-1}	
compd	Ar–H	CH_2	CH_2CH_2	funct group	CH_2	Ar–H
8a	6.17–6.84 (12 H, m)	4.39 (4 H, br)	2.65–3.25 (12 H, m)		2922, 2800, 1500, 1473	3010, 1600, 806
8b	6.42–7.14 (14 H, m)	4.04 (4 H, br)	2.21–3.23 (12 H, m)		2920, 2800, 1500, 1471	3010, 1600, 865, 750
8c	6.22–7.11 (12 H, m)	4.30 (4 H, br)	2.41–3.22 (12 H, m)	2.35 (6 H, s, CH_3)	2900, 2800, 1490, 1460	1595, 860, 750
8d	6.31–7.11 (12 H, m)	4.25 (4 H, br)	2.38–3.20 (12 H, m)	2.37 (6 H, s, CH_3)	2900–2800, 1490, 1465	3000, 1600
8e	6.29–7.13 (12 H, m)	4.35 (4 H, br)	2.35–3.27 (12 H, m)	2.30 (6 H, s, CH_3)	2950, 2852, 1372	3050, 1511, 804
8f	6.06–7.05 (12 H, m)	4.28 (4 H, br)	2.52–3.15 (12 H, m)	3.71 (6 H, s, OCH_3)	2950–2850, 1480	1518, 817

Table III. Mass Spectra of [2.2]Isoindolinophanes 8a-f

compd	MS (70 eV), *m/e* (rel intensity, %)
8a	512 (9, M^+ + H), 511 (15, M^+), 510 (8, M^+ – H), 255 (100, $M^+/2$), 218 (48, M^+ – CH_2–CH_2–N–C_6H_4–Cl, –CH_2–N–C_6H_4–Cl)
8b	443 (11, M^+ + H), 442 (29, M^+), 441 (7, M^+ – H), 351 (4, M^+ – N–Ph), 221 (100, $M^+/2$), 204 (30, M^+ – 2, Ph–N–$(CH_2)_2$)
8c	471 (16, M^+ + H), 470 (50, M^+), 379 (3, M^+–C_6H_4–CH_3), 364 (4, M^+ – N–C_6H_4–CH_3, –H), 235 (100, $M^+/2$)
8d	471 (7, M^+ + H), 470 (20, M^+), 379 (3, M^+ – C_6H_4–CH_3), 364 (2, M^+ – N–C_6H_4–CH_3, –H), 235 (100, $M^+/2$)
8e	471 (14, M^+ + H), 470 (37, M^+), 440 (24, M^+ – $2CH_3$), 365 (17, M^+ – N–C_6H_4–CH_3), 235 (100, $M^+/2$)
8f	503 (52, M^+ + H), 502 (33, M^+), 50 (84, M^+ – H), 251 (100, $M^+/2$), 232 (21, M^+ – $(CH_2)_2$–N–C_6H_4–OCH_3, –N–C_6H_4–OCH_3)

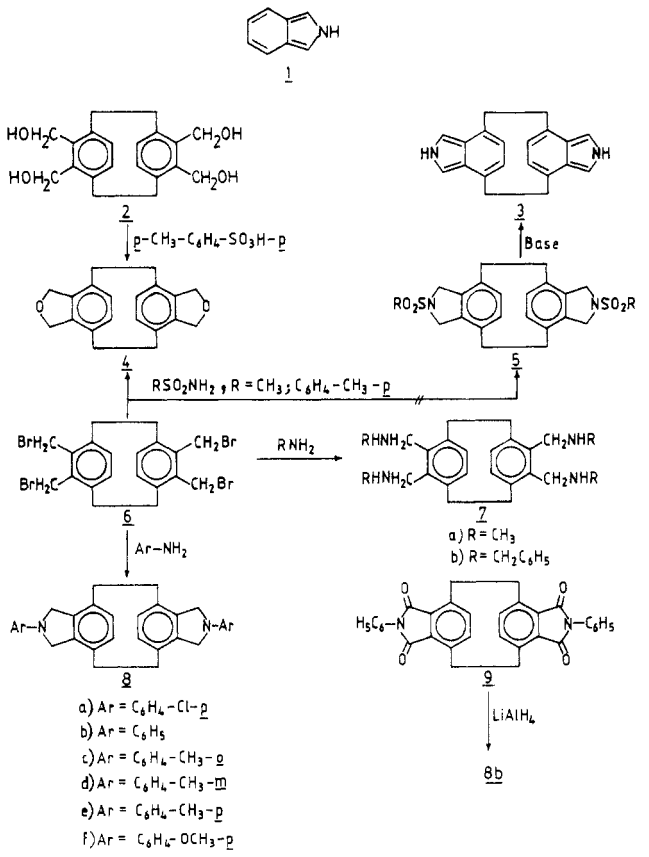

Figure 1.

minations with that prepared in experiment 5.

