Substituent Effects in the Photochemistry of 5-Aryl-3,3-diphenyl-2(3*H*)-furanones. Steady-State and Laser Flash Photolysis Studies[1]

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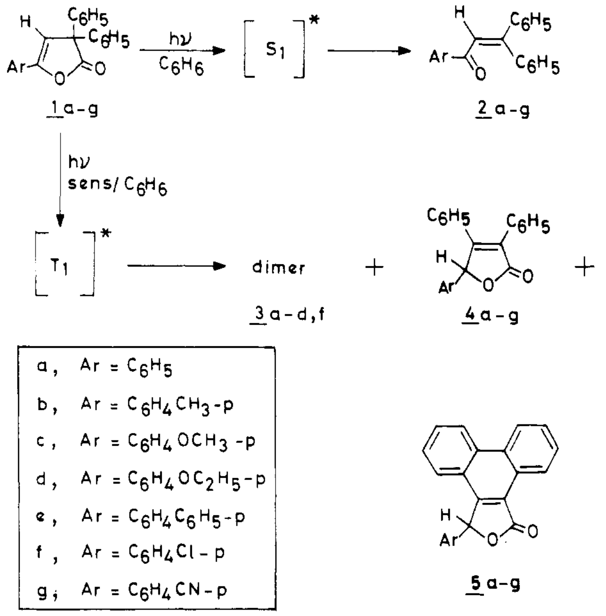
The photochemistry of a series of 5-aryl-3,3-diphenyl-2(3*H*)-furanones, containing electron-releasing as well as electron-withdrawing para substituents on the phenyl group at the C_5 position, has been investigated by steady-state photolysis, product analysis, and laser flash photolysis. While photodecarbonylation to 1-aryl-3,3-diphenylprop-2-en-1-ones dominates in the course of direct photolysis in methanol and benzene, triplet sensitization by *p*-methoxyacetophenone results in $C_3 \rightarrow C_4$ phenyl group migration leading to 5-aryl-3,4-diphenyl-2(5*H*)-furanones and, in certain cases, in the formation of photodimers. Under exhaustive photolysis, the 5(*H*)-furanones undergo electrocyclic reactions to dihydrophenanthrene-type products which, during workup, become oxidized to 3-arylphenanthro[9,10-*c*]furan-1(3*H*)-ones (isolable final products). The laser flash photolysis (337.1 or 355 nm) of aromatic ketones in the presence of 5–20 mM 2(3*H*)-furanones leads to the observation of their triplets (λ_{max}^T = 335–440 nm); data concerning absorption spectra and kinetic behaviors of these triplets are presented. From the observed triplet lifetimes, the phenyl group migration rates are estimated at $\leq 1 \times 10^6$ s^{-1}; apparently, these rates are slowed down by both electron-releasing and electron-withdrawing para substituents on the phenyl group at the C_5 position.

Introduction

In earlier papers, we have described various photochemical and thermal transformations of aryl-substituted 2(3*H*)-furanones.[3] The observed processes include decarbonylation, aryl group migration, fragmentation, electron-transfer-mediated bond cleavage, and rearrangement from [1,3]-sigmatropic shift. Some of these processes have been noted in the earlier studies of unsaturated lactones and related systems.[4] In the present work, we have varied the nature of para substituents on the phenyl group at the C_5 position of a series of 5-aryl-3,3-diphenyl-2(3*H*)-furanones (Scheme I) and examined whether the relative stabilization of the radical and/or carbocation center at the C_5 position by the substituents affects the phenyl group migrating rate in the triplet state.

Scheme I



Results

1. Preparative Photochemistry and Product Identification (Scheme I). Direct photolysis (Rayonet, RPR 3000 Å) of solutions of 2(3*H*)-furanones **1b–g** in benzene gave the decarbonylation products 1-aryl-3,3-diphenylprop-2-en-1-ones **2b–g** in high yields (87–96%). When the photolysis was performed in benzene in the presence of *p*-methoxyacetophenone, rearrangement products resulting from $C_3 \rightarrow C_4$ phenyl group migration (that is, 5-aryl-3,4-diphenyl-2(5*H*)-furanones, **4b–g**) as well as 3-arylphenantrho[9,10-*c*]furan-1(3*H*)-ones **5b–g** were obtained in 12–52% and 9–40% yields, respectively. Photodimers **3b–d,f** were also obtained under sensitized irradiation conditions. Except for the photodimers, the structures of the products were established by spectral data and comparison with authentic samples prepared through well-defined routes. The spectral characterization of the dimers was not possible because of their insolubility in suitable solvents; apparently, these are products of (2 + 2) → 4 reactions from the triplet states of 2(3*H*)- or 2(5*H*)-furanones. Interestingly, while the photosensitized irradiation of **1b** in hexane gave the dimer **3b** (70%) as the major product, that in acetonitrile did not produce even

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Table I. Absorption Spectral Data and Kinetic Properties of Triplets of 5-Aryl-3,3-diphenyl-2(3*H*)-furanones in Benzene at 295 K

substr	λ_{max}^T,[a] nm	ϵ_{max}^T,[b] 10^3 M^{-1} cm^{-1}	τ_T,[c] μs	k_q^T,[d] 10^9 M^{-1} s^{-1}		
				O_2	DMHD	ferrocene
1a[e]	335	13	0.92 (1.03)	1.6	0.98	5.0
1b	350	15	1.4 (1.9)	1.7	0.84	4.5
1c	355	13	1.9 (2.6)	2.2	0.73	4.6
1d	360	14	1.8 (1.8)	2.2	0.73	3.6
1e	440	39	7.7 (17)	1.4	0.40	5.1
1f	350	15	2.1 (2.1)	1.4	0.93	4.2
1g	365	21	3.0 (3.4)	1.1	1.2	5.0

[a] ±5 nm. [b] ±20%. [c] ±15%; the data in the parentheses are in methanol; substrate concentrations were 12.5 mM in benzene and 10 mM in methanol; sensitizers were acetophenone in benzene and *p*-methoxyacetophenone in methanol. [d] ±15%; k_q^Ts for oxygen were calculated from observed triplet decay rate constants in air-saturated and degassed solutions. [e] Data taken from ref 3a,b; τ^T in benzene was obtained from extrapolation to zero substrate concentration.

a trace amount of the dimer.

