A Tandem Hexaannulation Reaction of Benzyllithium Involving Base-Induced Cyclodehydrogenation

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Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

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The reaction of the tribenzo[3.3.3]propellane ketone **1** (triptindan-9-one) with benzyllithium/TMEDA affords an efficient one-pot *peri* annulation of a dihydronaphthalene across two wings of the propellane framework. The key step of this surprising tandem reaction was determined to be a nucleophilic cyclization of (*Z*)-9-benzylidenetriptindane (**4**) with concomitant hydride elimination. The formation of the novel centrotetracyclo[5.5.5.6] framework bearing a distorted (*E*)-stilbene unit was confirmed by single-crystal X-ray structure analysis.

Introduction

Our research into the chemistry of polycyclic hydrocarbons during the last decade has resulted in the systematic development of novel carbon frameworks containing centrically fused indane units, the centropolyindanes.[1] Special interest was directed to derivatives of triptindane **2**, the congener representing the C_{3v}-symmetrical tribenzo[3.3.3]propellane.[2][3] The conformationally flexible, three-dimensional molecular framework of **2** bears a high potential for further annulation reactions.[4] Thus, several three-fold C−C coupling reactions using the corresponding triketone led us to the syntheses of various centrohexacyclic propellanes.[1a,1c,1d,4a,4b] In a recent investigation that was aimed at the synthesis of three-fold phenanthro-anellated [3.3.3]propellanes,[4c,5] we prepared 9-benzylidenetriptindane **4** by Grignard reaction of benzyl bromide with triptindan-9-one (**1**)[3] followed by dehydration. Subsequent photocyclodehydrogenation of **4** gave the dibenzophenanthro-anellated propellane **5** in high yield.[5] In an attempt to replace the Grignard reagent by benzyllithium/TMEDA, we encountered an unexpected tandem reaction[6] (**1** → **3**, Scheme **1**), which formally consists of a condensation/cyclodehydrogenation sequence leading to an isomer of **5**, viz. the *trifuso*-tetracyclic propellane **3**. In this paper, we wish to report on this surprising *peri*-annulation reaction, some properties of the new hydrocarbon **3**, and on the mechanistic key step of its formation.

Results and Discussion

Alkylation/Cyclodehydrogenation Reaction of Triptindanone 1

The organolithium reagent was generated in situ by a transmetallation reaction between *n*-butyllithium (in hexanes) and toluene, the latter being also used as the solvent. An equimolar amount of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added to accelerate the reaction.[7][8] By adding a toluene solution of ketone **1** to a twenty-fold molar excess of the benzyllithium/TMEDA reagent in toluene, the typical orange color of the benzyllithium solution[9] changed rapidly to deep green and a voluminous black crystalline precipitate formed on the surface of the reaction flask. Aqueous workup of the reaction mixture followed by MPLC purification furnished a colorless, crystalline solid that proved to be distinct from the two expected products, 9-benzyltriptindan-9-ol (**6**) and 9-benzylidenetriptindan (**4**).[5] Spectroscopic analysis suggested the formation of the novel naphtho[1,2]-anellated [3.3.3]propellane, viz. hydrocarbon **3**, in which the benzylidene group has formed a new six-membered ring incorporating another benzylic position (C-10 or C-11) of the triptindane framework. X-ray single-crystal structure analysis confirmed the identity of the compound.

Spectroscopy and Molecular Structure of 3

The EI mass spectrum of **3** exhibits the highest mass signal as the base peak at *m*/*z* 380, indicating a molecular mass 2 Da lower than that of olefin **4** or the mass of the $[M - H_2O]^+$ fragment ion of the corresponding triptindanol **6** (see below). Besides the peak at *m*/*z* 289, corresponding to the loss of a benzyl radical to give ions $[M - C_7H_7]^+$, peaks

