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Photochemistry of Fullerenes

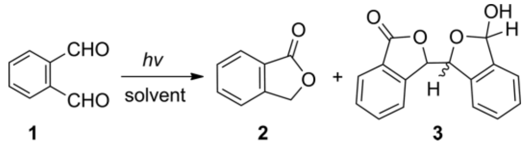
Photochemical Reaction of *o*-Phthalaldehyde with Fullerene C_{60}: The Stimulus for the Phthalide Additions to C_{60}

Manolis D. Tzirakis,*[a] Nikitas G. Malliaros,[a] and Michael Orfanopoulos*[a]

Abstract: A new, simple, and rapid photochemical reaction of *o*-phthalaldehyde with C_{60} has been disclosed. This reaction afforded exclusively the unanticipated C_{60}-phthalide derivative **11** in good yield. The formation of this product is consistent with the intervention of a key free-radical intermediate –a benzylic radical– in the course of the reaction. The structure of **11** has been determined by the combined use of experimental and theoretical NMR studies. In the course of this study we further disclosed a new mode of radical reactivity of C_{60} with a series of substituted phthalides (**2**, **15**–**17**) catalyzed by tetrabutylammonium decatungstate.

Introduction

The photochemical isomerization of *o*-phthalaldehyde (**1**) to phthalide (**2**) and an isomeric mixture of the corresponding dimers (**3**), has been the subject of several studies (Scheme 1).[1–7]



Scheme 1. Photochemical transformation of *o*-phthalaldehyde (**1**) to phthalide (**2**) and its dimer (**3**).

In general, these studies have given prominence to the important role of radical intermediates involved in this transformation (Figure 1). Nonetheless, there is a considerable controversy concerning the exact operating mechanism. Kagan has suggested the intermediacy of biradical intermediate **4** (Figure 1).[1] It was further shown that the relative ratio of **2** to **3** depends largely on the solvent used. For example, chlorinated solvents, such as CCl_4 and $CHCl_3$, favor the formation of **2**, while dimer **3** is favored in heptane or benzene.[1] Harrison et al. have shown that the irradiation of **1** at 77 K leads to the generation of radical intermediates **5** and **6** (Figure 1), which are stable at this low temperature.[3] They further proposed that the observed photochemistry of **1** that leads to **2** and **3** proceeds from the short-lived singlet excited state of **1**.[3] In contrast, Pappas and Blackwell have suggested that the phototransformations of **1** may proceed through the ketene-enol intermediate **7** (Figure 1) which can undergo an intramolecular cyclization to afford **8** (Figure 1), followed by ionic hydrogen transfer to give phthalide **2**.[2] The involvement of **7** has been confirmed by laser flash photolysis studies performed by Scaiano et al.[4] It was shown that the photochemistry of *o*-phthalaldehyde involves an intramolecular hydrogen transfer of two isomeric triplet states of **1** to afford a 1,4-biradical **9** (Figure 1), which then decays to an isomeric mixture of enols (*E*- and *Z*-**7**).[4] These enols revert back to **1** quite efficiently, and it was proposed that the formation of **2** and **3** should arise from an independent reaction pathway that involves the intermediacy of cyclic enol **10** (Figure 1). The suggested ketene-enol (**7**) involved in the decay of biradical **9** (from *o*-phthalaldehyde) has been further characterized by IR matrix-isolation spectroscopy.[5,6]

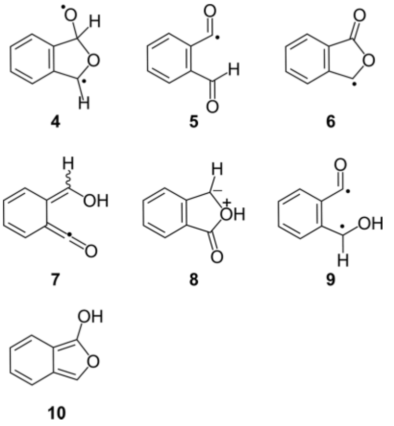


Figure 1. Suggested intermediate species **4**–**10** involved in the photochemical transformation of *o*-phthalaldehyde (**1**) to phthalide (**2**).

The aim of the present study was to investigate the photochemical reaction of **1** in the presence of [60]fullerene. We envisioned that C_{60} –a well-known radical scavenger–[8] would react promptly with the free-radical intermediates formed upon irradiation of *o*-phthalaldehyde, especially with acyl radical **5** as shown in a previous study that regards the prompt reactivity of C_{60} towards acyl radicals (Figure 1).[9] This reaction not only provides new evidence on the intermediate species involved in

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[a] *Department of Chemistry, University of Crete*
Voutes Campus, 71003, Heraklion, Crete, Greece
E-mail: tzirakis@chemistry.uoc.gr
morfanop@uoc.gr

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the photochemical transformation of **1**[1–7] but, at the same time, also provide a novel synthetic route for the functionalization of [60]fullerene and access to new nanostructures with potentially interesting properties.

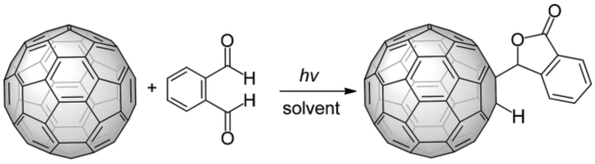
Results and Discussion

At the onset of our studies we investigated the reaction of C_{60} (20 mg, 0.028 mmol) with **1** by simply irradiating a solution of C_{60} with 15 equiv. of **1** in chlorobenzene (65 mL), using a 300 W Xenon lamp (Table 1, entry 1) at 5 °C. The reaction was followed by HPLC analysis of aliquots taken at varying time intervals. Under these conditions, the unanticipated monofunctionalized fullerene derivative **11** was detected by HPLC in 12 % yield after 6 min of irradiation. The reaction was greatly accelerated by using additional equivalents of **1** (Table 1, entries 2–3). Also, in contrast to C_6H_6 which did not alter the outcome of the reaction (Table 1, entry 4), the addition of CH_3CN as a polar cosolvent increased considerably the rate of the reaction (Table 1, entry 5), thus signifying the intermediacy of a polar transient species in the reaction mechanism. We further confirmed that the reaction proceeds efficiently also in ambient diffuse sunlight to afford **11** in 43 % isolated yield (Table 1, entries 7–8).