The sensitized irradiation of **1b** and **1g** in methanol gave only the corresponding methanol addition products **10b** (83%) and **10g** (62%), respectively. Similarly, **1b** in a mixture (9:1) of benzene and methanol gave **10b** (86%) as the only isolable product.

In order to ascertain the intermediacy of the 2(5*H*)-furanones **4b–g** in the formation of the phenanthrofuranones **5b–g** and possibly of the dimers **3b–d,f**, the irradiation of **4b,d** was carried out separately. The direct irradiation of **4b,d** gave the corresponding phenthrofuranones **5b,d** in high yields (83, 91%). The *p*-methoxyacetophenone-sensitized irradiation of **4b**, however, did not yield the dimer **3b**; the phenanthrofuranone **5b** arising through partial absorption of light by **4b** was isolated as the only product (66%). This result suggests that the dimer **3b** originates from the triplet state of **1b**, although its structure and stereochemistry remain undetermined.

2. Laser Flash Photolysis Studies. Upon 308-nm laser flash excitation of benzene solutions of **1b–g**, pronounced absorbance changes are observed at 300–400 nm within nanoseconds of the laser pulse; these show practically no sign of decay over our longest time scale (~150 μs) of observation. Based on their "permanent" nature and their spectral similarity with the difference absorption spectra of the 1-aryl-3,3-diphenylprop-2-en-1-ones **2b–g** vs the corresponding starting substrates **1b–g**, we attribute these spectral changes to prompt two-bond photocleavage resulting in the loss of CO. Employing benzophenone triplet formation in acetonitrile for actinometry ($\phi_T = 1.0$, $\epsilon_{max}^T = 6.5 \times 10^3$ M^{-1} cm^{-1} at 520 nm),[6] and using the ground-state extinction coefficients of the isolated photoproducts **2b–g**, we have determined the quantum yields of decarbonylation (ϕ_P) of **1b–g** in methanol. In these experiments, the solutions were optically matched at the laser excitation wavelength (absorbance = 0.2 at 308 nm in 2-mm cells) and the absorbance changes as a result of laser excitation were noted at 320–330 nm. The photoproduct difference absorption maxima in nm and ϕ_P data are as follows: **1b**: 305, 0.23; **1c**: 315, 0.20; **1d**: 315, 0.21; **1e**: 320, 0.12; **1f**: 305, 0.26; **1g**: 325, 0.10.

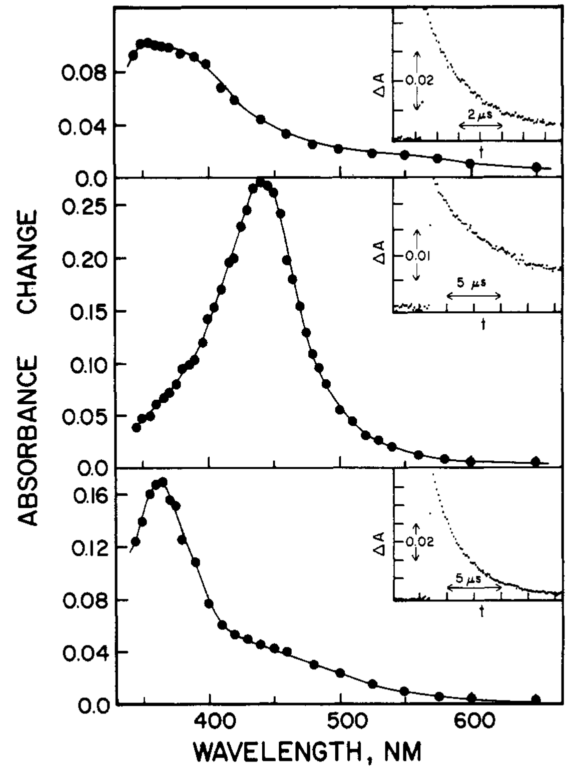

Figure 1. Triplet–triplet absorption spectra of (A) **1c**, (B) **1e**, and (D) **1g** observed at 1.0 μs following 337.1-nm laser flash photolysis of acetophenone (absorbance = 1.0 at 337.1 nm in 2-mm cells) in the presence of 12.5 mM substrates in benzene. The insets show representative decay traces for the triplets of the three systems in benzene.

Transient absorption spectra and decay kinetics attributable to the triplets of **1b–g** were investigated by 337.1-nm laser flash photolysis of acetophenone or *p*-methoxyacetophenone in benzene and methanol in the presence of 10–15 mM **1b–g**. Representative triplet absorption spectra and decay profiles are shown in Figure 1. The data concerning absorption maxima (λ_{max}^T) and lifetimes (τ^T) are compiled in Table I. In a previous study[3b] on related 3,3,5-triaryl-2(3*H*)-furanones, we have shown that the quenching of their triplets by the respective ground states (i.e., self-quenching) is insignificant ($k_{SQ}^T \leq 10^7$ M^{-1} s^{-1} in benzene). This aspect was not pursued in any detail in the present systems.

In order to confirm the triplet identification of the transients, their quenching behaviors toward oxygen, ferrocene, and 2,5-dimethyl-2,4-hexadiene (DMHD) were studied in detail. The bimolecular rate constants for triplet quenching and triplet–triplet extinction coefficients obtained by methods described earlier[3a,b,d] are given in Table I.

