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Photocyclization of 2,4,6-triethylbenzophenones in the solid state

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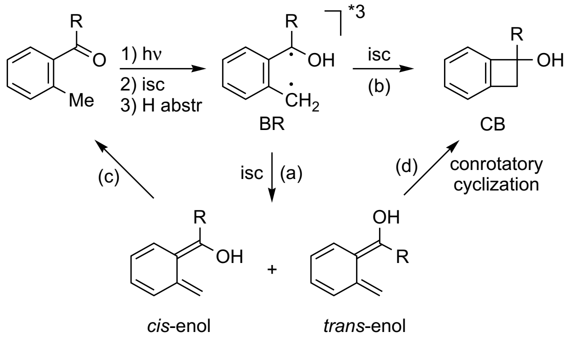
ABSTRACT

Photocyclization of 2,4,6-triethylbenzophenones (TEBPs) into (*E*)- or (*Z*)-benzocyclobutenols ((*E*)- or (*Z*)-CBs) is *E*-selective in solution. By contrast, upon solid-state photolysis, TEBP-3,4-diCl and especially TEBP-4-*t*-Bu gave (*Z*)-CB relative to (*E*)-CB with a much higher proportion than that in solution. For TEBP-4-*t*-Bu, the most major product in the solid state is an indanol derivative (Inol) (*E*/*Z*/Inol=1:3.9:10.3 at 9% conversion). On the basis of the X-ray crystallographic analysis, Inol and (*Z*)-CB are both topochemical products. Notably, the relative proportion of (*E*)-CB increased with increased conversion, namely with increased disruption of the crystal lattice. The DFT calculation of highly hindered 2,6-diisopropylbenzophenone (DIBP) was also conducted. These results in conjunction with the previous results on 2,4,6-triisopropylbenzophenones (TIBPs) indicate that CB is formed either via *trans*-enol followed by its conrotatory ring-closure (paths a and d) or through direct cyclization of biradical (BR) (path b) as shown in Scheme 1. Normally the former route is faster. However, in the crystalline state or in the case of sterically hindered phenyl ketones, path b tends to be adopted.

1. Introduction

There is a long-time controversy in the mechanism of photocyclization for *o*-alkyl phenyl ketones giving benzocyclobutenols (CBs) (either paths a and d or path b in Scheme 1).[1–4] In the 1990s, Wagner strongly insisted that CB should be formed solely through conrotatory cyclization of *trans*-enol (paths a and d), not at all directly via biradical (BR) (path b), as illustrated in Scheme 2.[1] On the other hand, one of the present authors had proposed in the 1980s that for 2,4,6-triisopropylbenzophenones (TIBPs), direct cyclization of BR accompanied by concomitant intersystem crossing (path b) occurred both in solution and in the solid state (Scheme 3).[2,3] The present investigation on the photocyclization of 2,4,6-triethylbenzophenones (TEBPs) (Eq. 1) was undertaken to make up this discrepancy.



Scheme 1. Possible mechanisms for photocyclization of *o*-alkyl phenyl ketones into their benzocyclobutenols.

TIBP is similar in molecular shape to the corresponding CB, but is very different from *trans*- or *cis*-enol,[3] as confirmed by the DFT calculation, which is described later. Therefore, if an intermediate such as *trans*-enol exists before cyclization to CB, the photocyclization will be very slow or do not occur in the crystal lattice because of the mobility constraint due to the rigid confined void-space, i.e., paths a and d will be unfeasible from the reaction cavity concept.[5,6] However, it has already been reported that several TIBPs (TIBP-X: X=*p*-OMe, *p*-*t*-Bu, *p*-Me, H) give the corresponding CBs very efficiently in the solid state, i.e., Φ(crystal)~Φ(solution)=0.1–0.5 (Scheme 4A).[3a] Furthermore, the solid-state photocyclization of chiral TIBP (*S*)-**7** (TIBP-X: X=*p*-(*S*)-phenylalaninocarbonyl methyl ester (p-COA^S)) proceeded with high diastereoselectivity (99% de at 34% conversion, Scheme 4B).[3b] The crystal structure (orthorhombic, space group $P2_12_12_1$) was retained during the transformation up to 100% conversion with small changes in lattice constants (*a*, *b*, and *c*) (Scheme 5).[3e] These results support that the solid-state photolysis

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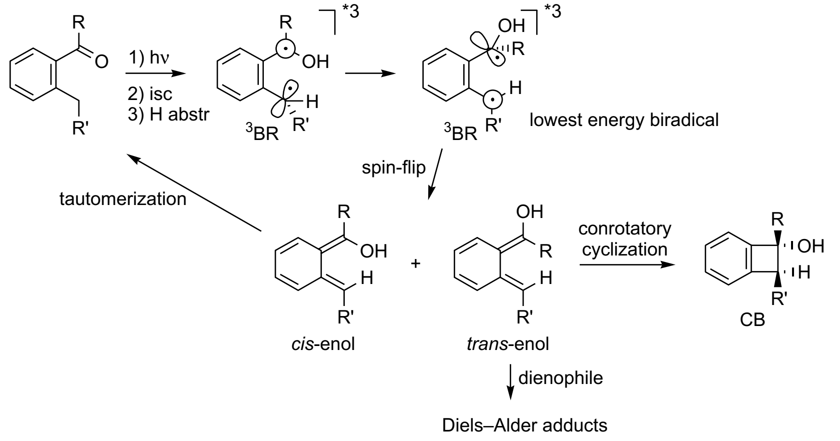
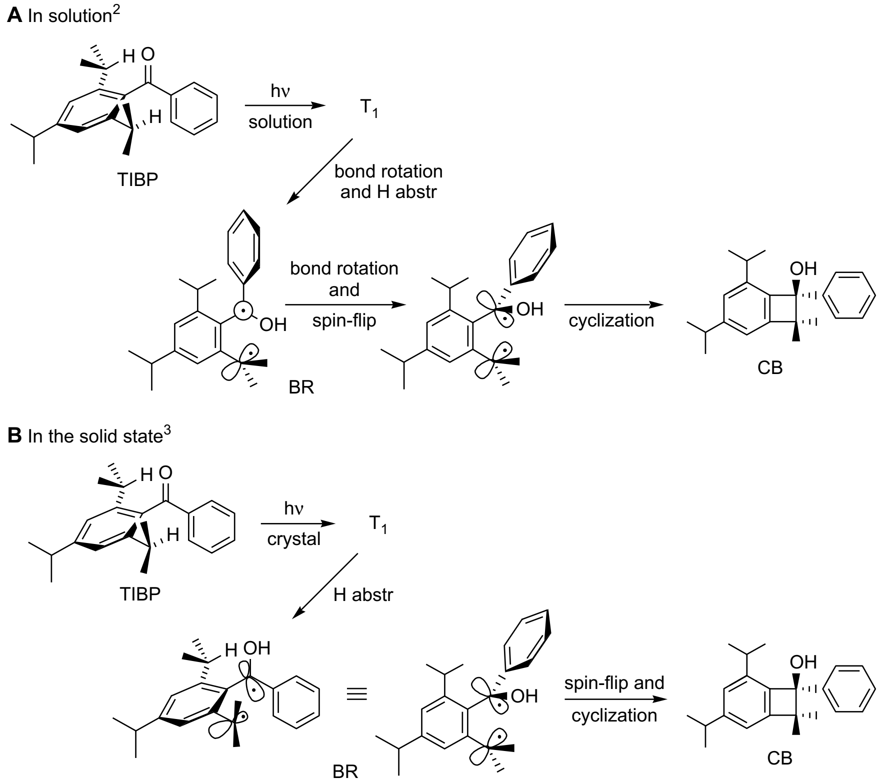
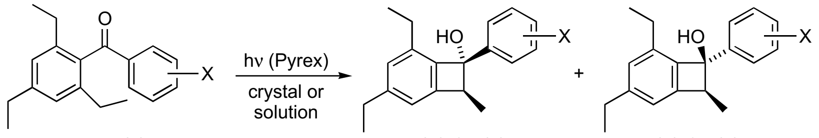


Scheme 2. Wagner's mechanism.



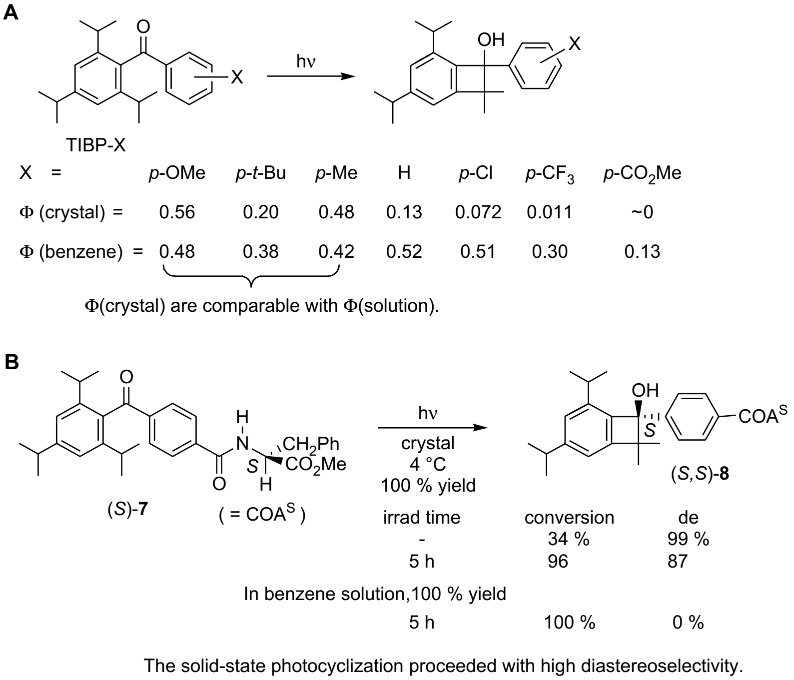
Scheme 3. Ito's mechanism for benzocyclobutenol formation.

of TIBPs gave CBs directly via BR, not via intermediacy of *trans*-enol. In order to further support this conclusion, we have now investigated the photocyclization of TEBPs. Since there are two possible stereoisomers for CB in this case ((*E*)- and (*Z*)-CB, Eq. 1), important information about the cyclization mechanism is expected to emerge from this investigation.