Control experiments showed that no reaction occurred in the absence of light for several hours. In addition, irradiation of **1** in the absence of C_{60} in chlorobenzene, benzene or a mixture of chlorobenzene/CH_3CN (85:15) solution afforded quantitatively phthalide **2** (see Experimental Section).

The structural assignment of **11** was deduced from the combined use of $^1H/^{13}C$ NMR, UV/Vis and FTIR spectroscopy, as well as from mass spectrometry [see the Experimental Section and Supporting Information (SI)]. Additional evidence for the proposed structure of **11** was obtained from the correlation between the DFT-calculated (δ_{calcd}; ppm) and experimental (δ_{expt}; ppm) ^1H and ^{13}C NMR chemical shifts (Table 2). All calculations were performed using the GAUSSIAN 09 package.[10] The ener-

Table 1. Reaction of C_{60} with **1**.[a]



1 **11**

Entry	Equiv. of **1**	Solvent	Irradiation time	Yield[%][b,c]
1	15	C_6H_5Cl	6 min	12
2	50	C_6H_5Cl	6 min	30 (19)
3	100	C_6H_5Cl	3 min	30 (21)
4	50	C_6H_6	6 min	30
5	50	C_6H_5Cl/CH_3CN (85:15)	3 min	33
6	100	C_6H_5Cl/CH_3CN (85:15)	3 min	56
7[d]	50	C_6H_5Cl/CH_3CN (85:15)	21 h	38
			72 h	55 (43)
8[d]	100	C_6H_5Cl/CH_3CN (85:15)	21 h	47 (33)

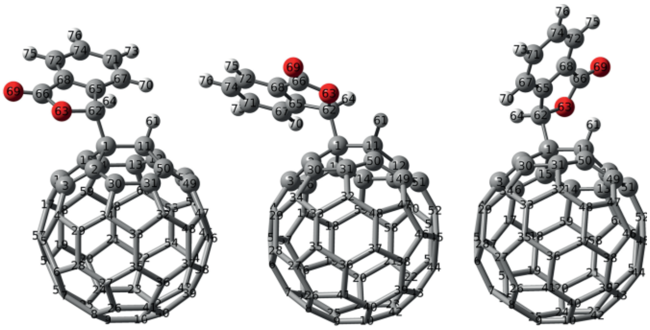
[a] For experimental details see the Experimental Section. [b] Yield based on integration of HPLC peaks. [c] Numbers in parentheses correspond to isolated yield. [d] The reaction was carried out with exposure to ambient light in 30 mL of solvent.

Table 2. Calculated [δ_{calcd}; ppm; B3LYP/6-311+G(2d,p)] and experimental (δ_{expt}, in ppm) ^1H and ^{13}C chemical shift values of **11** in chloroform.

Atom[a]	δ_{expt}[b]	δ_{calcd}[c]	$\lvert\delta_{calcd} - \delta_{expt}\rvert$	Atom[a]	δ_{expt}[b]	δ_{calcd}[d]	$\lvert\delta_{calcd} - \delta_{expt}\rvert$
C(1)	68.33	69.01	0.68	H(61)	6.31	6.45	0.14
C(11)	55.75	57.02	1.27	H(64)	7.16	6.76	0.40
C(62)	87.18	84.62	2.56	H(70)	8.27	8.42	0.15
C(66)	169.80	172.21	2.41	H(73)	7.95	7.87	0.08
C(67)	124.70	124.00	0.70	H(75)	8.26	8.55	0.29
C(71)	135.02	133.32	1.70	H(76)	7.83	7.72	0.11
C(72)	126.85	125.12	1.73			MAE[e] = 0.195	
C(74)	131.02	128.82	2.20				
		MAE[e] = 1.6563					

[a] All atoms are numbered according to the numbering system introduced in Figure 2. [b] NMR spectra were recorded on a 500 MHz spectrometer, in $CDCl_3$ at 25 °C. [c] Chemical shifts were derived from application of scaling factors (slope = –0.9854, intercept = 173.92) to the ^{13}C NMR shielding tensors computed at the B3LYP/6-311+G(2d,p) level of theory, followed by Boltzmann averaging over all three conformers at 298 K (further details are provided in the Experimental Section). [d] Chemical shifts were derived from application of scaling factors (slope = –0.5899, intercept = 28.358) to the ^1H NMR shielding tensors computed at the B3LYP/6-311+G(2d,p) level of theory, followed by Boltzmann averaging over all three conformers at 298 K (further details are provided in the Experimental Section). [e] MAE is defined as the sum of the absolute errors ($\Sigma\lvert\delta_{calcd} - \delta_{expt}\rvert$) divided by the total number (n) of chemical shifts values included in the comparison; $MAE=\Sigma\lvert\delta_{calcd} - \delta_{expt}\rvert/n$.

gies and optimal geometries of the three low-energy conformational isomers **11a**–**c** (rotation around the C1–C62 bond) were first determined at a higher level of theory, using the two-layer ONIOM [M06-2X/6-31+G(d,p):HF/3-21G] approach and implicit solvation in $CHCl_3$ (IEFPCM) (Figure 2; see also Section 7/Figure S25 in SI). At this level of theory, **11b** was found to be the lowest energy hence most highly populated conformer (Figure 2).