3. Triplet Yield Enhancement and Fluorescence Quenching by I⁻. The quantum yields of triplet formation (ϕ_T) are negligible for **1b–g** in methanol and benzene (<1%). However, the triplet formation in the case of **1e** and **1g** is induced by the presence of heavy atoms. Among the 2(3*H*)-furanones **1a–g**, **1e** and **1g** are the only systems

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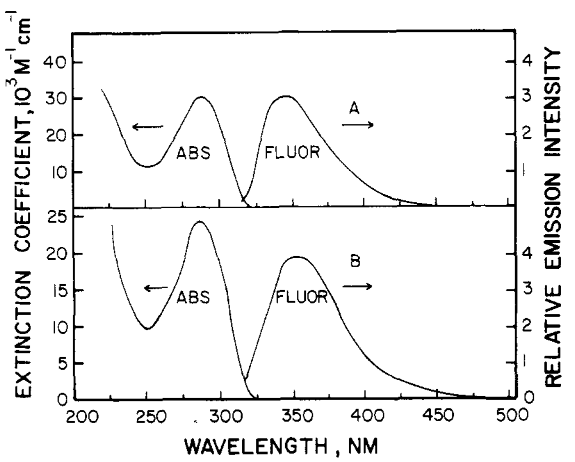


Figure 2. Absorption and fluorescence spectra of (A) **1e** and (B) **1g** in methanol.

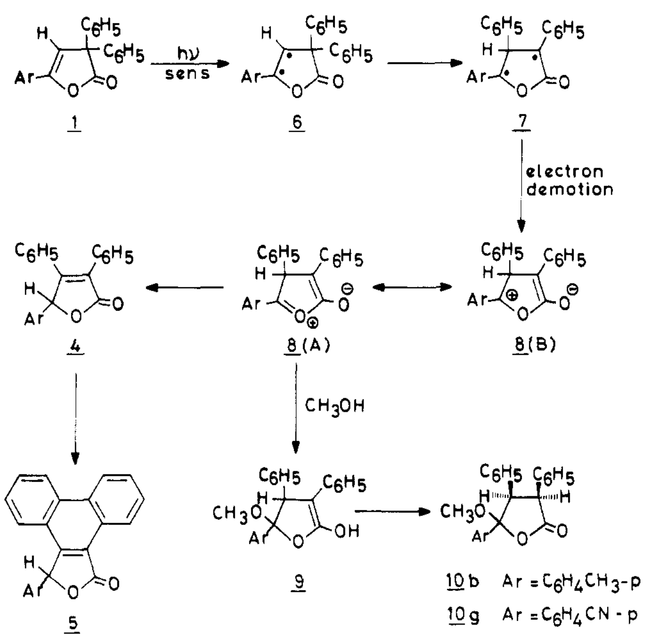
for which weak fluorescence (ϕ_F = 0.009 and 0.014, respectively) is observed under steady-state lamp excitation. The fluorescence spectra in methanol are presented in Figure 2. Upon oxygen saturation, the intensity of fluorescence from a methanolic solution of **1e** remains practically unchanged, while that in the case of **1g** undergoes a small decrease (~8%). On the basis of a typical value of 2×10^{10} M^{-1} s^{-1} for diffusion-controlled singlet quenching by oxygen in methanol,[8] the singlet excited state lifetimes for **1e** and **1g** are estimated to be <0.5 ns.

The effects of varying concentrations of KI (0–0.2 M) on fluorescence intensity (steady-state), triplet yield, and decarbonylation yield of **1e** and **1g** were investigated. From the slopes of linear Stern–Volmer plots for fluorescence quenching, the quenching constants (K_{SV}^F) are estimated to be 1 ± 0.5 and 2 ± 0.5 M^{-1} for **1e** and **1g**, respectively. The absorbance changes (ΔA_T) due to triplets were monitored at 435 and 380 nm for **1e** and **1g**, respectively, following 337.1-nm laser flash photolysis of methanol solutions (absorbance = 0.2 in 2-mm cells at 337.1 nm) containing varying [I^-]. The slope-to-intercept ratios from the double reciprocal plots of $1/\Delta A_T$ vs $1/[I^-]$ gave 2 ± 1 and 3 ± 1 for Stern–Volmer constants (K_{SV}^T) for triplet yield enhancement for **1e** and **1g**, respectively. Similar laser experiments for the decrease of photoproduct absorbance changes at 325–330 nm at increasing [I^-] gave Stern–Volmer constants (K_{SV}^P) for product quenching. K_{SV}^P's were comparable to K_{SV}^F's, except that the experimental errors were much larger for the former. The similarity of the values of K_{SV}^F, K_{SV}^T, and K_{SV}^P suggests that the triplets and the decarbonylation products originate from the same fluorescing states.

Discussion

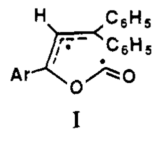
The triplet-mediated photorearrangement of the 2(3*H*)-furanones to 2(5*H*)-furanones can be explained in terms of the pathway shown in Scheme II. The quantum yields of the phenyl group migration processes from the triplet states are necessarily ≤1.0; therefore, the reciprocals of the observed triplet lifetimes represent the upper limits of the migration rates. From the τ_T data in Table I, these limits of migration rates are shown to be in the range (6×10^4) – (1.1×10^6) s^{-1}. Interestingly, compared to the unsubstituted system **1a**, both electron-releasing groups (e.g., *p*-methoxy) and electron-withdrawing groups (e.g., *p*-CN) cause lengthening in triplet lifetimes. The radical center at the C_5 position in the intermediate produced as a result of $C_3 \rightarrow C_4$ phenyl group migration is expected to be stabilized by both electron-withdrawing and -releasing groups at the para position of the phenyl group at this position. Thus, one would expect a resultant enhancement in the migration rate. Since, in practice, we observe a decrease in the observed triplet decay rate upon substitution, we conclude that the enhancement (if any) in the migration rate is more than compensated for by a decrease in the intersystem crossing rate, $T_1 \rightsquigarrow S_0$. It is, however, more plausible that the migration rates are slowed down upon introduction of the para substituents. This is particularly true for **1e**.