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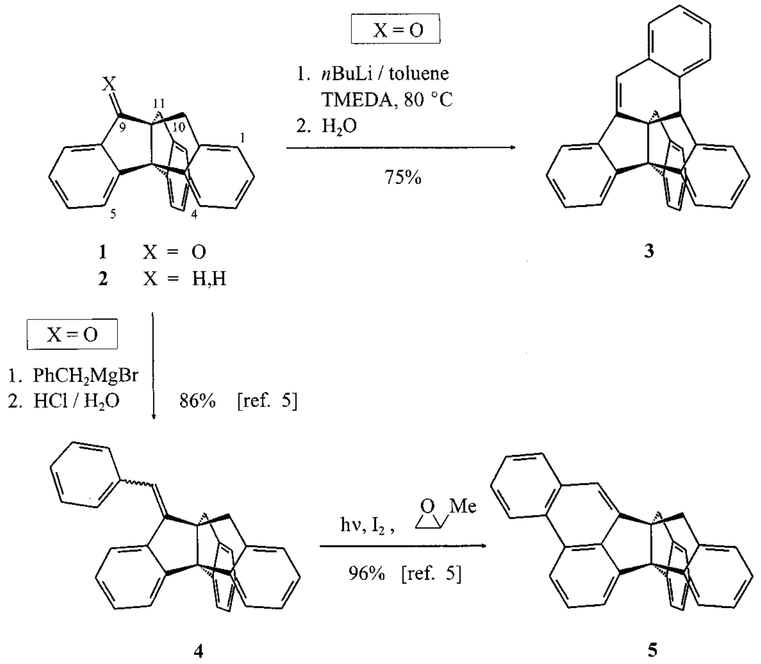


Scheme 1

at m/z 303 ($[M - C_6H_5]^+$) and m/z 302 ($[M - C_6H_6]^{+\bullet}$) are conspicuous. These fragmentations are much less pronounced for **3** than for the noncyclized olefin **4** and are of similarly low prominence as in the case of **5**. Expulsion of benzene after intramolecular isomerization of ionized alkylbenzenes (both in $M^{+\bullet}$ and $[M + H]^+$ ions) is known to reflect structural features.[10]

The ^{1}H-NMR spectrum of **3** shows the AB pattern of one methylene group only (14-CH$_2$) and, in addition, a characteristic singlet for a benzhydrylic methine group (13b-CH). Furthermore, a sharp singlet at $\delta = 6.78$ indicates the presence of a styryl proton (9-H). Among the arene signals, six distinct doublet resonances were found, among which one appears at high field ($\delta = 6.96$) and five at low field ($\delta = 7.42-7.66$). Three low-field doublets ($\delta = 7.56$, 7.64 and 7.66) exhibit mutual Nuclear Overhauser effects characteristic of the three protons in the molecular cavity of the triptindane skeleton (4-H, 5-H, 18-H). The ^{13}C-NMR spectrum of **3** corroborates its structure since it shows the maximum possible nine signals for quaternary arene and olefinic carbon atoms and 14 of 17 possible lines for tertiary arene and olefinic carbon atoms. Finally, two quaternary, one tertiary and one secondary signal in the aliphatic region were found, in accordance with the suggested structure of **3**.

Both the crystals and solutions of polycycle **3** exhibit a strong fluorescence upon irradiation at 366 nm. This finding can be traced to the unusual *peri* anellation of a 1,2-dialine to a C_s-diindane (4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene),[1] which gives rise to considerable distortion of the *trans*-stilbene unit about its olefinic double bond. In fact, X-ray single-crystal structure analysis of **3** (Figure 1, Tables 1 and 2) reveals a torsional angle of [C(8a)−C(8b)−C(9)−C(9a)] = 167.2°.[11] The indane "wing" of the triptindane backbone that makes part of the stilbene unit is forced into an envelope-like conformation. This is evident from the torsion about the C(4b)−C(8c) single bond, i.e. the propellane axis of **3**, as indicated by [C(8a)−C(8b)−C(8c)−C(4b)] = 28.7°.[11] Whereas the mean value of three equivalent torsion angles in the parent triptindane **2** is 22.8°,[12] the average of the three torsion angles about the propellane axis of **3** amounts to 29.4°.[11]