11a $\Delta G = 1.3$ kcal mol^{-1} 8.0%

11b $\Delta G = 0$ kcal mol^{-1} 68.0%

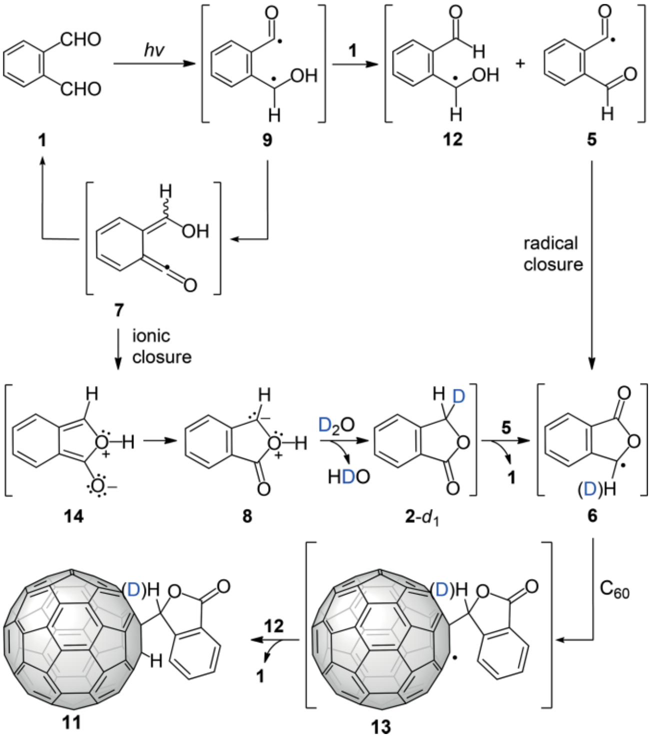
11c $\Delta G = 0.6$ kcal mol^{-1} 24.0%

Figure 2. Optimized geometries, relative Gibbs free energies (ΔG in kcal mol^{-1}) and calculated Boltzmann populations (%) calculated thereof, for the three low-energy conformers of **11**; geometry optimizations and energy calculations were carried out at the ONIOM2[M06-2X/6-31+G(d,p):HF/3-21G] [IEFPCM-chloroform] level of theory (298.15 K). The atoms treated at a high level in the ONIOM approach are shown in ball and stick representation, while the lower level atoms are represented in tube model. This figure also shows the numbering system adopted in the present work for identifying the relevant C- and H-atoms. Color code: white = H; gray = C; red = O. Cartesian coordinates and energies of all three conformers considered in our GIAO NMR calculations are provided in SI (Tables S4–S6).

Then, the NMR shielding tensors (σ; ppm) for each conformer were computed at the B3LYP/6-311+G(2d,p) level of theory using the gauge-including atomic orbital (GIAO) method in chloroform (IEFPCM solvation model). The computed set of isotropic magnetic shielding tensor values (σ_{iso}; ppm) for each nucleus in all conformers were scaled, referenced, and averaged (using the mole fraction of each conformation), to generate a set of Boltzmann-weighted average chemical shifts (δ_{calcd}; ppm) (Table 2). The mean absolute errors (MAEs) between the experimental and computed chemical shifts associated with each nucleus type (i.e. ^{1}H and ^{13}C) of **11** are given in the last row of Table 2. A perusal of this table indicates a good agreement between the experimental and the computed ^{1}H and ^{13}C chemical shifts (δ_{expt} vs. δ_{calcd}), which further supports the assigned structure of **11**. Full details on the computational methods, as well as the optimized geometries and energies of all three conformers of **11** are provided in the Experimental Section and SI (Tables S4–S6), respectively.

The reaction mechanism was next investigated by performing deuterium-labeling experiments. Initially, we performed the photocatalyzed reaction of **1** with C_{60} in a 85:15 mixture of C_6H_5Cl/CH_3CN containing 0.08 % D_2O. A significant percentage of deuterium incorporation (ca. 30 %) at the C(62) carbon atom of **11** was observed by ^{1}H NMR spectroscopy (Figure S22 in SI). Apparently, this result suggests that the reaction mechanism involves the intermediacy of a carbanionic species which can be effectively trapped by D_2O. To further probe this mechanistic hypothesis, we carried out the photochemical transformation of **1** in the presence of 0.08 % D_2O without adding C_{60}. Not surprisingly, deuterium incorporation was again observed at the same C-atom affording a mixture of **2**-*d*$_0$/**2**-*d*$_1$ in a ratio of ca. 70:30 (Figures S23–S24 in SI).

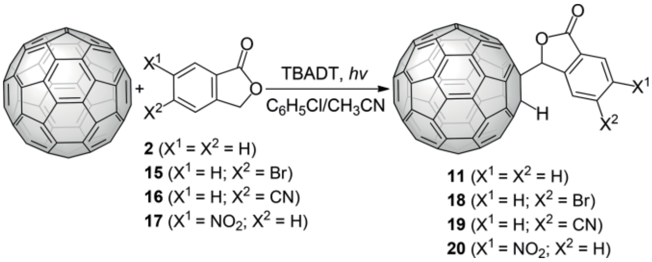
Scheme 2 depicts a plausible mechanistic scenario for the photochemical reaction of **1** with C_{60}, consistent with the experimental evidences described above and the preceding literature. The first step involves an intramolecular hydrogen atom transfer (HAT) by the triplet excited state of **1**. The resulting 1,4-biradical **9** can either (i) decay to intermediate ketene-enol **7** and revert back to **1**,[4] or (ii) react intermolecularly with **1** via a HAT process to afford radical intermediates **5** and **12**.[3] Acyl radical **5** rearranges to radical intermediate **6**, which is subsequently trapped by C_{60} to afford the final product **11** upon coupling with a H-atom derived from **12**. In another possible route, **7** undergoes intramolecular ionic closure to afford **14** which, in turn, rearranges to **8** and subsequently to **2** via an ionic hydrogen transfer.[2] In consistence with the mechanistic experiments described above, the presence of deuterated water in this latter step can result in the formation of deuterated phthalide, **2**-*d*$_1$. Phthalide **2** can subsequently enter the pathway of radical addition to C_{60} via a HAT process catalyzed by **5**. The significant increase of the reaction rate induced by the addition of CH_3CN as a polar co-solvent (Table 1, entries 5–6) further supports the intermediacy of polar transient species, i.e. **8** and **14**, in the reaction mechanism.