Scheme II



The fact that the rate constants for triplet quenching (k_q^T, Table I) by the diene, DMHD, are well below the limit of diffusion control suggests that the triplet energies (E_T) of the 2(3*H*)-furanones are lower than, but close to, E_T of DMHD (59 kcal mol^{-1}).[5] For **1e**, k_q^T by DMHD is significantly smaller; this suggests relatively large lowering in E_T upon *p*-phenyl substitution, which in turn may very well be responsible for the decrease in the phenyl migration rate. Note that the λ_{max}^T and ϵ_{max}^T are also much higher for **1e**, suggesting a pronounced difference in the electronic make-up of its triplet.

The phenyl and cyano groups also lower the efficiency of singlet-mediated decarbonylation (ϕ_P). From the onset of the lowest energy band systems of **1a–g**, no significant variation is noted in their singlet energy (E_S ~89 kcal mol^{-1}). Since the fluorescence and intersystem crossing are both negligible for these systems, the smaller value of ϕ_P must be due to the competing of "nonradiative" processes from the singlet state. The stabilization of the incipient product of initial bond cleavage (biradical I) by the *p*-phenyl or *p*-cyano substituent should render the



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photodecarbonylation process facile for **1e,g**. The experimental observation, contrary to this expectation, suggests that the substituents in question enhance the internal conversion more than the bond cleavage process.

Experimental Section

The equipment and procedures for melting point determination, spectral measurements, solvent purification, laser flash photolysis, and direct/sensitized photolyses are described in previous papers.[3a-e]

Preparation of 5-Aryl-3,3-diphenyl-2(3*H*)-furanones 1b-g. The 5-aryl-3,3-diphenyl-2(3*H*)-furanones **1b**,[10] mp 152–153 °C, **1c**,[11] mp 170–171 °C, and **1e**,[12] mp 193–194 °C, were prepared by the adaptation of the procedure reported for **1a**,[4b,i] mp 120–121 °C. A general procedure[4b,i] for the preparation of **1d,f,g** involved the neat heating of the appropriate 1-aryl-3,4-diphenylbut-2-ene-1,4-diones in glass tubes sealed under nitrogen at 270–280 °C for $^1/_2$ to $^3/_4$ h and workup of the thermolyzate by extraction with chloroform and chromatography over silica gel. The product thus obtained was purified by recrystallization from a mixture (1:3) of chloroform and ethanol.

1d: mp 95–96 °C; IR ν_{max} (KBr) 3080, 3040, 2960, 2900, 2860, (CH), 1770 (C=O), 1630 and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 306 nm (ϵ 6500, sh), 281 (22 700), 267 (17 400, sh), 247 (10 400, sh), 222 (19 600, sh); ^1H NMR ($CDCl_3$) δ 1.50 (3 H, t, J = 7.5 Hz, CH_3), 4.20 (2 H, q, J = 7.5 Hz, CH_2), 6.30 (1 H, s, vinylic) and 7.50 (14 H, m, aromatic).

Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.90; H, 5.62. Found: C, 80.68; H, 5.81.

1f: (76%); mp 173–174 °C;[13] IR ν_{max} (KBr) 3100, 3040, 3020 (CH), 1770 (C=O), 1635 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 299 nm (ϵ 4600, sh), 275 (18 900), 268 (17 800) sh), 261 (15 200, sh), 222 (21 700, sh), 214 (26 900, sh); ^1H NMR ($CDCl_3$) δ 6.30 (1 H, s, vinylic) and 7.50 (14 H, m, aromatic).

Anal. Calcd for $C_{22}H_{15}ClO_2$: C, 76.30; H, 4.34. Found: C, 76.43; H, 4.42.

1g: (78%); mp 188–189 °C; IR ν_{max} (KBr) 3080, 3050, 3010 (CH), 2220 (C≡N), 1790 (C=O), 1650 and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 286 nm (ϵ 24 600), 220 (28 700, sh); ^1H NMR ($CDCl_3$) δ 6.50 (1 H, S, vinylic) and 7.55 (14 H, m, aromatic).

Anal. Calcd for $C_{23}H_{15}NO_2$: C, 81.90; H, 4.45; N, 4.15. Found: C, 82.05; H, 4.50; N, 3.95.

Irradiation of 1a.[3a,b] A benzene solution of **1a** (320 mg, 1 mmol in 200 mL) was irradiated in the presence of *p*-methoxyacetophenone (150 mg, 1 mmol) for 2 h. Workup of the photolyzate yielded 30 mg (9%) of the dimer **3a**, mp >360 °C, 75 mg (23%) of unchanged **1a**, mp 120–121 °C (mixture melting point) (elution with a mixture (1:9) of benzene and petroleum ether and recrystallization from methanol), 30 mg (9%) of the phenanthrofuranone **5a**, mp 259–261 °C (mixture melting point) (elution with a mixutre (1:1) of benzene and petroleum ether and recrystallization from methanol), and 155 mg (48%) of the 2(5*H*)-furanone **4a**, mp 124–125 °C (mixture melting point) (elution with a mixture (7:3) of benzene and petroleum ether and recrystallization from methanol).

3a: IR ν_{max} (KBr) 3060, 3020, 2920 (CH) and 1765 (C=O) cm^{-1}.

Anal. Calcd for $C_{44}H_{32}O_4$: C, 84.62; H, 5.13. Found: C, 84.48; H, 5.27.