TEBP (**1**) (*E*)-CB (**2**) (*Z*)-CB (**3**) **(1)**

X = 4-*t*-Bu (**a**), 4-Cl (**b**), 3,4-diCl (**c**), 3,5-diCl (**d**), 2,4-diCl (**e**), 4-CO_2Me (**f**)



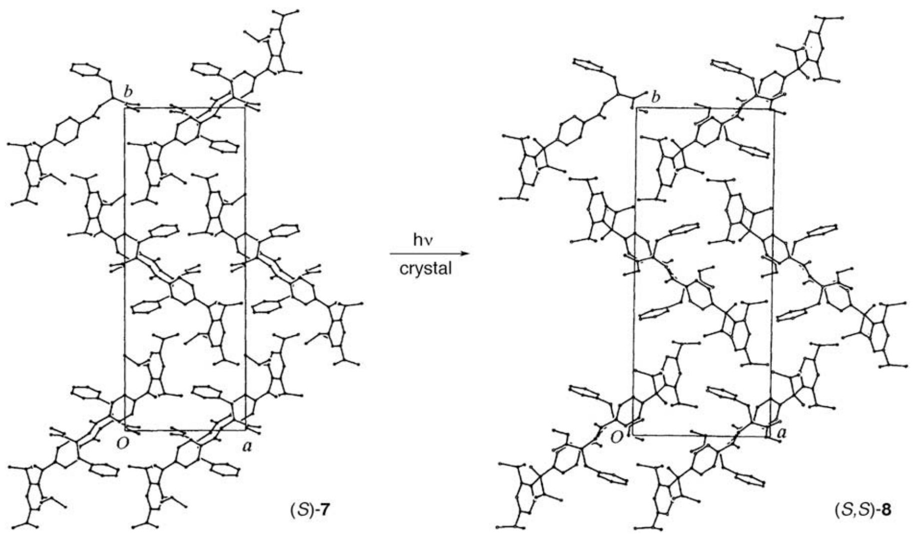
Scheme 4. Our previous results[3a,b] which are inconsistent with the Wagner's mechanism.

2. Results and discussion

2.1. Photolysis

It has already been reported that many of TEBPs are oil except 4-Cl-substituted TEBP.[2h] Cl substitution is known to be a good method to steer crystal packing.[5] Consulting also the substituted TIBPs having higher melting points,[3a] several new TEBPs (TEBP-X: X=3,4-diCl, 3,5-diCl, 2,4-diCl, 4-*t*-Bu, and 4-CO_2Me) were now prepared. Among them, TEBP-3,4-diCl and TEBP-4-*t*-Bu were found to be crystalline (Table 1). Therefore, the photochemistry of 4-Cl-, 3,4-diCl-, and 4-*t*-Bu-substituted TEBPs was here investigated.

As summarized in Table 2, irradiation of TEBP-4-*t*-Bu (**1a**), TEBP-4-Cl (**1b**), and TEBP-3,4-diCl (**1c**) in benzene or MeCN for 2 h at 10 or 2 °C with a 400-W high-pressure mercury lamp (Pyrex filter) under an argon atmosphere produced the corresponding (*E*)-CB (**2**) with high yield and efficiency. In agreement with the previous results,[2h] the other stereoisomer (*Z*)-CB (**3**) was yielded only in a little quantity: E/Z=18–32. The stereochemistry of (*E*)-CB was assigned on the basis of the unusually high-field ^1H NMR doublet signal of the 2-Me group (δ ~0.83, J~7.3 Hz),[2h,7] whereas the corresponding signal for (*Z*)-CB resonanced at δ ~1.35 (J~7.3 Hz). In addition to (*E*)- and (*Z*)-CB, a small amount of an anthrone derivative (An, **4**) was constantly produced, judging from the presence of a doublet peak at δ ~1.5 (J~7.3 Hz), which is attributable to the 10-Me group. Retention times on a C_{18} HPLC column eluted with MeOH–H_2O increased in the order (*E*)-CB<(*Z*)-CB<TEBP<An. Yields and proportions of the products listed in Tables 2 and 3 were determined by direct ^1H NMR and HPLC analyses of the photolysate.



Scheme 5. Crystal-to-crystal transformation of TIBP-*p*-COA^S (*S*)-**7**: projection of the crystal structure along *c*.[3e]

Table 1
Melting points of substituted 2,4,6-triethylbenzophenones (TEBPs)

TEBP-X	Mp (°C)	
4-OMe	Oil	[a]
4-*t*-Bu	41–42.5	This work
4-Me	Oil	[a]
H	Oil	[a]
4-Cl	43–44	[a]
3,4-DiCl	69.5–70.5	This work
3,5-DiCl	Oil	This work
2,4-DiCl	Oil	This work
4-CO$_2$Me	Oil	This work
4-CF$_3$	Oil	[a]

[a] Ref. 2h.

Next, the crystals of these three TEBPs were crushed and were irradiated in the solid-state apparatus[6] at 2–3 °C. While TEBP-4-Cl resisted to photoreact, TEBP-3,4-diCl reacted with reasonable efficiency to give (*E*)- and (*Z*)-CB (Table 3). The *E*/*Z* ratio was 3.9 after 1 h of irradiation (conversion 8%) and thus the relative yield of (*Z*)-CB is much higher than that in solution. Extended irradiation (10 h, 35% conversion) impaired the reaction stoichiometry, giving considerable amounts of uncharacterized byproducts.

Interestingly, the solid-state photoreaction of TEBP-4-*t*-Bu was facile and clean (Table 3). Only after 0.2 h of irradiation, a considerable conversion (9%) was reached, producing (*E*)-CB (**2a**), (*Z*)-CB (**3a**), and an indanol derivative (Inol, **5a**) (Eq. 2). Inol was stable under the HPLC conditions and was eluted between (*E*)-CB and (*Z*)-CB. However, it was fairly easily dehydrated in CDCl$_3$ or under the preparative TLC conditions to furnish an indene derivative (**6a**), which also underwent further decomposition during the separation procedure (Eq. 3). Inol is a product of δ-hydrogen abstraction by the carbonyl group.[8] Irradiation for a longer time (1 h, 35% conversion) resulted in a little melted appearance, spoiled somewhat the stoichiometry, and led to side formation of An. It should be noted that the most major product is Inol and that, at a short irradiation time (0.2 h, 9% conversion) where the regularity of the crystal lattice is not destroyed much, the yields of (*Z*)-CB and Inol overwhelmed that of (*E*)-CB, i.e., *E*/*Z*/Inol=1:3.9:10.3. Thus, as hoped, (*Z*)-CB became a main product in the solid state for both TEBP-3,4-diCl and TEBP-4-*t*-Bu. It should also be mentioned that the proportion of (*E*)-CB relative to (*Z*)-CB (and Inol) increased with the increase in conversion for both TEBP-3,4-diCl and TEBP-4-*t*-Bu.

For comparison, irradiation of 2,4,6-trimethylbenzophenone (TMBP) was carried out. As reported previously,[2c,7] a low yield of CB was produced in solution (Table 2). In the solid state, essentially no reaction products were observed (Table 3).

2.2. Crystal structure

Crystal structures of 12 TIBPs (TIBP-X: X=*p*-OMe, *m*-OMe, *p*-*t*-Bu, *p*-Me, H, *p*-CO$_2$Me, *m*-CO$_2$Me, *p*-CO$_2$Et, *p*-CO$_2$H, *p*-COCl, *m*-COCl, and *p*-COA$^{\text{S}}$) were already reported.[3a–e] The crystal structure of TIBP-*p*-Cl was successfully solved here (Fig. 1). In all these TIBPs, the carbonyl plane is almost perpendicular to the triisopropylphenyl ring (the torsion angles 79°–89°) and is near coplanar with the X-substituted phenyl ring (the torsion angles 3°–15°). The intramolecular distance between the carbonyl oxygen atom and the nearer *o*-isopropyl methine H in each TIBP is 2.7–3.0 Å, the distance to another *o*-isopropyl methine H being 2.9–3.2 Å.[†] With respect to the triisopropylbenzoyl moiety, each TIBP has a very similar conformation to the corresponding part of CB.[‡] Hence, the transformation of TIBP into CB may proceed with small distortion of the reaction cavity and be topochemically feasible,[5b] if there are no other obstacles. In fact, in the case of X=*p*-OMe, *p*-*t*-Bu, *p*-Me, H, and *p*-COA$^{\text{S}}$, the quantum yield in the solid state was comparable to or even larger than that in solution (see the data in Scheme 4).[3a,b] More data for the solid-state photoreactivity of TIBPs[3a–c] are summarized in Table 4.

Table 4 demonstrates that TIBP-*p*-CO$_2$Me and TIBP-*p*-COCl are photostable, TIBP-X with X=*p*-CO$_2$H, *m*-COCl, *p*-CO$_2$Et, and *p*-Cl react relatively slowly, and TIBP-X with X=*p*-OMe, *m*-OMe, *p*-*t*-Bu, *p*-Me, H, *m*-CO$_2$Me, and *p*-COA$^{\text{S}}$ are highly reactive. In order to understand these reactivity differences, their crystal structures were inspected again.[3a,d,e] The inspection has brought clear that, in the case of the stable or low-reactive TIBPs, the Ph-X groups are packed closely. The interplanar separations between the nearest Ph-X planes, which are related by a center of symmetry and are interacting through π–π interactions except the case of TIBP-*p*-CO$_2$H, are 3.4–3.6 Å. For example, see Figure 1b for TIBP-*p*-Cl; for the cases of *p*-CO$_2$Me, *p*-COCl, *m*-COCl, and *p*-CO$_2$Et, see Ref. 3d. With photostable TIBP-*p*-CO$_2$Me and TIBP-*p*-COCl, the two Ph-X planes are especially well overlapped, leading to the narrow reaction cavity.[3c,d] The Ph-CO$_2$H plane of TIBP-*p*-CO$_2$H form a cyclic hydrogen bond by the CO$_2$H group and the hydrogen-bonded dimers are all arrayed in the same way in three dimensions.[3d] In contrast to the stable or low-reactive TIBPs, the Ph-X planes of the highly reactive TIBPs (X=*p*-OMe, *m*-OMe, *p*-*t*-Bu, *p*-Me, H, *m*-CO$_2$Me, and *p*-COA$^{\text{S}}$) are much separated (the interplanar separation >7 Å) or are much slipped aside and thus the π–π overlapping interactions do not exist. As aforementioned, the conformation of the triisopropylbenzoyl moiety is similar to that of CB. Consequently, it can be viewed that the solid-state photocyclization of TIBPs was controlled by the confined space in crystal packing around the Ph-X moiety rather than around the triisopropylbenzoyl moiety. This is also understandable from molecular models, because it is the Ph-X moiety that is moved most when the cyclization to CB occurs. Small or negligible restriction from the confined space around the triisopropylbenzoyl moiety indicates that the TIBP crystals undergo photocyclization to CB via BR, not via *trans*-enol, since *trans*-enol is very different from TIBP and CB in molecular shape.