Scheme 2. Proposed mechanism for the photochemical reaction of **1** with fullerene C_{60}.

Next, in an attempt to provide solid experimental evidence for the suggested structure of **11**, we sought to access it from different synthetic pathways. We envisioned that structure **11** can result from the reaction of C_{60} with phthalide (**2**) in the presence of tetrabutylammonium decatungstate [TBADT, $(nBu_4N)_4W_{10}O_{32}$] through a Hydrogen Atom Transfer (HAT) mechanism (Table 3, entry 1). TBADT is a well-established photocatalyst for C–H bond activation in several classes of organic compounds.[11] For example, we have shown that TBADT can activate the benzylic C–H bond in toluenes[12] and also the α-C–H bond in ethers[13] to afford the corresponding C-centered radicals that can be effectively trapped by C_{60} and give the respective mono-functionalized hydrofullerenes in moderate to good yields. We therefore envisaged that TBADT can activate the benzylic C–H bond in **2** to afford the anticipated radical addition adduct of C_{60}, viz. **11**. To our delight this was indeed the case and product **11** was isolated in 20 % yield (see Experimental Section). This result not only provides further evidence in support of the structure suggested for the product obtained from the reaction of C_{60} with **1** (Table 1), but also constitutes a new synthetic example for the employment of TBADT catalysis in fullerene chemistry.[9,12–14] The scope of this new TBADT-catalyzed reaction was further explored by studying the reaction of C_{60} with three commercially available phthalides, namely 5-bromophthalide (**15**), 5-cyanophthalide (**16**), and 6-nitrophthalide (**17**) (Table 3, entries 2–4). Indeed, following the previous photocatalytic procedure, the corresponding radical intermediates were efficiently trapped by C_{60} to yield selectively the monofunctionalized fullerene derivatives **18**–**20**, respectively, in decent isolated yields (and almost quantitative recovery of unreacted C_{60}), thus validating the versatility and efficiency of this method.

Table 3. TBADT-catalyzed reaction of C_{60} with phthalide **2** and **15**–**17**.[a]

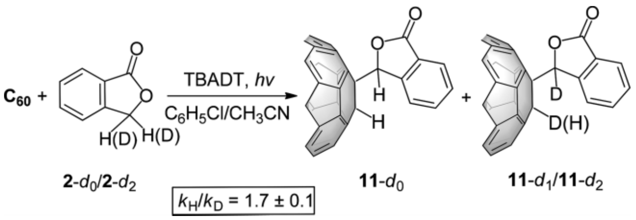


Entry	Substrate	Product	Irradiation time	Isolated yield [%]
1	**2**	**11**	1.5 h	20
2	**15**	**18**	3.5 h	15
3	**16**	**19**	4 h	17
4	**17**	**20**	1.5 h	14

[a] For experimental details see the Experimental Section.

To probe the mechanism of this reaction and obtain information on the extent of bond breaking we measured the primary intermolecular kinetic isotope effect (KIE) in the reaction of C_{60} with an equimolar mixture of phthalide-d_0 (**2**-d_0) and phthalide-d_2 (**2**-d_2) (Scheme 3; see also Figures S20–S21 in SI). This reaction was performed similarly with those described previously in this work (Table 3), using a 40-fold excess of **2**-d_0/**2**-d_2.

The ratio of products **11**-d_0 and **11**-d_1/**11**-d_2, which is the result of an intermolecular isotopic competition between the methylene $-CH_2-$ and $-CD_2-$ groups in **2**-d_0/**2**-d_2, is proportional to the primary isotope effect of k_H/k_D. ^1H NMR of the methine CH signal of **11**-d_0 as well as the phenyl hydrogens of both **11**-d_0 and **11**-d_1/**11**-d_2, determined the primary isotope effect $k_H/k_D = 1.7 \pm 0.1$ (Scheme 3; see also Figure S21 in SI). This substantial primary KIE indicates an extensive C–H(D) bond breaking in the transition state of the first slow radical forming step. Another important finding from this experiment concerns the source of the fullerenyl hydrogen. The adduct **11**-d_1 is partially deuterated (24 % D incorporation on the fullerene cage), which indicates, in consistence to the mechanism proposed in our previous studies,[9,12–14] that the intermediate C_{60} anion is mainly trapped by a proton originated from the residual moisture in the reaction mixture.



Scheme 3. Intermolecular primary KIE in the TBADT-mediated reaction of **2**-d_0/**2**-d_2 with C_{60}.

Conclusions

We disclosed a new mode of radical reactivity of C_{60}, which involves the photochemical addition of *o*-phthalaldehyde (**1**) to C_{60}. This simple and rapid reaction affords exclusively the unanticipated C_{60}-phthalide derivative **11** in good yield. The formation of this product is consistent with the intervention of a key free-radical intermediate in the course of the reaction, which is further supported by our mechanistic studies. The observed single addition of radicals to C_{60} is of particular interest, given the well-established high affinity of C_{60} (a "radical sponge") with free radicals,[8] which generally results in multiple radical additions, hence a difficult to separate mixture of multi-adducts. Thus, the present reaction is an excellent example concerning the isolation and characterization of C_{60} monoadduct via a single radical addition, especially in good yield and high purity. The structure of **11** has been determined by the combined use of experimental and theoretical NMR studies.