Irradiation of 1b. Irradiation (RPR, 300 nm, quartz vessel) of a benzene solution of **1b** (165 mg, 0.5 mmol in 100 mL) for 6 h yielded 140 mg (93%) of the decarbonylated product **2b**, mp 92–93 °C[14] (mixture melting point), after recrystallization from ethanol. In a repeat run, the irradiation of a solution of **1b** and excess piperylene in benzene yielded **2b** in 95% yield. In a separate experiment, a benzene solution of **1b** (325 mg, 1 mmol in 400 mL) was irradiated in the presence of *p*-methoxyacetophenone (150 mg, 1 mmol) for 2 h and worked up to separate 40 mg (12%) of **3b**, mp >360 °C, 75 mg (23%) of unchanged **1b**, mp 152–153 °C (*mixture melting point*) (*elution with a mixture* (1:4) of benzene and petroleum ether), 58 mg (18%) of **5b**, mp 254–255 °C (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from a mixture (1:1) of chloroform and ethanol), and 130 mg (40%) of **4b**, mp 119–120 °C[4e] (mixture melting point) (elution with a mixture (7:3) of benzene and petroleuim ether and recrystallization from ethanol).

3b: IR ν_{max} (KBr) 3020, 2960, 2920 (CH) and 1760 (C=O) cm^{-1}; mass spectrum, m/e (relative intensity) 652 (M$^+$, 1), 326 (100), 207 (48), 178 (73), 119 (80) and other peaks.

Anal. Calcd for $C_{46}H_{36}O_4$: C, 84.66; H, 5.52. Found: C, 84.60; H, 5.12.

5b: IR ν_{max} (KBr) 3040, 3020, 2960, 2910 (CH) and 1750 (C=O) cm^{-1}; UV λ_{max} (CH_3OH) 311 nm (ϵ 5700, sh), 300 (6850), 274 (8400), 256 (29 500), 250 (28 400, sh), 299 (28 600); ^{1} NMR ($CDCl_3$) δ 2.35 (3 H, s, CH_3), 6.70 (1 H, s, CH), 7.60 (10 H, m, aromatic), 8.80 and 9.30 (2 H, m, H^7 and H^8); mass spectrum, m/e (relative intensity 324 (M$^+$, 36), 295 (12), 205 (100), 176 (28), 119 (22) and other peaks.

Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.19; H, 4.94. Found: C, 85.31; H, 5.01.

In separate experiments, solutions of **1b** and *p*-methoxyacetophenone in hexane and acetonitrile were irradiated under analogous conditions. Workup as in the earlier case yielded **3b** (70%), **5b** (11%) and unchanged **1b** (3%) in hexane, and **5b** (31%), **4b** (23%) and unchanged **1b** (29%) in acetonitrile. In yet another experiment, a solution of **1b** (325 mg, 1 mmol) and *p*-methoxyacetophenone (150 mg, 1 mmol) in methanol (200 mL) was irradiated for 4 h. Removal of the solvent under reduced pressure gave 300 mg (83%) of **10b**, mp 126–127 °C, after recrystallization from a mixture (1:4) of benzene and petroleum ether. Similarly, sensitized irradiation of **1b** in a 9:1 benzene/methanol mixture for 4 h gave **10b** (86%) as the only isolable product. Attempted direct photolysis (RPR, 350 nm) of **1b** (325 mg, 1 mmol in 200 mL) in methanol for 5 h and workup of the photolyzate gave 295 mg (91%) of unchanged **1b**.

10b: IR ν_{max} (KBr) 3060, 3030, 2990, 2960, 2940, 2920, (CH), 1775 (C=O) and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 273 nm (ϵ 1900) 238 (18 700, sh), 226 (29 300, sh); ^1H NMR ($CDCl_3$) δ 2.20 (3 H, s, CH_3), 3.20 (3 H, s, OCH_3), 4.25 (1 H, d, J = 8 Hz, CH), 5.00 (1 H, d, J = 8 Hz, CH) and 7.05 (14 H, m, aromatic).

Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.45; H, 6.15. Found: C, 80.81; H, 6.23.

Irradiation of 4b. A benzene solution of **4b** (65 mg, 0.2 mmol in 50 mL) was irradiated for 4 h (RPR, 300 nm). Workup in the usual manner yielded 58 mg (90%) of **5b**, mp 254–255 °C (mixture melting point). In another experiment, the sensitized irradiation of **4b** in benzene for 4 h gave a mixture of **5b** (66%) and unchanged **4b** (25%).

Irradiation of 1c. A solution of **1c** (170 mg, 0.5 mmol) in benzene (100 mL) was irradiated and worked up in the usual manner to yield 150 mg (96%) of **2c**,[15] mp101–102 °C, after recrystallization from ethanol.

2c: IR ν_{max} (KBr) 3060, 3030, 2980, 2950 (CH), 1640 (C=O) and 1595 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 305 nm (ϵ 16 900), 229 (19 800); ^1H NMR ($CDCl_3$) δ 3.85 (3 H, s, OCH_3) and 7.40 (15 H, m, aromatic and vinylic).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.07; H, 5.73. Found: C, 84.35; H, 5.47.

In a separate experiment, a solution of **1c** (350 mg, 1 mmol) and *p*-methoxyacetophenone (150 m, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Workup in the usual manner yielded *120 mg (34%) of* **3c**, *mp >360 °C, 105 mg (30%) of unchanged* **1c**, mp 170–171 °C (mixture melting point) (elution with a mixture (7:3) of benzene and petroleum ether), 30 mg (9%) of **5c**, mp 238–239 °C (elution with a mixture (7:3) of benzene and petroleum ether and recrystallization from a mixture (1:1) of chloroform and ethanol), and 65 mg (19%) of **4c**, mp 112–113 °C[4e] (mixture melting point) (elution with benzene and recrystallization from ethanol).