5. Interaction of 4,5,12,13-Tetrakis(bromomethyl)-[2.2]paracyclophane (6) with Aromatic Amines: Preparation of [2.2]Isoindolinophanes 8a-f; General Procedure. A mixture of 1 g (0.0017 mol) of **6** and the requisite amine (0.0034 mol) in 25 mL of dimethylformamide was heated under reflux for 2 h. The reaction mixture was concentrated and allowed to cool at room temperature. The solid product was collected and dried. Recrystallization from dimethylformamide gave the corresponding [2.2]isoindolinophanes **8a-f**. The physical data are summarized in Tables I–III.

6. Interaction of 6 with Aliphatic Amines. One gram (0.0017 mmol) of **6** was heated under reflux in excess of the aliphatic amine as a solvent for 6 h. The precipitated solid was collected and recrystallized from dimethylformamide to give the corresponding secondary amines (Tables I and IV).

TCNE (Janssen Chimica, Belgium), DDQ, and CHL (Merck, West Germany) were used without further purification. CNIND was prepared from 1,3-indanedione and TCNE according to the published procedure (*9*).

Methylene chloride (Merck) was used as a solvent for all CT complexes studied without further purification.

Table IV. Mass and IR Spectra of 7a and 7b

compd	MS(70 eV), *m/e* (rel intensity)	IR(KBr), cm^{-1}
7a	380 (31, M^+), 318 (36, M^+ – $2CH_3NH_2$), 303 (14, M^+ – $2CH_3NH_2$, –CH_3), 190 (100, $M^+/2$)	2900–2800 (CH_2), 1580, 855 (Ar–H), 3350 (NH)
7b	684 (24, M^+), 470 (17, M^+ – $2PhCH_2NH_2$), 379 (31, M^+ – $2PhCH_2NH_2$, –$PhCH_2$)	2900–2800, 1480, 1450 (CH_2), 1650, 860, 750 (Ar–H), 3400 (NH)

Table V. CT Complexes of [2.2]Isoindolinophanes 8a-f with π-Acceptors

donor	acceptor	λ_{max}, nm	ε, $L \cdot mol^{-1} \cdot cm^{-1}$	*K*, $L \cdot mol^{-1}$	*E*, eV
8a	TCNE	551	525	1.14	2.26
8b	TCNE	560	770	1.41	2.22
8c	TCNE	557	435	1.60	2.23
8d	TCNE	464	475	1.68	2.20
8e	TCNE	575	555	1.69	2.16
8f	TCNE	580	410	1.70	2.14
8b	CNIND	560 (sh)			
8c	CNIND	455 (sh)			
8d	CNIND	640	870	0.77	1.94
8e	CNIND	710	870	0.65	1.75
8f	CNIND	750	830	0.48	1.66
8c	CHL	525 (sh)			
8d	CHL	625	1170	0.57	1.99
8e	CHL	628	1250	0.53	1.98
8f	CHL	500 (sh)			

Association constant (K) values of the CT complexes studied were determined by using the Scott-modified (*10*), Benesi-Hildebrand (*11*) equation for a 1:1 complex

$$\frac{[A]\,[D]l}{d} = \frac{1}{K\epsilon} + \frac{[D]}{\epsilon}$$

where [A] and [D] are the initial molar concentration of the electron acceptor and donor, respectively, l is the optical path length of the cell, d is the optical density of the complex, K is the association constant ($L \cdot mol^{-1}$), and ϵ is the molar extinction coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$).

The wavelengths of maximum absorption, λ_{max}, molar extinction coefficients, ϵ, association constants, K, and transition energies, E, of the charge-transfer complexes of [2.2]isoindolinophanes **8a-f** with π acceptors are listed in Table V.