In the course of this study, we further disclosed a new mode of radical reactivity of C_{60} with a series of substituted phthalides catalyzed by tetrabutylammonium decatungstate (TBADT). The operating mechanism for this latter reaction was investigated by determining the intermolecular kinetic isotopic effect of the reaction of C_{60} with **2**-d_0/**2**-d_2. The presence of a normal isotope effect ($k_H/k_D = 1.7 \pm 0.1$) shows that the rate-determining step of the reaction is the cleavage of the C–H or C–D bond as similarly found in our previous reactions on the TBADT-catalyzed reaction of C_{60} with different substrates.[9,11–14] This latter reaction expands further the synthetic utility of TBADT catalyst in fullerene functionalization chemistry by providing a new route to previously unexplored fullerene-based structures.

Experimental Section

General: Reagents and solvents were purchased in *reagent grade* quality from Fluka, Merck, and Sigma-Aldrich and used without further purification. Tetrabutylammonium decatungstate (TBADT) was prepared according to procedure reported in the literature.[15] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-500 MHz (125 MHz for ^{13}C) spectrometer in $CDCl_3$ solutions.

Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane using the residual deuterated solvent signals as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). For ^{1}H NMR, coupling constants *J* are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). All spectra were recorded at 25 °C. UV/Vis spectra were performed on a Shimadzu MultiSpec-1501 UV/Visible spectrometer. HPLC analysis was conducted on a Marathon III instrument equipped with a 5C18-MS (4.6 × 250 mm, Nacalai Tesque) reversed phase column with detection at 310 nm. A mixture of toluene/acetonitrile (1:1 v/v) was used as eluent at 1 mL/min flow rate. Flash column chromatography was carried out on SiO_2 (silica gel 60, SDS, 230–400 mesh ASTM) by applying an overpressure of 0.1–0.6 bar. Evaporation of the solvents was accomplished with a rotary evaporator or by high vacuum distillation. Photochemical reactions were carried out by using a 300-W xenon lamp as the light source. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer (ATR, Golden Gate) and values are reported as wavenumbers (cm^{-1}) with band intensities indicated as: s (strong), m (medium), and w (weak).

Experimental Procedures and Spectroscopic Data

Photochemical Reaction of C_{60} with 1: In a typical experiment, a solution of C_{60} (20 mg, 0.028 mmol) in 65 mL of solvent (C_6H_5Cl) was added in a 100-mL glass flask followed by addition of 50 equiv. *o*-phthalaldehyde (188 mg, 1.4 mmol). The resulting solution was septum capped and deoxygenated in the absence of light by purging with argon for 20 min. This solution was subsequently irradiated for 6 min with a 300 W Xenon lamp at 5–10 °C using an ice water bath. A constant, slow argon stream was maintained over the solution. The progress of all reactions was monitored by HPLC. The solvent was distilled from the reaction mixture under reduced pressure, and the remaining crude product was centrifuged three times with acetonitrile HPLC grade to remove excess *o*-phthalaldehyde. The isolated product was further purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **11** in 19 % yield (4.5 mg, 0.0053 mmol).

11: IR (KBr): $\tilde{\nu}$ = 1775 (s), 1720 (w), 1702 (w), 1688 (w), 1655 (m), 1638 (w), 1618 (w), 1561 (m), 1543.3 (w), 1499 (w), 1509 (w), 1459 (m), 1439 (w), 1261 (s), 1015 (s), 800 (s), 527 (s) cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (nm) = 326, 405, 433; ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H = 8.26 (2H, m), 7.95 (1H, m), 7.83 (1H, m), 7.16 (1H, s), 6.31 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ_C = 169.80, 152.97, 152.57, 151.05, 149.18, 147.80, 147.52, 146.95, 146.92, 146.83, 146.79, 146.77, 146.65, 146.61, 146.52, 146.50, 146.48, 146.44, 146.42, 146.11, 146.06, 146.01, 145.83, 145.77, 145.66, 145.59, 145.58, 145.00, 144.97, 144.66, 144.47, 143.47, 143.40, 143.25, 142.89, 142.85, 142.80, 142.53, 142.46, 142.35, 142.31, 142.22, 142.16, 141.93, 141.90, 141.81, 141.76, 141.74, 141.55, 140.63, 140.62, 140.16, 140.11, 138.51, 137.85, 136.41, 136.06, 135.02, 131.02, 128.36, 126.85, 124.70, 87.18, 68.33, 55.75 ppm; HR-MALDI-MS (DCTB): *m/z* (%): 856.0424 (18), 855.0393 (48), 854.0361 (67, M^+, calcd. for $C_{68}H_6O_2^+$: 854.0362), 721.0073 (100, $C_{60}H^+$, calcd. for $C_{60}H^+$: 721.0073).

Photochemical Reaction of C_{60} with 1 at Ambient Light: In a typical experiment, a solution of C_{60} (20 mg, 0.028 mmol) in 30 mL of chlorobenzene/acetonitrile (85:15) was added in a 50-mL glass flask followed by addition of 50 equiv. *o*-phthalaldehyde (190 mg, 1.4 mmol). The resulting mixture was septum capped and deposited on the lab bench next to the window exposed to ambient, diffused sunlight. The progress of the reaction was monitored by HPLC. After 72 hours the solvent was distilled from the reaction mixture under reduced pressure, and the remaining crude product was centrifuged three times with acetonitrile HPLC grade to remove excess *o*-phthalaldehyde. The isolated product was further purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **11** in 43 % isolated yield (10.2 mg; 0.012 mmol), C_{60} (2 mg; 0.0028 mmol), and a small amount of a complex mixture of several unidentified by-products.