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3c: IR ν_{max} (KBr) 3060, 3030, 2980, 2840 (CH), 1775 (C=O), 1610 and 1580 (C=C) cm^{-1}; mass spectrum, m/e (relative intensity) 342 ($M^+/2$, 60), 207 (12), 179 (26), 135 (100) and other peaks.

Anal. Calcd for $C_{46}H_{36}O_6$: C, 80.70; H, 5.26. Found: C, 80.60; H, 5.08.

5c: IR ν_{max} (KBr) 3080, 3060, 2960 (CH), 1750 (C=O) and 1600 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 314 nm (ϵ 5900, sh), 301 (6600), 276 (8000), 257 (28 900), 251 (27 600, sh), 237 (31 800); ^{1}H NMR (CDCl$_3$) δ 3.80 (3 H, s, OCH$_3$), 6.67 (1 H, s, CH), 7.40 (10 H, m, aromatic), 8.80 and 9.35 (2 H, m, H^7 and H^8); mass spectrum, *m/e* (relative intensity) 340 (M^+, 52), 311 (14), 205 (100), 177 (33), 176 (35), 135 (80) and other peaks.

Anal. Calcd for $C_{23}H_{16}O_3$: C 81.18; H, 4.71. Found: C, 81.42; H, 4.93

Irradiation of 1d. Direct irradiation of a benzene solution of **1d** (180 mg, 0.5 mmol in 100 mL) followed by workup in the usual manner yielded 155 mg (95%) of **2d**, mp 103–104 °C, after recrystallization from petroleum ether.

2d: IR ν_{max} (KBr) 3040, 3020, 2970, 2920 (CH), 1640 (C=O) 1590 and 1560 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 222 (ϵ 19 600, sh), 247 (10 400, sh), 267 (17 400, sh), 281 (22 700), 306 (6500, sh); ^{1}H NMR (CDCl$_3$) δ 1.40 (2 H, t, J = 7.5 Hz, CH$_3$) 3.95 (2 H, q, J = 7.5 Hz, CH$_2$) and 7.30 (15 H, m, aromatic and vinylic).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.15; H, 6.10. Found: C, 84.38; H, 5.95.

In a separate experiment, a solution of **1d** (355 mg, 1 mmol) and *p*-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Workup of the photolysate in the usual manner gave 215 mg (61%) of the dimer **3d**, mp >360 °C, 35 mg (10%) of unchanged **1d**, mp 95–96 °C (mixture melting point) (elution with a mixture (2:3) of benzene and petroleum ether), 23 mg (6%) of the phenanthrofuranone **5d**, mp 219–220 °C (elution with a mixture (3:2) of benzene and petroleum ether and recrystallization from a mixture (1:4) of chloroform and ethanol), and 43 mg (12%) of the 2(5*H*)-furanone **4d** as a waxy material that could not be crystallized (elution with benzene).

3d: IR ν_{max} (KBr) 3070, 3040, 2980, 2940, 2890, 2840 (CH), 1770 (C=O), 1610 and 1590 (C=C) cm^{-1}; mass spectrum, *m/e* (relative intensity) 711 ($M^+ - 1$, 1), 356 (84), 206 (10), 178 (22), 149 (100), 121 (28) and other peaks.

Anal. Calcd for $C_{48}H_{40}O_6$: C, 80.90; H, 5.62. Found: C, 80.81; H, 5.38.

5d: IR ν_{max} (KBr) 3060, 3030, 2970, 2030 (CH), 1750 (C=O) and 1600 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 314 nm (ϵ 5150, sh), 302 (5850), 275 (7900), 257 (25 800), 251 (23 900, sh), 231 (28 400); ^{1}H NMR (CDCl$_3$) δ 1.40 (3 H, t, J = 7.5 Hz, CH$_3$), 4.03 (2 H, q, J = 7.5 Hz, CH$_2$), 6.63 (1 H, s, CH), 7.73 (10 H, m, aromatic), 8.80 and 9.25 (2 H, m, H^7 and H^8); mass spectrum, *m/e* (relative intensity) 354 (M^+, 73), 325 (17), 205 (100), 176 (33), 149 (100) and other peaks.

Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.36; H, 5.08. Found: C, 81.30; H, 5.00.

4d: IR ν_{max} (thin film) 3060, 2980, 2930, (CH), 1745 (C=O), 1600 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.66 (3 H, t, J = 7.5 Hz, CH$_3$), 3.95 (2 H, q, J = 7.5 Hz, CH$_2$), 6.20 (1 H, s, CH) and 7.25 (14 H, m, aromatic).

Irradiation of 4d. A solution of **4d** (70 mg 0.2 mmol) in benzene (50 mL) was irradiated for 4 h. Removal of the solvent followed by crystallization of the residue from a mixture (1:4) of chloroform and ethanol gave 60 mg (89%) of **5d**, mp 219–220 °C (mixture melting point).

Irradiation of 1e. Irradiation and workup of a solution of **1e** (1.95 mg, 0.5 mmol) in benzene (100 mL) in the usual manner gave 165 mg (92%) of **2e**, mp 121–122 °C, after recrystallization from ethanol.

2e: IR ν_{max} (KBr) 3040, 3020 (CH), 1654 (C=O) and 1590 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 307 nm (ϵ 16 900), 229 (20 600); ^{1}H NMR (CDCl$_3$) δ 7.60 (m, aromatic and vinylic).

Anal. Calcd for $C_{27}H_{20}O$: C, 90.00; H, 5.56. Found: C, 90.30; H, 5.84.

In a separate experiment, a solution of **1e** (390 mg, 1 mmol) and *p*-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 6 h. Workup as in the earlier cases yielded 150 mg (38%) of unchanged **1e**, mp 193–194 °C (mixture melting point) (elution with a mixture (1:4) of benzene and petroleum ether), 155 mg (40%) of **5e**, mp 284–286 C (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from chloroform), and 45 mg (12%) of **4e**, mp 169–170 °C (elution with a mixture (7:3) of benzene and petroleum ether and recrystallization from ethanol).