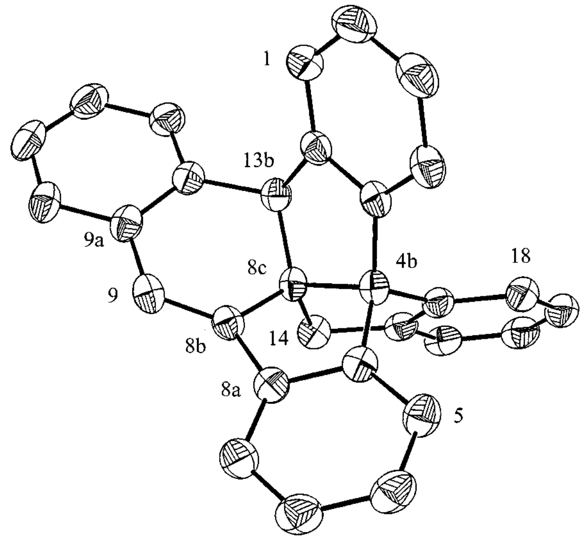


Figure 1. X-ray molecular structure of compound **3** (ORTEP plot), viewed onto the concave side of the *trifuso*-tricyclo[5.5.6] part of the *trifuso*-centrotetracyclo[5.5.5.6] framework; hydrogen atoms are not shown

From these findings, the structure of **3** has been elucidated unequivocally. Hydrocarbon **3** represents a novel polycyclic carbon framework that may be classified as a benzoanellated *trifuso*-centrotetracyclane.[13] This rare class

Table 1. Crystal data and structure refinement for compound **3**

	3
Empirical formula	$C_{30}H_{20}$
Molecular mass	380.46
Crystal color and habit	colorless, irregular
Crystal size [mm]	0.60 × 0.40 × 0.30
T [K]	173(2)
Wavelength (graphite monochromator) [Å]	0.71073
Space group	$P\bar{1}$
a [Å]	8.9780(10)
b [Å]	10.645(2)
c [Å]	11.874(2)
α [°]	108.400(10)
β [°]	94.920(10)
γ [°]	109.830(10)
V [Å^3]	989.0(3)
Z	2
$D_{\mathrm{calcd.}}$ [mg/m^3]	1.278
Absorption coefficient [mm^{-1}]	0.072
$F_{(000)}$	400
Range for data collection [°]	1.85−25.05
hkl range (min./max.)	0/10, −12/11, −14/14
Reflections collected	3721
Independent reflections	3480
R_{int}	0.0334
Absorption correction	none
Data/restraints/parameters	3473/0/271
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$], wR_2	R_1 = 0. 0437 for 2754 reflections, 0.1014
R indices (all data),wR_2	0.0606, 0.1171
Largest and mean Δ/σ	0.000 and 0.000
Largest diff. peak and hole [eÅ^{-3}]	0.2 and −0.2

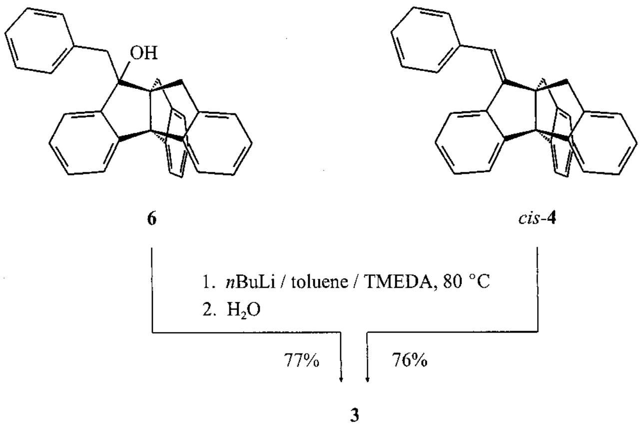
Table 2. Selected C−C bond lengths [Å] and bond angles [°] for compound **3**