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Registry No. **2**, 102419-27-2; **4**, 102343-34-0; **8**, 102419-26-1; **7a**, 102343-41-9; **7b**, 102343-42-0; **8a**, 102343-36-2; **8a**·TCNE, 102343-43-1; **8b**, 102343-35-1; **8b**·TCNE, 102343-44-2; **8b**·CNIND, 102343-50-0; **8c**, 102343-37-3; **8c**·TCNE, 102343-45-3; **8c**·CNIND, 102343-51-1; **8c**·CHL, 102343-55-5; **8d**, 102343-38-4; **8d**·TCNE, 102343-46-4; **8d**·CNIND, 102343-52-2; **8d**·CHL, 102343-56-6; **8e**, 102343-39-5; **8e**·TCNE, 102343-47-5; **8e**·CNIND, 102343-53-3; **8e**·CHL, 102343-57-7; **8f**, 102343-40-8; **8f**·TCNE, 102343-48-6; **8f**·CNIND, 102343-54-4; **8f**·CHL, 102343-58-8; **9**, 102419-28-3; p-$ClC_6H_4NH_2$, 106-47-8; $PhNH_2$, 62-53-3; o-$CH_3C_6H_4NH_2$, 95-53-4; m-$CH_3C_6H_4NH_2$, 108-44-1; p-$CH_3C_6H_4NH_2$, 106-49-0; p-$CH_3OC_6H_4NH_2$, 104-94-9; CH_3NH_2, 74-89-5; $PhCH_2NH_2$, 100-46-9; p-toluenesulfonamide, 70-55-3; methanesulfonamide, 3144-09-0.

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The Stobbe Condensation. 5. Reactions of Aryl Aldehydes with α,α-Disubstituted Succinic Esters

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The condensation of some aryl aldehydes (Ia-i) with dimethyl 2,2-dimethylsuccinate gave predominantly the corresponding (*E*)-half-esters (IIIa-i). Hydrolysis of III produced the dibasic acids (V), which were dehydrated to the anhydrides (VI). These were converted to the acids VIII. Cyclization of III revealed the formation of VII or IX, depending on reaction conditions.

The Stobbe condensation of α,α-disubstituted succinic esters with carbonyl compounds has not been thoroughly investigated (*1*, *2*). Thus, dimethyl 2,2-dimethylsuccinate was condensed with benzaldehyde, o-chloro-, m-chloro-, o-methoxy-, and p-methoxybenzaldehydes and 1-naphthaldehyde, as well as thiophene- and 1-methylpyrrole-2-carboxaldehydes (Ia-i), to form almost exclusively the (*E*)-half-esters (III) (cf. Scheme I).

The structure of the half-esters (III) was evident from their spectral data (*3a,b*; *4*) and chemical behavior (cf. Table I and II). Saponification of the half-esters afforded the acids (Vb-i), which were converted to the anhydrides (VIb-i). These anhydrides were also obtained from the half-esters upon treatment with sodium acetate-acetic anhydride mixtures (*5*).

The (*E*) configuration of the half-esters (III) is established by their cyclization under mild conditions (*7*) to the ketonic esters (VII) (cf. Scheme II). It should also be noted that the precursors of these (*E*)-half-esters, the δ-lactones, are free from steric and polar interactions (*6*).

Table I. Infrared and Mass Spectra of Some Representatives of Compounds III-IX

compd	infrared spectra(KBr) ν, cm^{-1}		mass spectra m/e	% of base peak	assign.
IIIc	1710 (s), 1720 (s)	C=O	278	4.44	$M^{\cdot+}$
			174	100	$[C_{12}H_{14}O]^+$
			159	41.76	$[C_{11}H_{11}O]^+$
	2980 (br)	OH	151	38.38	$[C_{10}H_{15}O]^+$
Vc	1685 (s), 1710 (s)	C=O			
	2980 (br)	OH			
VIc	1775 (s), 1820 (s)	C=O			
VIIg	1710 (s), 1745 (s)	C=O	265	8.44	$M^{\cdot+}$
			170	92.06	$[C_{12}H_{10}O]^+$
			142	100	$[C_{10}H_6O]^+$
			141	92.47	$[C_{10}H_5O]^+$
VIIIc	1702 (s), 1710 (s)	C=O	246	25.67	$M^{\cdot+}$
			201	100	$[M\text{-}CO_2H]^+$
	2990 (br)	OH			
IXc	1704 (s), 1775 (s)	C=O	246	94.88	$M^{\cdot+}$
			159	100	$[C_{10}H_7O_2]^+$

Treatment of the anhydrides (VI) with aluminum chloride and cyclization of the produced oxoindenyl acids (VIII) gave the ketonic lactones (IX). These were also obtained by treatment of half-esters (III) with concentrated sulfuric acid under more drastic conditions (*7-9*), to affect isomerization of the inter-

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