5e: IR ν_{max} (KBr) 3060, 3020 (CH) and 1750 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 315 nm (ϵ 6000, sh), 301 (7100), 275 (8500), 257 (26 600), 252 (25 900, sh), 233 (28 300); ^{1}H NMR (CDCl$_3$) δ 6.80 (1 H, s, methine), 7.65 (15 H, m, aromatic), 8.85 and 9.35 (2 H, m, H^7 and H^8); mass spectrum, *m/e* (relative intensity) 386 (M^+, 25), 357 (5), 340 (14), 252 (13), 205 (100), 181 (18), 176 (15) and other peaks.

Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.05; H, 4.66. Found: C, 86.63; H, 5.04.

4e: IR ν_{max} (KBr) 3060, 3020 (CH), 1740 (C=O) and 1590 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 269 nm (ϵ 22 200, sh), 245 (25 300); ^{1}H NMR (CDCl$_3$) δ 6.35 (1 H, s, CH) and 7.48 (19 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 388 (M^+, 33), 360 (27), 359 (40), 207 (26), 181 (79), 178 (100), 176 (100), 153 (55) and other peaks.

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.60; H, 5.15. Found: C, 86.75; H, 5.26.

Irradiation of 1f. Direct irradiation of a benzene solution of **1f** (175 mg, 1 mmol in 100 mL) gave 150 mg (94%) of the decarbonylated product **2f**, mp 100–101 °C, after recrystallization from ethanol.

2f: IR ν_{max} (KBr) 3060, 3040 (CH), 1650 (C=O), 1590 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 311 nm (ϵ 11 000), 291 (11 100, sh), 264 (14 300), 231 (15 600, sh); ^{1}H NMR (CDCl$_3$) δ 7.53 (m, aromatic and vinylic).

Anal. Calcd for $C_{21}H_{15}ClO$: 79.25; H, 4.72. Found: C, 79.61; H, 4.51.

In a separate experiment, the sensitized irradiation of **1f** (350 mg, 1 mmol) in benzene (200 mL) followed by workup in the usual manner yielded a mixture of **3f** (30 mg, 9%), mp >360 °C, unchanged **1f** (95 mg, 29%), mp 173–174 °C (mixture melting point) (elution with a mixture (1:4) of benzene and petroleum ether), **5f** (55 mg, 16%), mp 25–256 °C (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from a mixutre (1:1) of chloroform and ethanol), and **4f** (135 mg, 39%), mp 132–133 °C (elution with a mixture (7:3) of benzene and petroleum ether and recrystallization from ethanol).

3f: IR ν_{max} (KBr) 3050, 3020 (CH) and 1765 (C=O) cm^{-1}; mass spectrum, *m/e* (relative intensity) 693 (M^+, 1), 691 ($M^+ - 2$, 1), 346 (80), 207 (68), 179 (100), 139 (23) and other peaks.

Anal. Calcd for $C_{44}H_{30}Cl_2O_4$: C, 76.19; H, 4.33. Found: C, 76.56; H, 4.64.

5f: IR ν_{max} (KBr) 3060, 3020 (CH) and 1750 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 314 nm (ϵ 4500, sh), 301 (5100), 275 (10 900), 257 (22 000), 251 (20 600, sh), 236 (22 100); ^{1}H NMR (CDCl$_3$) δ 6.67 (1 H, s, CH), 7.55 (10 H, m, aromatic), 8.80 and 9.25 (2 H, m, H^7 and H^8); mass spectrum, *m/e* (relative intensity) 344 (M^+, 22), 315 (5), 265 (11), 263 (11), 205 (100), 176 (33), 139 (5) and other peaks.

Anal. Cacld for $C_{22}H_{13}ClO_2$: C, 76.74; H, 3.78. Found: C, 77.06; H, 3.90.

4f: IR ν_{max} (KBr) 3020 (CH), 1570 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 277 nm (ϵ 2500, sh), 264 (25 900), 232 (46 600); ^{1}H NMR (CDCl$_3$) δ 6.33 (1 H, s, CH) and 7.40 (14 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 346 (M^+, 24), 207 (48), 179 (100), 178 (60), 139 (20) and other peaks.

Anal. Calcd for $C_{22}H_{15}ClO_2$: C, 76.30; H, 4.34. Found: C, 76.25; H, 3.98.

Irradiation of 1g. A solution of **1g** (170 mg, 0.5 mmol) in benzene (100 mL) was irradiated for 6 h. Workup of the photolyzate by preparative TLC over silica gel yielded 10 mg (6% of unchanged **1g**, mp 188–189 °C (mixture melting point), and 135 mg (87%) of the decarbonylated product **2g**, mp 141–142 °C, after recrystallization from ethanol.

2g: IR ν_{max} (KBr) 3050, 3020 (CH), 2220 (C≡N), 1650 (C=O), 1600 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH$_3$O) 321 nm (ϵ 9800), 300 (9800), 254 (19 600, sh), 247 (19 900); ^{1}H NMR (CDCl$_3$) δ 7.50 (m, aromatic and vinylic).

Anal. Calcd for $C_{22}H_{15}NO$: C, 85.44; H, 4.85; N, 4.53. Found: C, 85.11; H, 4.63; N, 4.51.

In a separate experiment, a solution of **1g** (340 mg, 1 mmol) and *p*-methoxyacetophenone (155 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Workup in the usual manner yielded 60 mg (18%) of unchanged **1g**, mp 188–189 °C (mixture melting point) (elution with a mixture (1:1) of benzene and petroleum ether), 35 mg (10%) of **5g**, mp 235–236 °C (elution with a mixture (7:3) of benzene and petroleum ether and recrystallization from a mixture (1:1) of chloroform and ethanol), and 177 mg (52%) of **4g**, mp 117–118 °C[4e] (mixture melting point) (elution with benzene and recrystallization from ethanol).