Figures 2 and 3 show the crystal structures for three TEBPs (TEBP-X: X=4-*t*-Bu, 4-Cl, 3,4-diCl) and one TMBP. Like TIBPs,[3a,d,e] the carbonyl plane is almost perpendicular to the trialkyl-substituted Ph ring (the torsion angles: 88°, 89°, 89°, and 71°, respectively), and is near coplanar with the other Ph ring (the torsion angles: 7°, 12°, 12°, and 11°, respectively). The intramolecular distances between the carbonyl O and the nearest *o*-alkyl α-H (O1⋯H14) are 3.09, 2.95, 3.13, and 2.47 Å, respectively (Table 5).[†] The terminal Me groups of the *o*-Ets in each TEBP are directed toward the side of the carbonyl O atom (Fig. 2). As described above for TIBPs, the neighboring Ph-X planes of photostable TEBP-4-Cl or TMBP and low-reactive TEBP-3,4-diCl are related by a center of symmetry and are overlapped through π–π interactions (the interplanar distances: 3.14, 3.39, 3.66 Å, respectively) (Fig. 3b–d). On the other hand, the neighboring Ph-X planes of highly reactive TEBP-4-*t*-Bu are much slipped aside (Fig. 3a) and thus the π–π interactions do not exist. Hence, in the solid-state photocyclization of TEBPs and TMBP, the Ph-X moiety rather than the trialkylbenzoyl

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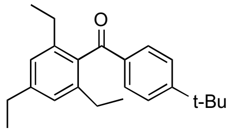
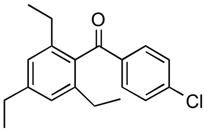
[†] These values are almost within the maximum distance for the intramolecular hydrogen abstraction process to take place. The optimum distance between the carbonyl oxygen and the to-be-abstracted hydrogen is 2.72 Å, but the distances as great as 3.1 Å can be tolerated.[9,10]

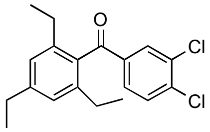
[‡] Since it was difficult to obtain good quality of crystals for CB, only the crystal structures of CB-*m*-OMe and CB-*p*-COA$^{\text{S}}$ were successfully obtained so far.[3e] However, the molecular shape of CB can be quite precisely known from molecular modeling, e.g., the DFT calculation (vide infra).



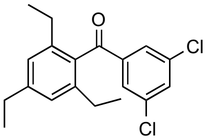
TEBP-4-*t*-Bu (**1a**)



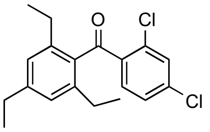
TEBP-4-Cl (**1b**)



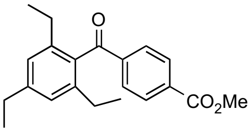
TEBP-3,4-diCl (**1c**)



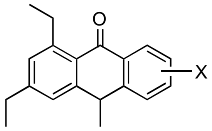
TEBP-3,5-diCl (**1d**)



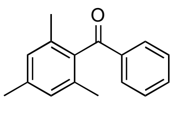
TEBP-2,4-diCl (**1e**)



TEBP-4-CO$_2$Me (**1f**)



An (**4**)



TMBP

Table 2
Photochemistry of 2,4,6-triethylbenzophenones (TEBPs) in solution[a]

TEBP-X	Solvent	Temp (°C)	Irrad time (h)	Conv (%)	Product yield (%)			*E*/*Z* ratio
					(*E*)-CB	(*Z*)-CB	An	
4-*t*-Bu	Benzene	10	2	100	92	5	3	18:1
4-Cl	Benzene	10	2	99	88	3	3	27:1
3,4-DiCl	Benzene	10	2	99	83	4	3	20:1
	MeCN	2	2	87	86	4	5	32:1
TMBP[b]	Benzene	10	10	97	29		—	—

[a] Irradiation was carried out with a 400-W high pressure mercury lamp (Pyrex) at 10 or 2 °C under the Ar atmosphere.
[b] 2,4,6-Trimethylbenzophenone.

moiety appears to suffer the confined-space-restriction of the crystal lattice, like the cases of TIBPs (vide supra).

Reactions in crystals proceed with minimum movement of atoms and molecules.[5a] On the basis of this topochemical principle, the X-ray molecular structures of the three TEBPs (Fig. 2) predict that a *Z* isomer rather than an *E* isomer of CB should be produced by their solid-state photolysis. We are fortunate to have obtained such results (Table 3). Thus, upon short-time solid-state photolysis, TEBP-3,4-diCl and especially TEBP-4-*t*-Bu gave (*Z*)-CB relative to (*E*)-CB with much higher proportions than in solution, i.e., the *E*/*Z* ratios are 3.9:1 (solid) and 20–32:1 (solution) for TEBP-3,4-diCl and are 1:3.9 (solid) and 18:1 (solution) for TEBP-4-*t*-Bu. The *E* isomers were probably formed at the imperfect crystal lattice or surface. For TEBP-4-*t*-Bu, the most major product in the solid state is Inol (*E*/*Z*/Inol=1:3.9:10.3 at 9% conversion). Formation of Inol is also rationalizable from the topochemical principle, because the carbonyl O is very close to *o*-Et β-H (O1···H19=2.68 Å) as compared with α-H (O1···H14=3.09 Å) (Table 5). For TEBP-4-Cl and TEBP-3,4-diCl, the relevant O···β-H distances are 2.88 and 2.81 Å, respectively, and the corresponding Inol derivatives were not formed.

Table 3
Photochemistry of 2,4,6-triethylbenzophenones (TEBPs) in the solid state[a]

TEBP-X	Irrad time (h)	Conv (%)	Product yield (%)				*E*/*Z*/Inol ratio
			(*E*)-CB	(*Z*)-CB	An	Inol	
4-*t*-Bu	0.2	9	6	26	0	68	1:3.9:10.3
	0.5	20	9	24	Trace	67	1:2.6:7.2
	1	35	15	18	7	52	1:1.2:3.5
4-Cl	2	~0	No reaction				—
3,4-DiCl	1	8	69	18	0	—	3.9:1:-
	2	13	62	15	0	—	4.1:1:-
	5	19	63	16	0	—	4.3:1:-
	10	35	37	9	0	—	5.4:1:-
TMBP[b]	10	~0	No reaction				—

[a] Irradiation was carried out with a 400-W high pressure mercury lamp (Pyrex) at 2–3 °C under the Ar atmosphere.
[b] 2,4,6-Trimethylbenzophenone.

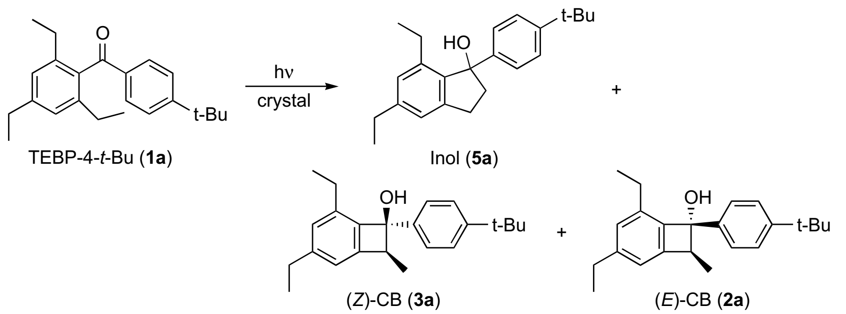
2.3. DFT calculation

The DFT calculations at the level of B3LYP/6-31G(d) were performed on 2,6-diisopropylbenzophenone (DIBP) and 2-methylbenzophenone (MBP), a typical example of sterically hindered and unhindered *o*-alkylbenzophenones, respectively, and on the possible intermediates and products formed photochemically thereof. The calculated stable conformations and energies of these molecules are summarized in Figures 4 and 5. The changes of energy levels relative to the ketone ground state are shown in Figure 6. The twisted conformations of DIBP and MBP (Figs. 4 and 5) are consistent with the X-ray structures of TIBPs, TEBPs, and TMBP described above. As expected from the previous publication,[9,11] the conformations of DIBP and MBP are not altered by excitation to their triplet states ^{3}DIBP* and ^{3}MBP*.[§] ^{3}DIBP* has a slightly higher energy (0.4 kcal/mol) than ^{3}MBP*.[¶] There is one stable form of BR (or enol triplet) in the case of DIBP and are two stable forms of BR (or enol triplet) in the case of MBP.[‖] In both cases, BR converged to nearly the same conformation and energy as enol triplet, supporting a notion that BR and enol triplet are different names of the same species.[17,18] The conformations of these stable BRs are essentially equivalent to the conformer ^{3}tw,co in Scheme 6 (vide infra). Calculations of *trans*- and *cis*-enols and CB have disclosed that (a) both enols are considerably less stable than CB and (b) CB from DIBP is more stable than CB

[§] Dichotomous observations, i.e., the existence of either one triplet[12,19] or two kinetically distinct triplets,[13] were reported for ^{3}MBP*.