Photochemical Isomerization of 1 to 2: A solution of *o*-phthalaldehyde **1** (200 mg, 1.49 mmol) in 70 mL of solvent (C_6H_5Cl, or $CHCl_3$, or C_6H_6, or chlorobenzene/acetonitrile, 85:15) was added in a 100-mL glass flask. The resulting solution was septum capped, purged for 20 min with argon, and was subsequently irradiated with a 300 W Xenon lamp at 5–10 °C using an ice water bath. A constant, slow argon stream was maintained over the solution. The progress of all reactions was monitored by NMR. The irradiation time was varied from 25 min ($CHCl_3$) to 40 min (C_6H_5Cl/CH_3CN, C_6H_5Cl, C_6H_6). Then, the solvent was distilled from the reaction mixture under reduced pressure to afford substantially pure **2** as a white solid. The identity of **2** was confirmed by comparison with a commercial sample.

Phthalide (2): R_f = 0.3 (SiO_2; hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H = 5.33 (2H, s), 7.49–7.56 (2H, m), 7.67–7.69 (1H, m), 7.94 (1H, d, $^{3}J_{HH}$ = 8 Hz), 4.88 (1H, m), 5.43 (1H, dd, $^{3}J_{HH}$ 8.4, 15.0 Hz), 5.79 (1H, d, $^{3}J_{HH}$ 11.0 Hz), 6.45 (1H, dd, $^{3}J_{HH}$ 11.0, 15.0 Hz), 7.46–7.24 (10H, m) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ_C = 69.79, 122.22, 125.93, 125.97, 129.20, 134.15, 146.66, 171.24 ppm.

General Photocatalytic Procedure for the TBADT-Mediated Photochemical Reaction of C_{60} with Phthalides (2, 15, 16, or 17): A solution of C_{60} (20 mg, 0.028 mmol) in 65 mL of chlorobenzene/acetonitrile (85:15) was added in a 100-mL glass flask followed by addition of 100 equiv. phthalide (**2**, **15**, **16**, or **17**) (2.8 mmol) and 0.2 equiv. TBADT (19 mg, 0.0055 mmol). The resulting mixture was septum capped and degassed in the absence of light by purging with argon for 20 min. This solution was subsequently irradiated with a 300 W Xenon lamp for 1.5–4 h at 5–10 °C in an ice water bath, while a constant, slow argon stream was maintained over the solution. The progress of the reaction was monitored by HPLC. Then, the solvent was distilled from the reaction mixture under reduced pressure, and the remaining crude product was centrifuged three times with acetonitrile HPLC grade to remove excess phthalide (**2**, **15**, **16**, or **17**) and TBADT. The crude product was further purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v).

TBADT-Mediated Photochemical Reaction of C_{60} with Phthalide 2: The reaction was carried out following the general photocatalytic procedure described above using phthalide **2** (375 mg, 2.8 mmol). The reaction mixture was irradiated for 90 min. The crude product was purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **11** in 20 % isolated yield (4.7 mg; 0.0055 mmol), along with a small amount of a complex mixture of several unidentified by-products.

TBADT-Mediated Photochemical Reaction of C_{60} with 5-Bromophthalide (15): The reaction was carried out following the general photocatalytic procedure described above using 5-bromophthalide **(15)** (600 mg, 2.8 mmol). The reaction mixture was irradiated for 3.5 h. The crude product was purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **18** in 15 % isolated yield (4.0 mg; 0.0043 mmol).

18: IR (KBr): $\tilde{\nu}$ = 2372.9 (m), 2346 (s), 1871 (w), 1846.2 (w), 1832 (w), 1774.6 (s), 1735.7 (m), 1719.6 (m), 1702.4 (m), 1686 (w), 1676.5 (m), 1671.1 (w), 1664.1 (w), 1655.2 (s), 1648.1 (m), 1637.9 (m), 1628.9 (w), 1618.3 (m), 1603.7 (w), 1578.1 (m), 1570.9 (m), 1560.7 (s), 1543.1 (s), 1523.5 (m), 1508.7 (s), 1499.3 (m), 1491.4 (w), 1475.5 (m), 1465.8 (w), 1459.2 (s), 1449.9 (w), 1438.8 (m), 1421.2 (m), 1388.9 (w), 1325 (w) 1294.1 (w), 1261.7 (w), 1211.1 (m), 1182.7 (w), 1058.3 (w), 999.3 (m), 845.9 (w), 753.4 (s), 708.6 (w), 670 (w), 661.2 (w), 573.9 (w), 526.9 (s), 420 (w) cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} (nm) = 329, 405, 431; ^{1}H NMR (CDCl$_3$, 500 MHz, 25 °C): δ_H = 8.37 (1H, br. s), 8.10 (1H, d, $^3J_{HH}$ = 8.0 Hz), 7.95 (1H, dd; $^3J_{HH}$(1)= 8.0 Hz, $^3J_{HH}$(2)= 2.0 Hz), 7.11 (1H, s), 6.34 (1H, s) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz, 25 °C): δ_C = 168.82, 159.90, 152.70, 152.24, 151.16, 148.72, 148.62, 148.56, 148.15, 147.88, 147.81, 147.48, 146.86, 146.81, 146.65, 146.62, 146.54, 146.49, 146.46, 146.20, 146.15, 146.13, 145.95, 145.83, 145.81, 145.65, 145.59, 145.57, 145.44, 145.40, 144.98, 144.95, 144.74, 144.62, 144.44, 143.47, 143.24, 142.87, 142.50, 142.34, 142.21, 142.16, 141.94, 141.93, 141.56, 140.68, 140.14, 138.54, 137.42, 135.94, 134.67, 130.38, 128.01, 127.24, 86.52, 68.11, 55.90. ppm; ESI-MS (negative ion mode): *m/z* 930.926 ([M – H]$^-$, calcd. for $C_{68}H_4BrO_2^-$: 930.939).

TBADT-Mediated Photochemical Reaction of C_{60} with 5-Cyanophthalide (16): The reaction was carried out following the general photocatalytic procedure described above using 5-cyanophthalide **16** (445 mg, 2.8 mmol). The reaction mixture was irradiated for 4 h. The crude product was purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **19** in 17 % isolated yield (4.3 mg; 0.0049 mmol), along with a small amount of a complex mixture of several unidentified by-products.