C(8c)−C(4b)	1.560(2)
C(8c)−C(8b)	1.514(2)
C(8c)−C(13b)	1.536(2)
C(8c)−C(14)	1.546(2)
C(4b)−C(4a)	1.516(2)
C(4b)−C(4c)	1.521(2)
C(4b)−C(18a)	1.519(2)
C(8b)−C(8a)	1.468(2)
C(8b)−C(9)	1.336(2)
C(9)−C(9a)	1.459(2)
C(13b)−C(13a)	1.517(2)
C(13b)−C(13c)	1.526(2)
C(4b)−C(8c)−C(8b)	102.74(13)
C(4b)−C(8c)−C(13b)	106.68(13)
C(4b)−C(8c)−C(14)	104.77(13)
C(8b)−C(8c)−C(13b)	112.04(13)
C(8b)−C(8c)−C(14)	115.54(14)
C(13b)−C(8c)−C(14)	113.74(14)
C(8a)−C(8b)−C(9)	130.0(2)
C(8a)−C(8b)−C(8c)	106.78(13)
C(8b)−C(9)−C(9a)	121.3(2)
C(9)−C(8b)−C(8c)	122.3(2)

of polycycles is characterized by four rings that are mutually fused at three C−C bonds of a neopentane core. They may also be considered [*m.n.o*]propellanes bearing an additional ring that is *peri*-fused across two of its wings. Apart from *trifuso*-centrotetraindane,[14] a regular centropolyindane[1a,15] bearing four indane units anellated in this way, as well as some related cyclopenta-anellated [4.3.3]propellanes were reported recently.[16][17]

Mechanism of Cyclodehydrogenation

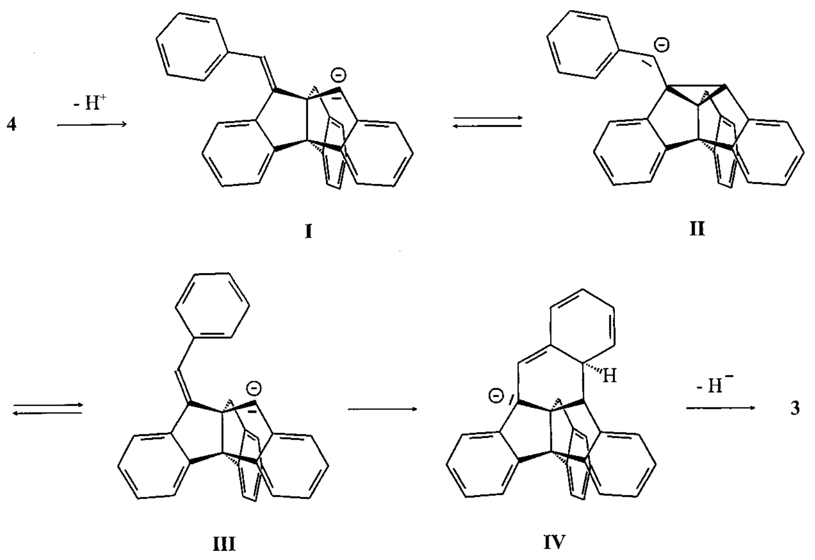
The formation of polycycle **3** from triptindan-9-one (**1**) and benzyllithium is very surprising. Formation of **3** requires incorporation of a methylene group of the triptindane framework into the newly formed ring with concomitant hydride elimination, in contrast to the photochemically induced cyclodehydrogenation of **4** to **5**.[5] In fact, 9-benzylidenetriptindane (**4**) turned out to be the reactive intermediate of the base-induced cyclodehydrogenation to **3**, as will be shown below.



Scheme 2

Olefinic hydrocarbons have been dehydrogenated by metallation/elimination.[18] The driving force for the reaction is the favorable expulsion of a hydride ion (preferably as LiH) in the second step.[19][20] Recently, polycyclic hydrocarbons such as triquinacene[21] and several tribenzotriquinacenes[22] have been dehydrogenated by treatment with superbasic reagents (Lochmann−Schlosser bases).[23] Tribenzotriquinacene, a centrotriindane related to **2**,[1] was found to react much more readily owing to benzylic activation of the deprotonation and/or elimination steps.[22a] Various other (two-fold) metallation reactions of acyclic isobutene derivatives by *n*-butyllithium in the presence of TMEDA, but without concomitant dehydrogenation, were also reported recently.[24]