[¶] It has been reported previously[2h] that ^{3}TIBP* has a slightly higher triplet energy (~0.5 kcal/mol) than benzophenone triplet ^{3}BP*, but the triplet energy transfer occurs from BP to TIBP. This unusual event was interpreted in terms of the effect of internal rotational entropy.[2h] More investigations on the effects of molecular structure, temperature, and solvation are desirable in order to attribute this outcome to the entropy effect.[14]

[‖] By means of laser photolysis, one BR was detected for the MBP case[18–20] and BR was undetectable for the TIBP case because of its short lifetime (≪100 ns).[15–17] In the former case, the *syn* and *anti* forms of BR were proposed to interconvert so rapidly that only one species can be apparently observed.



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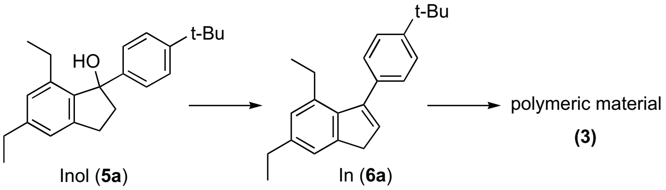

(3)

from MBP, while the opposite is the case for the enols. Relative to CB, the energies of BR and *trans*-enol, which are possible immediate precursors to CB, were found to be, respectively, 28 and 16 kcal/mol for DIBP and, respectively, 23 and 10 kcal/mol for MBP. The larger exothermicity of the cyclization process for DIBP than for MBP (Fig. 6) is consistent with the experimental fact that 2,6-dialkyl substitution enhances the photocyclization of *o*-alkyl phenyl ketones and the thermal stability of the resultant CB.[7] As expected, the shape of DIBP is similar to that of CB, whereas the shape of *trans*- or *cis*-enol is very different from that of DIBP (Fig. 4). The isopropyl-substituted benzene rings of these enols are far from planar. Therefore, it is unlikely that *trans*-enol is efficiently formed as the intermediate in the perfect crystalline state of TIBP.

2.4. Final mechanism

As described above, the solid-state photocyclization reactions of a series of *o*-alkylbenzophenones (TIBPs, TEBPs, and TMBP) are interpretable in terms of the reaction cavity concept and the topochemical principle. The findings a–c about the photochemistry of TEBP-4-*t*-Bu in crystals, (a) high solid-state photoreactivity, (b) formation of Inol and (*Z*)-CB with very minor formation of (*E*)-CB, and (c) both Inol and (*Z*)-CB are topochemically controlled products, are strong evidences that CB can be formed directly via BR (path b in Scheme 1). However, as seen from Table 3, the relative yield of (*E*)-CB-4-*t*-Bu or (*E*)-CB-3,4-diCl increased with the increase in conversion, i.e., the increased disruption of the crystal lattice. This indicates that without restriction due to the confined space of rigid crystals, TEBP tends to yield (*E*)-CB through conrotatory cyclization of *trans*-enol as in solution (paths a and d in Scheme 1). In the case of more sterically hindered TIBP, CB appears to be produced along path b until 100% conversion, since the crystal-to-crystal photocyclization of (*S*)-**7** was highly diastereoselective even at high conversion (87% de at 96% conversion).[3b,e] Therefore, it is natural to presume that path b is also occurring in solution to a certain extent in the case of TIBP. We would like to point out that the rotation around a single bond linking the triisopropylphenyl group and the carbonyl group is hindered on the NMR time scale, the observed rotational rate being 1.4–68 s^{-1},[2b] which is very much slower than the BR decay, since the lifetimes of photoenol biradicals are generally 100–5000 ns.[17] Accordingly, the situation for BR to reach conformational equilibrium within its lifetime (a prerequisite for the Wagner's mechanism[1a–d]) is unlikely to happen for TIBP.[††]

A problem concerning the Wagner's mechanism[1a–d] is that the competition between conformational interconversion and intersystem crossing in BR is not properly considered. BR lifetimes are usually determined by the isc rate.[25,26] The same drawback of his mechanism was indicated also in the case of the Norrish type II reaction.[27] In the photoenolization mechanism of Scheme 2, the reason for the complete neglect of the direct cyclization of BR to CB (path b in Scheme 1) is unclear. Eventually, in order to accommodate these problems, we wish to propose Scheme 1 as a final mechanism or Scheme 6 as a detailed explanation of Scheme 1.

In Scheme 6, the radical centers of BR are represented as either twisted 90° (tw) or coplanar (co) with the triisopropylphenyl ring. Although the conformers ^{3}co,tw, ^{3}tw,tw, and ^{3}co,co are not stable forms of BR, they are shown in this mechanistic scheme for convenience, because these geometries correspond to nascent species of solution (^{3}co,tw) or solid-state (^{3}tw,tw) hydrogen abstraction and to immediate precursors to products (^{1}co,co to enol and ^{1}tw,tw to CB). The conformer ^{3}tw,co is the most stable form of BR (see Section 2.3). It has a favorable orthogonal geometry for efficient intersystem crossing to occur concomitantly with the reaction (reaction 5 or reaction 6) and this phenomenon is called a coupled spin-flip and bond rotation.[2e,28] The reaction 5 or 6 involves a hypothetical intermediate ^{1}co,co or ^{1}tw,tw, respectively. In crystals or in the case of sterically hindered compounds, the paths leading to the congested molecules ($^{1\text{ or }3}$co,co and *cis*- or *trans*-enol) are

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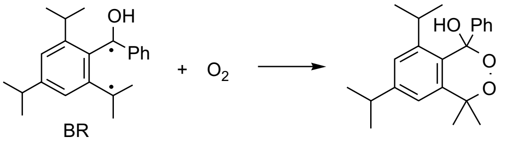
[††] Laser photolysis study of TIBP successfully revealed the existence of the short-lived transients such as ketone triplet (280 ns), *cis*-enol (∼4 μs), and *trans*-enol (>100 μs), but failed to detect BR due to its short lifetime (≪100 ns).[16,17] As pointed out there,[16,17] the BR assignment in our joint work with the laser spectroscopists[24] was found to be in error. The both enols were shown to be unreactive toward molecular oxygen.[16] This fact indicates that it is not the enol but BR that reacts with oxygen (Eq. 4), since TIBP easily afforded the cyclic peroxide upon irradiation in the presence of oxygen.[2f,7] This piece of conclusion is consistent with most of the previously published papers[2e,f,21–23] (and the references cited in Refs. 2e and 2f). Concerning this point, a part of the discussion in Refs. 1a and 1b needs reconsideration.



(4)

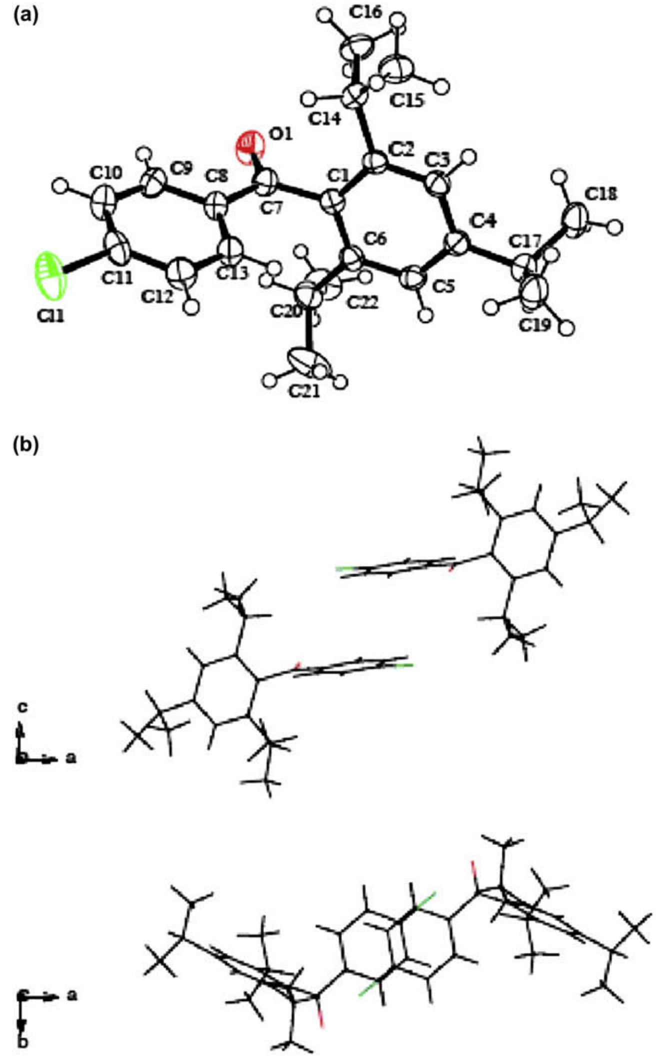


Figure 1. (a) The molecular structure of TIBP-*p*-Cl. (b) The dimeric structure of TIBP-*p*-Cl, where weak π–π interactions exist between the adjacent phenyl-Cl planes; symmetry operation $1-x$, $1-y$, $1-z$, the interplanar distance 3.60 Å. Projections in two directions are shown.

slowed down, and thus a spin-flip leading to ^{1}tw,tw followed by CB formation (Eq. 6) will be faster than the enol formation (Eq. 5).[‡‡]

$$^{3}\text{tw, co}\xrightarrow{\text{isc}}{}^{1}\text{co, co}\rightarrow \textit{cis}\text{- or }\textit{trans}\text{-enol} \qquad (5)$$

$$^{3}\text{tw, co}\xrightarrow{\text{isc}}{}^{1}\text{tw, tw}\rightarrow \text{CB} \qquad (6)$$

3. Conclusion

In conclusion, CB is formed either via *trans*-enol (paths a and d) or through direct cyclization of BR (path b) as shown in Scheme 1. Normally the former route is faster. However, in crystals or in the case of sterically hindered compounds, path b tends to be adopted. Crystalline medium is not a sufficient condition to suppress path a, considering the results that (a) both TEBP-3,4-diCl and TEBP-4-*t*-Bu yielded (*E*)-CB along with (*Z*)-CB (and Inol) even at a low conversion in crystals (Table 3) and (b) mesitaldehydes, which are much less crowded than TIBP, formed *trans*-enols upon irradiation in crystals.[4] Hence, steric hindrance of the molecule is an important factor as well. Finally, as exemplified in this and other articles,[5,9,10,27] the crystalline state can be an important approach to elucidate reaction mechanisms.