19: IR (KBr): $\tilde{\nu}$ = 2370.8 (m), 2345.8 (s), 1871 (w), 1846.2 (w), 1832 (w), 1774.7 (s), 1735.6 (m), 1719.5 (s), 1702.4 (m), 1686 (s), 1676.5 (m), 1671 (w), 1664.2 (w), 1655.2 (s), 1648.1 (m), 1637.9 (s), 1628.8 (w), 1618.2 (s), 1577.9 (m), 1570.9 (w), 1560.7 (s), 1543.1 (s). 1523.5 (m), 1508.7 (s), 1499.2 (m), 1491.3 (w), 1475.5 (m) 1466 (w), 1459 (m), 1438.7 (m), 1421.3 (m), 1406.7 (w), 1389 (w), 1301.5 (w), 1272.2 (w), 1200.9 (w), 1043 (w), 1002.2 (w), 849.3 (w), 752.5 (s), 708.8 (w), 670.3 (w), 658.1 (w), 543.2 (w), 526.8 (s), 453 (w) cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} (nm) = 328, 405, 431; ^{1}H NMR (CDCl$_3$, 500 MHz, 25 °C): δ_H = 8.48 (1H, s), 8.36 (1H, d, $^3J_{HH}$ = 8 Hz), 8.09 (1H, d, $^3J_{HH}$ = 8 Hz) 7.21 (1H, s), 6.41 (1H, s) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz, 25 °C): δ_C = 167.74, 152.39, 151.88, 147.89, 147.87, 147.56, 146.90, 146.87, 146.74, 146.68, 146.66, 146.59, 146.52, 146.51, 146.26, 146.18, 146.18, 146.16, 145.96, 145.90, 145.88, 145.78, 145.70, 145.67, 145.65, 145.03, 145.02, 144.59, 144.42, 143.51, 143.45, 143.26, 142.99, 142.93, 142.91, 142.86, 142.50, 142.46, 142.39, 142.21, 142.20, 142.16, 142.01, 141.98, 141.97, 141.92, 141.82, 141.59, 141.56, 140.80, 140.77, 140.29, 140.17, 138.69, 138.03, 136.17, 135.89, 134.70, 131.92, 128.54, 127.71, 118.41, 117.52, 87.05, 67.98, 56.27 ppm; HR-MALDI-MS (DCTB): *m/z* (%): 879.089 (100, *M*$^+$, calcd. for $C_{69}H_6NO_2^+$: 879.031), 721.116 (80, $C_{60}H^+$, calcd. for $C_{60}H^+$: 721.007).

TBADT-Mediated Photochemical Reaction of C_{60} with 6-Nitrophthalide (17): The reaction was carried out following the general photocatalytic procedure described above using 6-nitrophthalide **(17)** (500 mg, 2.8 mmol). The reaction mixture was irradiated for 90 min. The crude product was purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **20** in 14 % isolated yield (3.5 mg; 0.0039 mmol).

20: IR (KBr): $\tilde{\nu}$ = 2375.1 (w), 2346.1 (m), 1832.0 (w), 1782.5 (s), 1735.7 (w), 1719.8 (m), 1702.5 (w), 1686 (m), 1676.5 (w), 1664.2 (w), 1655.2 (m), 1648.0 (w), 1637.9 (m), 1617.9 (m), 1578.0 (w), 1570.9 (w), 1560.8 (m), 1532.9 (s), 1508.8 (w), 1499.5 (w), 1491.4 (w), 1475.3 (w), 1459.3 (m), 1438.7 (w), 1427.7 (w), 1342.5 (s), 1298.8 (w), 1252.1 (w), 1209.6 (w), 1183.3 (w), 1092.5 (s), 1042.0 (w), 998.1 (m), 837.9 (w), 811.3 (w), 794.8 (w), 752.5 (s), 705.0 (m), 669.5 (w), 577.3 (m), 554.0 (w). 527.0 (s), 475.7 (w) cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} (nm) = 329, 405, 431; ^{1}H NMR (CDCl$_3$, 500 MHz, 25 °C): δ_H = 9.05 (1H, d, $^3J_{HH}$ = 2.0 Hz), 8.77 (1H, dd, $^3J_{HH}$(1) = 8.5 Hz; $^3J_{HH}$(2) = 2.0 Hz), 8.41 (1H, d, $^3J_{HH}$ = 8.5 Hz), 7.28 (1H, s), 6.46 (1H, s) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz, 25 °C): δ_C = 167.31, 159.80, 152.43, 151.87, 150.94, 150.18, 149.28, 147.89, 147.87, 147.52, 146.89, 146.85, 146.73, 146.68, 146.66, 146.64, 146.57, 146.56, 146.52, 146.50, 146.24, 146.20, 146.19, 146.09, 145.89, 145.87, 145.86, 145.74, 145.70, 145.66, 145.61, 145.04, 145.01, 144.55, 144.39, 143.50, 143.44, 143.24, 142.98, 142.98, 142.90, 142.85, 142.42, 142.38, 142.17, 142.13, 141.97, 141.92, 141.89, 141.80, 141.57, 141.47, 140.82, 140.77, 140.15, 140.14, 138.73, 138.07, 136.13, 135.89, 130.16, 129.53, 126.17, 122.26, 111.38, 101.48, 87.28, 68.00, 56.40 ppm; ESI-MS (negative ion mode): *m/z* 898.016 ([M – H]$^-$, calcd. for $C_{68}H_4NO_4^-$: 898.013).

TBADT-Mediated Photochemical Reaction of C_{60} with Equimolar Quantities of Phthalide-d_0 (2-d_0) and Phthalide-d_2 (2-d_2): The reaction was carried out following the general photocatalytic procedure described above using **2**-d_0/**2**-d_2 (150 mg, 1.1 mmol). The reaction mixture was irradiated for 13 h. The crude product was purified by flash column chromatography (eluent: hexane/toluene, 4:1 v/v) to afford fullerene adduct **11-d_0** and **11-d_1/d_2** in 18 % isolated yield (4.2 mg; 0.0050 mmol).