5g: IR $\nu_{\max}$ (KBr) 3060, 3040 (CH) 2240 (C≡N), 1750 (C=O) and 1610 (C=C) cm^{-1}; UV $\nu_{\max}$ (CH_3OH) 313 nm (ϵ 6200, sh), 301 (6750), 275 (8400), 257 (25 800), 251 (23 900, sh), 231 (28 400); ^1H NMR ($CDCl_3$) δ 6.77 (1 H, s, CH), 7.35 (10 H, m, aromatic), 8.85 and 9.30 (H^7 and H^8); mass spectrum, m/e (relative intensity) 335 (M^+, 23), 305 (5), 291 (5), 252 (10), 205 (100), 176 (72) and other peaks.

Anal. Calcd for $C_{23}H_{13}NO_2$: C, 82.39; H, 3.88; N, 4.18. Found: C, 82.01; H, 4.13; N, 4.27.

In another experiment, a solution of **1g** (340 mg, 1 mmol) and *p*-methoxyacetophenone (150 mg, 1 mmol) in methanol was irradiated for 3 h. Workup of the photolyzate in the usual manner yielded 70 mg (31%) of unchanged **1g**, mp 188–189 °C (mixture melting point) (elution with a mixture (1:1) of benzene and petroleum ether), and 230 mg (62%) of **10g**, mp 152–153 C (elution with a mixture (3:2) of benzene and petroleum ether and recrystallization from carbon tetrachloride).

10g: IR $\nu_{\max}$ (KBr) 3060, 3020, 3000, 2930, 2900 (CH), 2215 (C≡N), 1770 (C=O) and 600 (C=C) cm^{-1}; UV $\nu_{\max}$ (CH_3OH) 292 nm (ϵ 2000), 278 (2250), 254 (19 600, sh), 244 (22 800); ^1H NMR ($CDCl_3$) δ 3.25 (3 H, s, OCH_3), 3.30 (1 H, d, J = 8 Hz, CH), 5.07 (1 H, d, J = 8 Hz, CH) and 7.20 (14 H, m, aromatic).

Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.05; H, 5.15; N, 3.79. Found: C, 78.21; H, 5.01; N, 3.93.

Registry No. **1b**, 36165-25-0; **1c**, 1955-40-4; **1d**, 117252-11-6; **1e**, 1955-55-1; **1f**, 87575-49-3; **1g**, 117252-12-7; **2b**, 106552-37-8; **2c**, 24845-42-9; **2d**, 117252-13-8; **2e**, 117252-14-9; **2f**, 106552-38-9; **2g**, 117252-15-0; **4b**, 68727-79-7; **4c**, 56258-96-9; **4d**, 117252-16-1; **4e**, 117252-17-2; **4f**, 117252-18-3; **4g**, 68727-72-0; **5b**, 117252-19-4; **5c**, 117252-20-7; **5d**, 117252-21-8; **5e**, 117252-22-9; **5f**, 117252-23-0; **5g**, 117252-24-1; **10b**, 117252-25-2; **10g**, 117252-26-3; I^-, 20461-54-5; DMHD, 764-13-6; ferrocene, 102-54-5; oxygen, 7782-44-7; *p*-methoxyacetophenone, 100-06-1.

Design of Roof-Shaped Clathrate Hosts.[1] Inclusion Properties and X-ray Crystal Structures of a Free Host and of Inclusion Compounds with 1-BuOH and DMF

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A series of new clathrate hosts characteristic of a roof-shaped molecular backbone and specifically attached functional groups have been synthesized and studied with regard to their inclusion behavior (68 different inclusion species). Formation, stoichiometries, and selectivities of the clathrates depend in a systematic manner on the structural features of the hosts including the number, the nature, the flexibility, and the geometry of functional groups. X-ray structure analyses of two inclusion compounds [**1a**·1-BuOH (1:1), $P\bar{1}$, a = 11.979 (8) Å, b = 10.233 (9) Å, c = 8.974 (6) Å, α = 84.79 (4)°, β = 76.68 (6)°, γ = 68.06 (5)°, Z = 2; and **1a**·DMF (1:1), $P2_1/c$, a = 10.889 (8) Å, b = 9.126 (3) Å, c = 19.005 (13) Å, β = 98.53 (4)°, Z = 4] illustrate that cyclic H bonding between host and guest and dimer clustering of the host molecule play a fundamental role in clathrate binding. The free host **1a** shows infinite H-bonded zigzag chains in its crystal structure [$P\bar{1}$, a = 14.346 (11) Å, b = 12.496 (15) Å, c = 9.432 (6) Å, α = 113.76 (7)°, β = 78.76 (8)°, γ = 107.48 (8)°, Z = 4].

In the last years, the collection of compounds that show the unique property of clathration has increased considerably.[3] Unfortunately, many of these new host molecules have remained individual examples rather than suggesting some structural analogy or fitting in a particular class of substances. They reflect the clathrate chemistry as being rather complex. On the other hand, host compounds having a structural relationship are more conducive to throwing light upon the problem by making a thorough discussion of inclusion properties possible, e.g., based on a designed structural modification.[4,5]

Here we report on such a family of new clathrate hosts whose common feature is a roof-shaped rigid overall structure;[6] we give a demonstration of their inclusion capabilities and support by X-ray crystallographic evidence two isolated inclusion compounds and a free host.

Results and Discussion

Design Strategy. In a former paper we developed the design principle for a new host type called "coordinatoclathrand".[4b,7] The procedure involves a molecule with both a bulky basic skeleton (BS, see Figure 1) and suitably positioned (coordinating) functional groups (FG), i.e., a specific combination of topological and coordinative host–guest interactions in the solid state. Se-

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