4. Experimental

4.1. Instruments and materials

^{1}H and ^{13}C NMR spectra were measured on a JEOL AL-300 or EX-400 spectrometer. Mass and IR spectra were gathered with JEOL JMS-HX 110A and SHIMADZU FTIR-8400 spectrometers, respectively. LC–MS was recorded on a PE SCIEX API-2000 spectrometer. HPLC analyses were performed with a JASCO PU-980 pump and a SHIMADZU SPD-6AV detector (fixed at 217 nm) by using a Cosmosil 5C$_{18}$-AR column (4.6 mm i.d.×150 mm) and were eluted with a mixture of MeOH–H$_2$O. Preparative HPLC was carried out by JAI LC-9101 (fixed at 217 nm) by using a Cosmosil 5C$_{18}$ column (20 mm i.d.×250 mm) and was eluted with MeOH.

2,4,6-Triisopropyl-4′-chlorobenzophenone (TIBP-*p*-Cl) and 2,4,6-trimethylbenzophenone (TMBP) were available from our previous work.[2] These were recrystallized from MeOH and hexane, respectively, prior to use. 2,4,6-Triethylbenzophenones (TEBPs **1a**–**1f** or TEBP-X: X=4-*t*-Bu (**1a**), 4-Cl (**1b**), 3,4-diCl (**1c**), 3,5-diCl (**1d**), 2,4-diCl (**1e**), and 4-CO$_2$Me (**1f**)) were prepared from 1,3,5-triethylbenzene and the corresponding benzoyl chlorides by the Friedel–Crafts reaction as described previously.[2b–d,h]

Spectroscopic data for new TEBPs are as follows.

4.1.1. *2,4,6-Triethyl-4′-tert-butylbenzophenone or (4-tert-butylphenyl)(2,4,6-triethylphenyl)methanone (TEBP-4-t-Bu,* ***1a****)*

Colorless plates, mp 41–42.5 °C (from hexane); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 (2H, d, J=8.6 Hz), 7.41 (2H, d, J=8.6 Hz), 6.94 (2H, s), 2.65 (2H, q, J=7.7 Hz), 2.38 (4H, q, J=7.7 Hz), 1.31 (9H, s), 1.26 (3H, t, J=7.5 Hz), 1.07 (6H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 200.43, 157.22, 144.91, 140.43, 136.35, 135.39, 129.46, 125.53, 125.36, 35.16, 31.09, 28.82, 26.34, 15.53, 15.48; IR (neat) 2964, 1667, 1605, 1279, 934 cm^{-1}; MS (EI^{+}) m/z 322 (M^{+}, 14), 265 (100), 250 (16), 236 (14); HRMS (EI^{+}) calcd for C$_{23}$H$_{30}$O 322.2297, found 322.2291.

4.1.2. *2,4,6-Triethyl-3′,4′-dichlorobenzophenone or (3,4-dichlorophenyl)(2,4,6-triethylphenyl)methanone (TEBP-3,4-diCl,* ***1c****)*

Colorless plates, mp 69.5–70.5 °C (from hexane); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.90 (1H, s),[§§] 7.57 (1H, d, J=8.4 Hz),[§§] 7.49 (1H, d, J=8.4 Hz), 6.96 (2H, s), 2.34 (4H, q, J=7.5 Hz), 1.26 (3H, t, J=7.5 Hz), 1.07 (6H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 198.40, 145.68, 140.53, 138.12, 137.59, 134.78, 133.46, 131.03, 130.83, 128.57, 125.71, 28.79, 26.39, 15.54, 15.37; IR (neat) 2966, 1674, 1580, 1464, 1381, 1283, 1236, 1175, 1031, 946 cm^{-1}; MS (EI^{+}) m/z 336 (M^{+}, 54), 334 (M^{+}, 83), 299 (100), 284 (36), 189 (43); HRMS (EI^{+}) calcd for C$_{19}$H$_{20}$O^{35}Cl^{37}Cl 336.0862, found 336.0862.

4.1.3. *2,4,6-Triethyl-3′,5′-dichlorobenzophenone or (3,5-dichlorophenyl)(2,4,6-triethylphenyl)methanone (TEBP-3,5-diCl,* ***1d****)*

Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.63 (2H, s),[§§] 7.53 (1H, s),[§§] 6.96 (2H, s), 2.66 (2H, q, J=7.6 Hz), 2.34 (4H, q, J=7.6 Hz), 1.27 (3H, t, J=7.5 Hz), 1.07 (6H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 198.04, 145.84, 140.57, 140.47, 135.75, 134.49, 133.13, 127.63, 125.78, 28.80, 26.42, 15.53, 15.32; IR (neat) 2966, 1679, 1566, 1271, 1243, 1178, 873, 806 cm^{-1}; MS (EI^{+}) m/z 336 (M^{+}, 39), 334 (M^{+}, 58), 299 (100), 189 (41); HRMS (EI^{+}) calcd for C$_{19}$H$_{20}$O^{35}Cl^{37}Cl 336.0862, found 336.0856.

[‡‡] As assumed in Ref. 2h, the step BR(=enol triplet)→CB can even be a symmetry-allowed disrotatory ring-closure.

[§§] Each peak is finely split (J=1–2 Hz).

Table 4
Summary for the photoreactivity of TIBPs in the solid state[3a–c]

TIBP-X	*p*-OMe	*m*-OMe	*p*-*t*-Bu	*p*-Me	H	*p*-Cl	*p*-CO_2Me	*m*-CO_2Me	*p*-CO_2Et	*p*-CO_2H	*p*-COCl	*m*-COCl	*p*-COA^S
Irrad time (h)	2	2	2	2	4	8	10	2	4	4	10	4	5
Conv (%)	100	100	100	100	100	89	0	100	76	28	0	35	96

*4.1.4. 2,4,6-Triethyl-2′,4′-dichlorobenzophenone or (2,4-dichlorophenyl)(2,4,6-triethylphenyl)methanone (TEBP-2,4-diCl, **1e**)*

Colorless oil (this contains an impurity in 9%, which is probably 2,4,5-triethyl-2′,4′-dichlorobenzophenone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (1H, s),[§§] 7.40 (1H, d, J=8.4 Hz), 7.21 (1H, d, J=8.4 Hz),[§§] 6.93 (2H, s), 2.64 (2H, q, J=7.6 Hz), 2.41 (4H, q, J=7.6 Hz), 1.24 (3H, t, J=7.6 Hz), 1.08 (6H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.84, 146.00, 141.03, 138.53, 136.21, 135.65, 134.55, 133.33, 131.55, 126.98, 125.96, 28.78, 26.51, 15.56, 15.31; IR (neat) 2966, 1682, 1582, 1462, 1373, 1285, 1236, 932, 874 cm^{-1}; MS (EI$^+$) *m*/*z* 336 (M$^+$, 9), 334 (M$^+$, 14), 299 (100), 284 (19), 270 (17); HRMS (EI$^+$) calcd for $C_{19}H_{20}O^{35}Cl^{37}Cl$ 336.0862, found 336.0857.

*4.1.5. 2,4,6-Triethyl-4′-methoxycarbonylbenzophenone or methyl 4-(2,4,6-triethylbenzoyl)benzoate (TEBP-4-CO_2Me, **1e**)*

A colorless viscous substance; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (2H, d, J=8.8 Hz), 7.84 (2H, d, J=8.8 Hz), 6.96 (2H, s), 3.92 (3H, s), 2.66 (2H, q, J=7.6 Hz), 2.35 (4H, q, J=7.5 Hz), 1.26 (3H, t, J=7.6 Hz), 1.05 (6H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.15, 166.24, 145.51, 141.06, 140.57, 135.46, 134.19, 129.88, 129.32, 125.65, 52.44, 28.79, 26.39, 15.52, 15.39; IR (neat) 2966, 1728, 1674, 1276, 1105, 933, 729 cm^{-1}; MS (EI$^+$) *m*/*z* 324 (M$^+$, 45), 309 (36), 265 (100); HRMS (EI$^+$) calcd for $C_{21}H_{24}O_3$ 324.1725, found 324.1722.

4.2. Photolysis of TEBPs and TMBP

Irradiation was carried out with a 400-W high-pressure mercury lamp. A solution of TEBP or TMBP in benzene or MeCN (ca. 0.01 M, 5–100 mL) was placed in a suitable Pyrex tube. After bubbling Ar gas for 0.5–0.6 h, the tube was sealed with a rubber septum and was irradiated at 10 or 2 °C. The temperature controls were conducted by thermostated circulating water. In the case of the solid-state photolysis, a crystal sample (10–120 mg) was crushed and sandwiched between two Pyrex plates, then set in a special photolysis vessel[6] and was irradiated under the stream of Ar gas at 2–3 °C.

The yields of photoproducts were determined by direct ^{1}H NMR and HPLC analyses of the photolysate. When necessary for structural identification of the photoproducts, they were separated by preparative TLC (Merck silica gel 60-PF_{254}, 2 mm, hexane–AcOEt) or by preparative TLC and subsequent preparative HPLC. Their spectroscopic data are described below.

4.3. Characterization of the photoproducts

*4.3.1. Products from TEBP-4-t-Bu (**1a**)*

A photolysate from 3.5 h irradiation of 458 mg of **1a** in benzene (100 mL) was separated with preparative TLC (12:1 hexane–AcOEt) to afford 298 mg (65% yield) of (*E*)-1-(4-*tert*-butylphenyl)-4,6-diethyl-2-methyl-1,2-dihydrobenzocyclobuten-1-ol ((*E*)-CB-4-*t*-Bu, **2a**) as a colorless viscous substance.

*4.3.1.1. Compound **2a**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (2H, d, J=8.8 Hz),[§§] 7.17 (2H, d, J=8.8 Hz),[§§] 6.98 (1H, s), 6.88 (1H, s), 3.61 (1H, q, J=7.2 Hz), 2.65 (2H, q, J=7.6 Hz), 2.62–2.43 (2H, m), 1.29 (9H, s), 1.25 (3H, t, J=7.5 Hz), 1.17 (3H, t, J=7.5 Hz), 0.82 (3H, d, J=7.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.08, 147.37, 146.42, 141.73, 139.57, 138.23, 127.06, 126.37, 124.76, 119.41, 84.58, 54.66, 34.45, 31.36, 29.69, 24.86, 15.99, 15.42, 14.81; IR (neat) 3385, 2961, 1463, 1200, 1056, 1017, 822 cm^{-1}; MS (FAB$^+$) *m*/*z* 321 (M$^+$−1, 80), 305 (100), 265 (45); HRMS (FAB$^+$) calcd for $C_{23}H_{29}O$ 321.2218, found 321.2212.