Computational Methods: All calculations were performed using the GAUSSIAN 09 package (Revision A.02).[10] The energies and optimal geometries of the three conformers **11a**–**c** were determined at the B3LYP/6-31G(d) level of theory, in the gas phase (Tables S1–S3 in SI). All optimized structures were verified as ground-state minima by performing frequency calculations at the same level of theory (no imaginary frequencies were found). For NMR calculations, the energies and optimal geometries of **11a**–**c** were first determined at a higher level of theory, using the two-layer ONIOM [M06-2X/6-31+G(d,p):HF/3-21G] approach and implicit solvation in CHCl$_3$ (IEFPCM; integral equation formalism variant of the polarizable continuum model), as implemented in Gaussian 09 software package (Revision A.02)[10] (Tables S4–S6 in SI). Solute cavities were constructed using default united-atom radii (UA0). A pruned (99,590) integration grid (99 radial shells and 590 angular points per shell; "*ultrafine*" grid in Gaussian 09) was employed. All optimized structures were verified as ground-state minima by performing frequency calculations at the same level of theory (no imaginary frequencies were found), the data from which were also used to compute their Boltzmann distribution at 298 K. All optimized structures were then used for NMR calculations. NMR shielding tensors (σ, in ppm) were computed with the gauge-independent atomic orbitals (GIAO) method at the B3LYP/6-311+G(2d,p) level of theory, including chloroform solvation effects (using the IEFPCM solvation model), while employing solute cavities built from Bondi radii as implemented in Gaussian 09. A pruned (99,590) integration grid was employed. The computed isotropic magnetic shielding tensors (σ_{iso}, in ppm) for each nucleus in all conformers was converted to referenced and empirically scaled chemical shifts (δ_{scaled}, in ppm) by applying scaling and referencing factors (slope and intercept, respectively) according to the equation: $\delta_{\text{scaled}} = (\sigma_{\text{iso}} - \text{intercept})/\text{slope}$, where δ_{scaled} is the referenced/scaled chemical shift (in ppm), and σ_{iso} is the isotropic computed NMR shielding tensor (in ppm). The slope and intercept values are typically obtained by linear regression analysis of a plot of the calculated isotropic magnetic shielding tensors (σ_{iso}) against the corresponding experimental chemical shifts (δ_{expt}). In the present study, we used generic-scaling factors obtained from large datasets [i.e. obtained from linear regression analysis of a plot of calculated isotropic magnetic shielding tensors (σ_{iso}) against experimental chemical shifts (δ_{expt}) of a large series of compounds]; these scaling/referencing factors are specific of the level of theory used. For the level of theory used herein [B3LYP/6-311+G(2d,p)//M06-2X/6-31+G(d,p)] the following values have been calculated by Willoughby et al.:[16] for ^{1}H: intercept = 31.9477, slope = –1.0767; for ^{13}C: intercept = 181.2412, slope = –1.0522. The final calculated chemical shift values (δ_{calcd}, in ppm; Table 2) were determined by Boltzmann averaging the scaled chemical shift values (δ_{scaled}, in ppm), based on the calculated Gibbs free energy values of each conformer. Specifically, by using the free energy data (kcal mol^{-1}) obtained from the frequency calculations, a Boltzmann weighting factor [$e^{(-E/RT)}$, where E is the relative energy (kcal mol^{-1}) with respect to the most stable conformer, T is the temperature (in K), and R is the gas constant (0.001986 kcal mol^{-1} K^{-1})] was determined for each conformer at 298 K, which was, in turn, converted into the relative mole fraction by dividing the calculated Boltzmann factor of each conformer by the sum of all the Boltzmann factors of all contributing conformers. The resulting weighting factors (mole fraction contributions) were applied to the scaled chemical shift values (δ_{scaled}, in ppm) for each nucleus of each individual conformer. Summation of the weighted chemical shifts across all conformers generates the final Boltzmann-weighted average chemical shifts (δ_{calcd}, in ppm) used to compare against experimental data (δ_{expt}, in ppm; Table 2). It should be noted that only one enantiomer [i.e. the one having (*S*)-configuration at C(62)] was considered in our computational NMR studies.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H NMR, ^{13}C NMR, FT-IR, and UV/Vis spectra of **11** and **18**–**20**; optimized geometries (in Cartesian coordinates), total energies, relative free energies, and Boltzmann populations of the three conformers of **11**. Experimental Details.

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Keywords: Fullerene C_{60} · Photochemistry · Radical reactions · *o*–Phthalaldehyde · Phthalides

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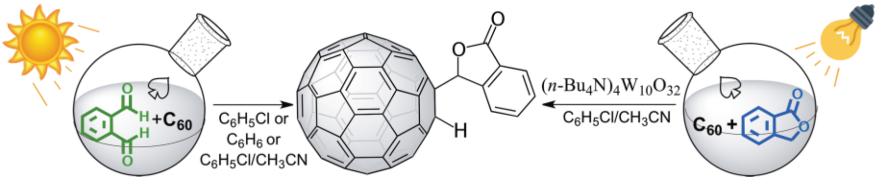
Photochemistry of Fullerenes

M. D. Tzirakis, N. G. Malliaros, M. Orfanopoulos** 1–8

Photochemical Reaction of *o*-Phthalaldehyde with Fullerene C_{60}: The Stimulus for the Phthalide Additions to C_{60}



C_{60} reacts under ambient light with *o*-phthalaldehyde to afford an unanticipated C_{60}-phthalide derivative in 43 % yield. Alternatively, this hydrofullerene can be accessed via a novel tetrabutylammonium decatungstate photocatalyzed reaction of C_{60} with phthalides (4 examples).

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