A combined photolysate from the four experiments of the solid-state photolysis of **1a** (irradiation time 0.2–2 h, total weight ca. 130 mg) was separated with preparative TLC (20:1 hexane–AcOEt) to afford 96 mg of recovered **1a**, 12 mg of a mixture of (*Z*)-CB (**3a**) and Inol (**5a**), and 17 mg of a mixture of **5a** and (*E*)-CB (**2a**). The latter two fractions were further separated with repeated preparative HPLC to

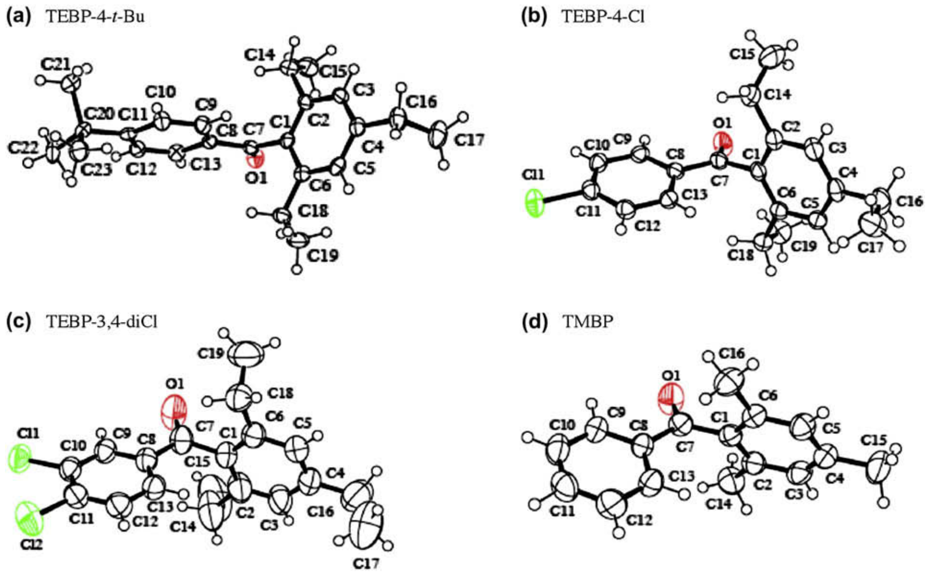


Figure 2. The molecular structures of (a) TEBP-4-*t*-Bu, (b) TEBP-4-Cl, (c) TEBP-3,4-diCl, and (d) TMBP.

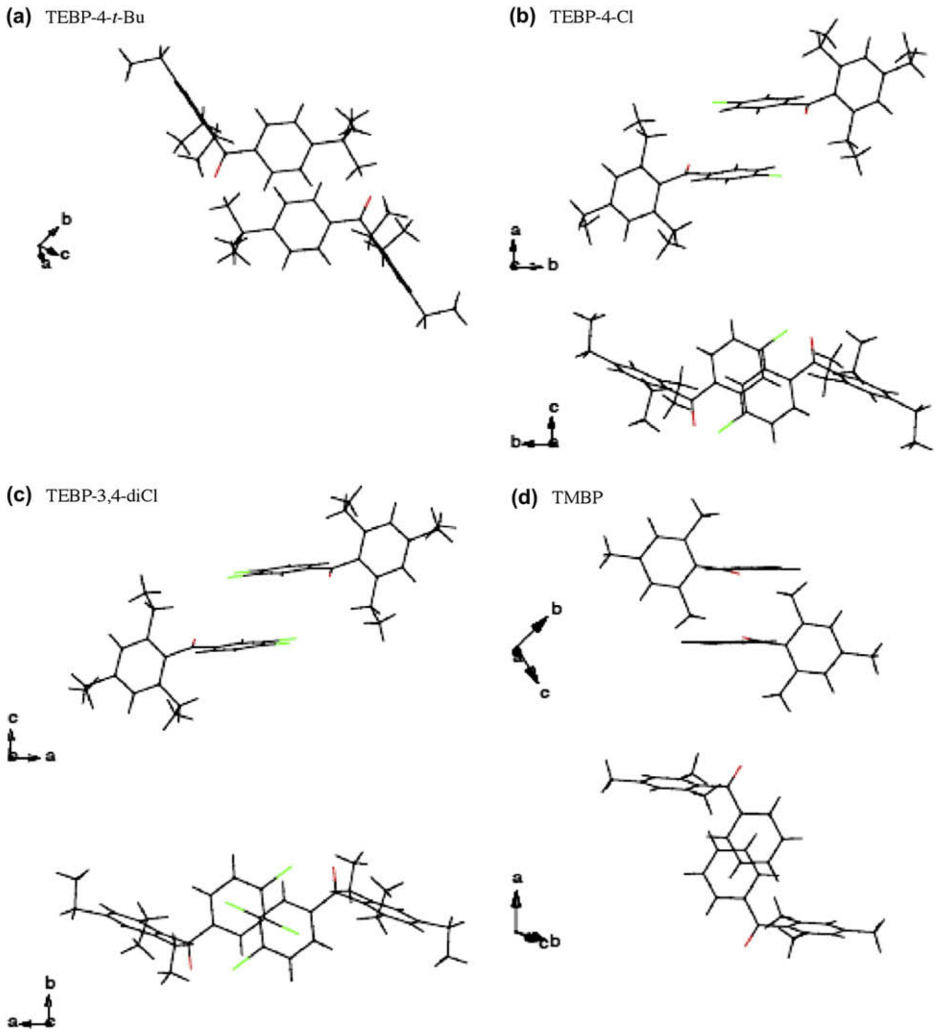


Figure 3. The dimeric structures of (b) TEBP-4-Cl, (c) TEBP-3,4-diCl, and (d) TMBP, where π–π interactions exist between the neighboring phenyl-X planes; symmetry operations $1-x, 1-y, 1-z$; $1-x, -y, 1-z$; and $-x, -y, -z$, respectively, the interplanar distances 3.14, 3.39, and 3.66 Å, respectively. Projections in two directions are shown. For (a) TEBP-4-*t*-Bu, the dimeric interactions do not exist between the neighboring phenyl-X planes (symmetry operation $1-x, 1-y, 1-z$), because they are much slipped aside.

isolate **3a** and **5a**, affording 8 mg of **3a** and 10 mg of a mixture of **5a** and **2a** (molar ratio 75:25). Both of these isolated samples were contaminated with a small amount of the fillings of the preparative HPLC column. Inol (**5a**) was gradually dehydrated during the separation treatments (e.g., in $CDCl_3$ or under the preparative HPLC conditions), giving an indene derivative In (**6a**), which was further decomposed to insoluble white materials in several days.

4.3.1.2. (Z)-1-(4-tert-Butylphenyl)-4,6-diethyl-2-methyl-1,2-dihydrobenzocyclobuten-1-ol ((Z)-CB-4-t-Bu, ***3a****).* A colorless substance; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, d, J=8.8 Hz), 7.27 (2H, d, J=8.3 Hz), 6.93 (1H, s), 6.87 (1H, s), 3.58 (1H, q, J=7.3 Hz), 2.64 (2H, q, J=7.5 Hz), 2.56–2.40 (2H, m), 2.37 (1H, s, OH), 1.37 (3H, d, J=7.3 Hz), 1.28 (9H, s), 1.24 (3H, t, J=7.6 Hz), 1.10 (3H, t, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.68, 148.38, 146.34, 143.31, 141.53, 139.49, 127.15, 125.03, 124.55, 119.25, 81.89, 53.45, 34.41, 31.36, 29.70, 24.71, 15.95, 14.71, 14.60; IR (neat) 3469, 2962, 2913, 1205, 1179, 1066, 1014, 915, 816 cm^{-1}; MS (FAB$^+$) m/z 321 (M$^+$−1, 17), 305 (100), 265 (49); HRMS (FAB$^+$) calcd for $C_{23}H_{29}O$ 321.2218, found 321.2220.

4.3.1.3. 1-(4-tert-Butylphenyl)-5,7-diethylindan-1-ol (Inol, ***5a****).* A colorless substance; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, J=8.5 Hz), 7.19 (2H, d, J=8.3 Hz), 6.96 (1H, s), 6.89 (1H, s), 3.04–2.97 (1H, m), 2.88–2.80 (1H, m), 2.64 (2H, q, J=7.5 Hz), 2.52–2.35 (3H, m), 2.32–2.22 (1H, m), 1.28 (9H, s), 1.24 (3H, t, J=7.6 Hz), 0.93 (3H, t, J=7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.28, 145.12, 144.43, 144.20, 141.99, 141.31, 127.22, 124.85, 124.75, 121.58, 86.24, 46.57, 34.37, 31.37, 29.71, 28.78, 24.31, 15.67, 14.79; ^{1}H NMR (400 MHz, CD_3COCD_3) δ 7.30 (2H, d, J=8.8 Hz), 7.21 (2H, d, J=8.8 Hz), 6.94 (1H, s), 6.86 (1H, s), 3.01–2.93 (1H, m), 2.85–2.77 (1H, m), 2.61 (2H, q, J=7.4 Hz), 2.49–2.35 (3H, m), 2.34–2.24 (1H, m), 1.28 (9H, s), 1.21 (3H, t, J=7.5 Hz), 0.86 (3H, t, J=7.5 Hz); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 149.37, 146.62, 145.20, 144.81, 143.96, 142.16, 127.79, 125.65, 125.27, 122.04, 85.98, 47.25, 34.81, 31.69, 30.08, 29.35, 24.82, 16.30, 15.19; MS (FAB$^+$) m/z 321 (M$^+$−1, 11), 305 (100), 265 (16); HRMS (FAB$^+$) calcd for $C_{23}H_{30}O$ 322.2297, found 322.2293.

Table 5

The intramolecular distances between the carbonyl O and the *o*-alkyl α-Hs or *o*-Et β-Hs at both *ortho* positions for the crystals analyzed here

	O···α-H (Å)		O···β-H (Å)	
	O1···H14	O1···H18	O1···H15	O1···H19
TEBP-4-*t*-Bu	3.09	3.23	2.84	2.68
TEBP-4-Cl	2.95	3.16	3.67	2.88
TEBP-3,4-diCl	3.13	3.16	2.81	3.30
TMBP	2.47	3.37 (O1···H16)	—	—
TIBP-*p*-Cl	2.93	3.03 (O1···H20)	—	—

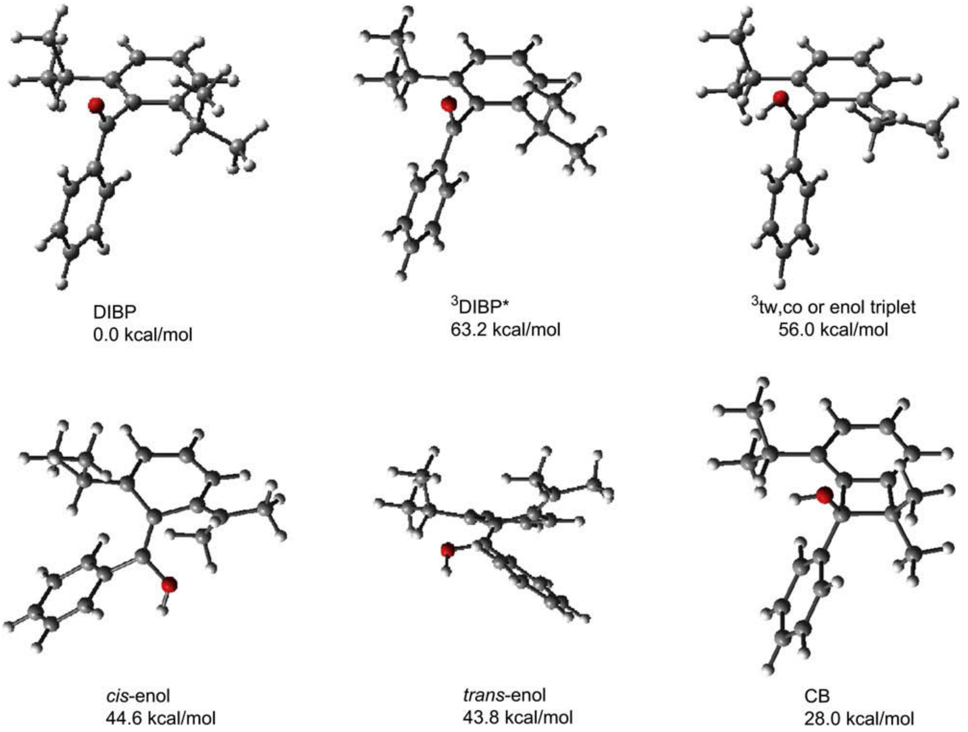


Figure 4. DFT calculations on 2,6-diisopropylbenzophenone (DIBP) and on the possible intermediates and products formed photochemically thereof.

4.3.1.4. 3-(4-tert-Butylphenyl)-4,6-diethylindene (In, ***6a****).* A colorless substance; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (2H, d, J=8.4 Hz), 7.28 (2H, d, J=8.4 Hz), 7.20 (1H, s), 6.91 (1H, s), 6.26 (1H, t, J=2.0 Hz), 3.40 (2H, d, J=2.0 Hz), 2.67 (2H, q, J=7.5 Hz), 2.38 (2H, q, J=7.5 Hz), 1.35 (9H, s), 1.26 (3H, t, J=7.5 Hz), 0.88 (3H, t, J=7.5 Hz); LC–MS (Inertsil ODS-3, acetonitrile, ESI^+) m/z 305 (M^++1, 100).

*4.3.2. Products from TEBP-3,4-diCl (**1c**)*

A photolysate from 3 h irradiation of 329 mg of **1c** in benzene (75 mL) was separated with preparative TLC (15:1 hexane–AcOEt) to afford 230 mg (70% yield) of (*E*)-1-(3,4-dichlorophenyl)-4,6-diethyl-2-methyl-1,2-dihydrobenzocyclobuten-1-ol ((*E*)-CB-3,4-diCl, **2c**) as a colorless viscous substance. This isolated **2c** contained as an

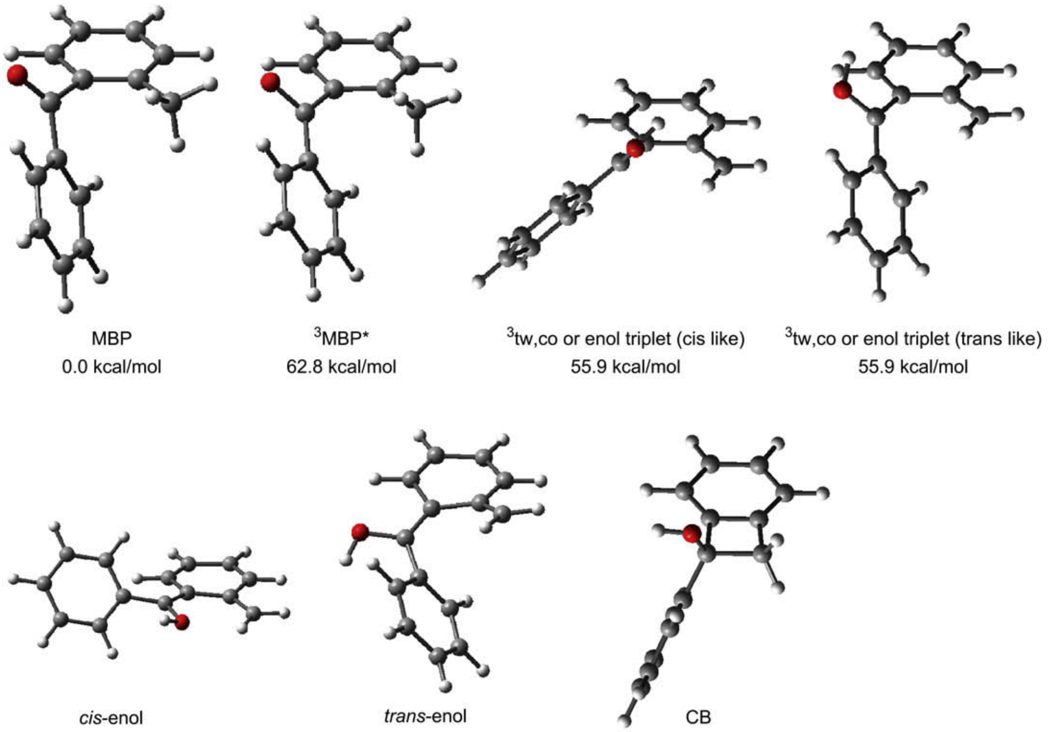


Figure 5. DFT calculations on 2-methylbenzophenone (MBP) and on the possible intermediates and products formed photochemically thereof.

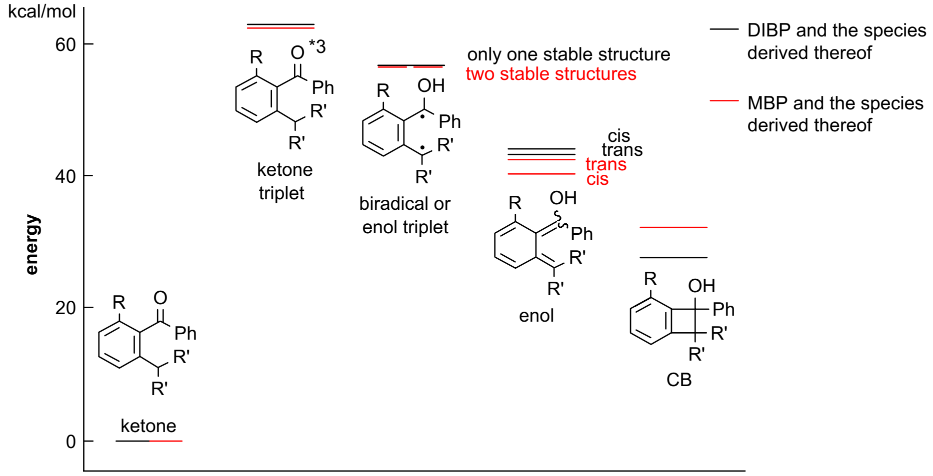
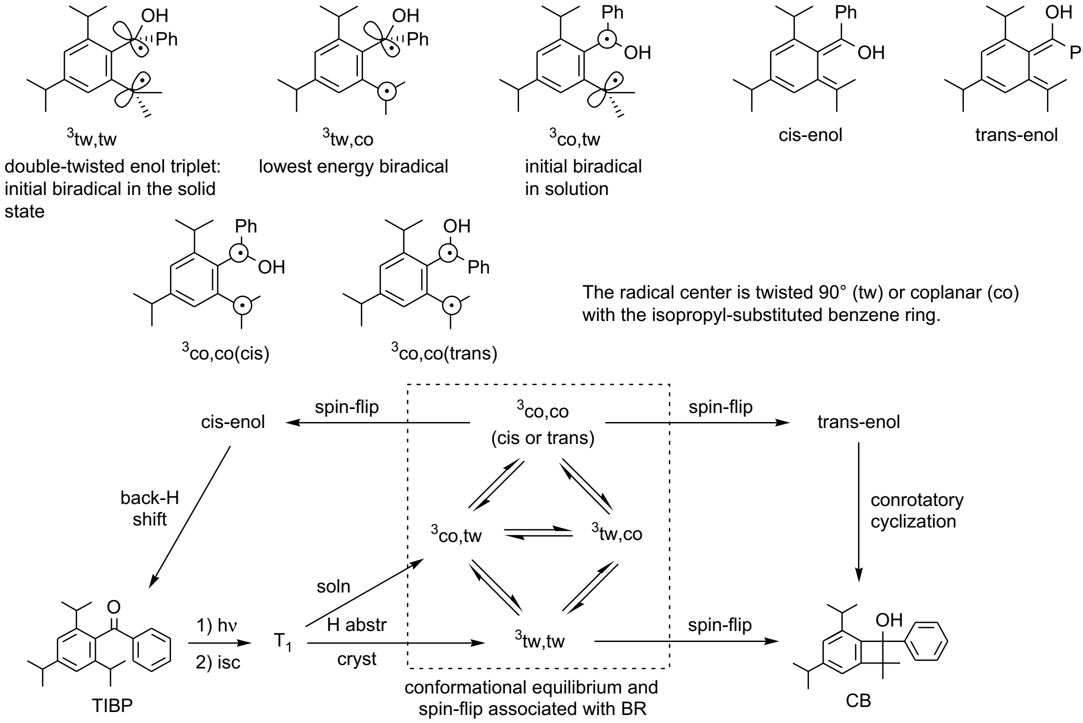


Figure 6. Potential energies relative to the ketone ground state.

impurity a tiny amount of (*Z*)-1-(3,4-dichlorophenyl)-4,6-diethyl-2-methyl-1,2-dihydrobenzocyclobuten-1-ol ((*Z*)-CB-3,4-diCl, **3c**). The **3c** content was increased by repeated preparative TLC to afford 43 mg of a colorless mixture of **3c** and **2c** (molar ratio 16:84). Further purification of **3c** was not attempted.

*4.3.2.1. Compound **2c**.* ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 (1H, s),[§§] 7.35 (1H, d, J=8.1 Hz), 7.03 (1H, d, J=8.2 Hz),[§§] 6.99 (1H, s), 6.89 (1H, s), 3.60 (1H, q, J=7.2 Hz), 2.655 (2H, q, J=7.6 Hz), 2.56–2.38 (2H, m), 2.28 (1H, br), 1.255 (3H, t, J=7.6 Hz), 1.13 (3H, t, J=7.5 Hz), 0.85 (3H, d, J=7.0 Hz); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 147.14, 147.08, 141.95, 140.69, 139.45, 132.19, 131.21, 129.79, 128.67, 127.61, 126.17, 119.61, 83.62, 55.28, 29.68, 24.76, 15.92, 15.25, 14.70; IR (neat) 3385, 2964, 1471, 1378, 1198, 1030, 817 cm^{-1}; MS (FAB^{+}) m/z 335 (45), 333 (66), 317 (100); MS HR(FAB^{+}) calcd for $C_{19}H_{21}O^{35}Cl_2$ 335.0969, found 3335.0959.

*4.3.2.2. Compound **3c**.* ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 (1H, s),[§§] 7.33 (1H, d, J=8.1 Hz), 7.12 (1H, d, J=8.2 Hz),[§§] 6.95 (1H, s), 6.93 (1H, s), 3.53 (1H, q, J=7.2 Hz), 2.645 (2H, q, J=7.6 Hz), ca. 2.55–2.36 (2H, m), 1.36 (3H, d, J=7.0 Hz), 1.25 (3H, t, J=7.6 Hz), 1.07 (3H, t, J=7.5 Hz).



The radical center is twisted 90° (tw) or coplanar (co) with the isopropyl-substituted benzene ring.

Hypothetical BR conformers ^{3}tw,tw and ^{3}co,co are taken into consideration, because a spin-flip to reactive ^{1}BR may be competitive with the conformational interconversions of BR. In crystals or in the case of the sterically crowded compounds, the spin-flip may be faster than the conformational equilibrium.

Scheme 6. Detailed photocyclization mechanism proposed for TIBP: idealized conformations of BR and their notations are illustrated.

Table 6
Crystallographic parameters

	TIBP-*p*-Cl	TEBP-4-*t*-Bu	TEBP-4-Cl	TEBP-3,4-diCl	TMBP
Empirical formula	$C_{22}H_{27}OCl$	$C_{23}H_{30}O$	$C_{19}H_{21}OCl$	$C_{19}H_{20}OCl_2$	$C_{16}H_{16}O$
Formula weight	342.91	322.49	300.83	335.27	224.30
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*Pbca* (#61)	*C*2/*c* (#15)	*P*2$_1$/*c* (#14)	*Pbca* (#61)	*P*$\bar{1}$ (#2)
a (Å)	16.4264(11)	20.977(2)	10.4106(4)	17.0159(6)	7.8788(7)
b (Å)	11.5254(7)	8.8971(8)	15.8700(7)	10.8347(4)	8.2646(7)
c (Å)	20.5096(14)	22.7043(19)	10.7195(4)	19.1795(9)	10.7054(9)
α (°)	—[a]	—[a]	—[a]	—[a]	100.877(2)
β (°)	—[a]	110.152(2)	110.9680(13)	—[a]	91.960(2)
γ (°)	—[a]	—[a]	—[a]	—[a]	108.996(2)
V (Å^3)	3882.9(4)	3978.0(6)	1653.75(12)	3536.0(2)	643.85(9)
Z	8	4	4	8	2
D_{calcd} (g/cm^3)	1.173	1.077	1.208	1.259	1.157
No. observations	4434	4564	3782	4017	2557
No. variables	326	339	215	220	191
R_1	0.0647	0.0758	0.0588	0.0774	0.0729
wR_2	0.1589	0.2761	0.1928	0.2623	0.289
GOF	1.038	1.110	1.115	1.080	1.034

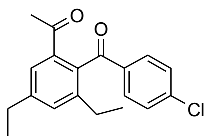
[a] 90° by definition.

4.3.3. Products from TEBP-4-Cl (**1b**)

The photocyclization of **1b** in benzene into (*E*)-1-(4-chlorophenyl)-4,6-diethyl-2-methyl-1,2-dihydrobenzocyclobuten-1-ol ((*E*)-CB-4-Cl, **2b**) was previously studied.[2h] The isolated **2b** contained a tiny amount of (*Z*)-CB-4-Cl (**3b**), characteristic peaks of which were clearly visible at δ 1.35 (3H, d, J=7.3 Hz) and other regions (δ 6.94 (1H, s), 6.92 (1H, s), 3.53 (1H, q, J=7.2 Hz)).

*4.3.3.1. Compound **2b**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (2H, d, J=8.8 Hz), 7.18 (2H, d, J=8.8 Hz), 6.98 (1H, s), 6.89 (1H, s), 3.60 (1H, q, J=7.2 Hz), 2.65 (2H, q, J=7.6 Hz), 2.53–2.41 (2H, m), 1.24 (3H, t, J=7.7 Hz), 1.13 (3H, t, J=7.7 Hz), 0.82 (3H, d, J=7.0 Hz).

When the photolysis was carried out under bubbling of Ar (not in the closed system as above), a considerable amount of 2-(4-chlorobenzoyl)-3,5-diethylacetophenone (**9**) was produced. Residual oxygen in Ar is probably responsible for the formation of **9**. Thus, a photolysate from 2 h irradiation of 302 mg of **1b** in benzene (75 mL) was separated with repeated preparative TLC (15–10:1 hexane–AcOEt) to afford 194 mg (64%) of **2b**, 24 mg (8%) of 6-chloro-1,3-diethyl-10-methylanthrone (**4b**) containing 13 mg (4%) of recovered **1b**, and 25 mg (8%) of **9**. Unlike the related anthrones, which were previously reported,[2d,e,g,h] anthrone **4b** was not very stable on silica gel. Therefore, the above mixture of **4b** and **1b** (molar ratio 63:37) could not be further separated by preparative TLC.



9

*4.3.3.2. Compound **4b**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (1H, d, J=8.4 Hz), 7.40 (1H, s),[§§] 7.35 (1H, d, J=8.4 Hz),[§§] 7.11 (1H, s), 7.06 (1H, s), 4.16 (1H, q, J=7.2 Hz), 3.19 (2H, q, J=7.2 Hz), 2.69 (2H, q, $J\sim$7.2 Hz), 1.52 (3H, d, J=7.3 Hz), 1.31–1.24 (6H, m).

*4.3.3.3. Compound **9**.* A pale yellow substance; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (2H, d, J=8.6 Hz), 7.59 (1H, s), 7.34 (2H, d, J=8.6 Hz), 7.34 (1H, s), 2.75 (2H, q, J=7.6 Hz), 2.49 (3H, s), 2.41 (2H, q, J=7.6 Hz), 1.31 (3H, t, J=7.7 Hz), 1.07 (3H, t, J=7.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.98, 197.75, 145.45, 142.22, 138.98, 136.99, 136.52, 136.12, 133.23, 129.79, 128.81, 127.32, 28.63, 26.96, 25.88, 15.51, 15.41; IR (neat) 2967, 1680, 1586, 1284, 1256, 1089, 932 cm^{-1}; MS (EI$^+$) *m*/*z* 314 (M$^+$, 100), 299 (51), 279 (60), 203 (82); HRMS (EI$^+$) calcd for $C_{19}H_{19}O_2{}^{35}Cl$ 314.1073, found 314.1073.

4.4. X-ray crystal structure analysis

The diffraction data were collected at −100±1 °C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation to a maximum 2θ value of 54.9°. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[29] and expanded using Fourier techniques.[30] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Some hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[31] crystallographic software package except for refinement, which was performed using SHELXL-97.[32] The crystal structure parameters for TIBP-*p*-Cl, TEBP-4-*t*-Bu, TEBP-4-Cl, TEBP-3,4-diCl, and TMBP are summarized in Table 6. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 704821–704825, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.5. Computational methods

The B3LYP functional was used for the DFT calculation of 2,6-diisopropylbenzophenone (DIBP) and 2-methylbenzophenone (MBP), and of the possible intermediates and products formed photochemically thereof (i.e., ketone triplet, biradical, enol triplet, *trans*- and *cis*-enols, and benzocyclobutenol). All of the possible conformations in the biradical triplet state (^{3}co,tw, ^{3}tw,co, and ^{3}tw,tw) were considered as the initial guess of the geometry optimization. In DIBP, the three starting structures converged a ^{3}tw,co structure (see Fig. 4). In MBP, two ^{3}tw,co structures having cis-like and trans-like conformations (see Fig. 5) were obtained, although the potential energies of the cis- and trans-like structures are very similar to each other (see Fig. 5). The 6-31G(d) basis set was used for the optimization of the geometry. Computations were performed using Gaussian03 package.[33–35]

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