When either 9-benzyltriptindan-9-ol **6**[5] or (*Z*)-9-benzylidenetriptindane **4**[5] were treated under the reaction conditions that were used for the attempted benzylation of triptindanone **1** (cf. Scheme 1), polycycle **3** was again formed as the sole product and isolated in virtually the same yields (Scheme 2). Thus, the alcoholate formed upon addition of benzyllithium/TMEDA to ketone **1** leads to elimination of alkoxide, thus generating olefin **4**. Once formed, this hydrocarbon is deprotonated and undergoes cyclization. Clearly the (*E*) stereochemistry of the stilbene moiety, which is required for cyclization, is achieved upon deprotonation when the stereochemically pure isomer (*Z*)-**4** is used (Scheme 3). The ease of the (*Z*)-to-(*E*) isomerization points to a favorable bonding interaction between the benzylic positions C-9 and C-10 in the deprotonated triptindane framework (cf. anion **II**), an effect that enables free rotation of the former stilbene double bond to give anion **III**. Subsequent nucleo-



Scheme 3

philic addition of the benzylic anion to one of the *ortho* positions of the benzylidene group gives rise to a cyclohexadienyl anion (**IV**) from which the *ortho*-hydrogen atom is eventually lost by hydride elimination. Related hydride elimination reactions are known to take place favorably when conjugated electron systems, such as styrene and stilbene-type species, are generated.[25][26] However, to the best of our knowledge, a base-induced "aromatic cyclodehydrogenation" reaction such as the formation of **3** from **4** presented here is unprecedented.

Conclusion

In summary, an interesting base-induced cyclization has been found as a variant of the deprotonation/hydride elimination sequence known for simpler unsaturated hydrocarbons. In the present case, hydride elimination occurs from an (electronically nonactivated) arene ring; hence the cyclization process can be considered a nucleophilic aromatic substitution. The ease of cyclization may be due to favorable preorientation and anionic hyperconjugation. In this view, the general scope of the reaction remains open so far. Besides the base-induced cyclodehydrogenation of a particular benzylidene-substituted [3.3.3]propellane, however, the base-induced tandem condensation/cyclodehydrogenation reaction of benzyllithium with a polycyclic ketone, viz. triptindanone **1**, has enabled a highly efficient hexaannulation procedure leading to a novel *trifuso*-centrotetracyclic framework, a [5.5.5.6]centrotetracyclane.

Experimental Section

General: Melting points were determined with Model 512 (Büchi) and Melting Point Apparatus (Electrothermal) and are uncorrected. − IR spectra were measured with a Perkin−Elmer IR-841. − ^{1}H- and ^{13}C-NMR spectra were measured with a DRX 500 instrument (Bruker); $^{13}C\{^{1}H\}$ spectra were measured using the DEPT technique. ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY spectroscopy of compound **3** was performed using the same instrument. − Mass spectra were obtained with a double-focusing instrument, Autospec (Fisons), using electron impact ionization (EI, 70 eV). Exact masses were determined with the same instrument at a resolution of $m/\Delta m \approx 8000$. − Column chromatography was performed using silica gel (Kieselgel 60, 0.063 × 0.200 mm, Merck). − Reactions were carried out in dried glass flasks under argon. Solvents were redistilled and dried and stored over molecular sieves (4 Å). TMEDA was used directly after distillation.

13b*H*-4b,13c-[1,2](Benzenomethano)benzo[*b*]indeno(1,2,3-*lm*)-fluorene (3)

(A) From Triptindan-9-one (1): *n*-Butyllithium [13.0 mL (20.0 mmol) of a 1.6 M solution in hexanes] was rapidly injected under argon through a septum into a solution of 2.32 g (20 mmol) of freshly distilled TMEDA in 50 mL of toluene. The orange-red solution was heated to 80 °C for 30 min and its color changed to deep red. The solution was allowed to cool to ambient temperature and a solution of triptindan-9-one (**1**) (630 mg, 2.04 mmol) in 8.0 mL of toluene was added. Upon addition, the color of the solution changed to deep green. The reaction mixture was heated with stirring to 80 °C for 6 h and then stirred at room temperature for another 16 h during which the solution turned black and a black-green precipitate formed on the surface of the reaction flask. Hydrolysis by dropwise addition of water gave a clear, colorless, two-phase mixture that showed a strong fluorescence upon irradiation at 366 nm. The organic layer was separated and the aqueous solution extracted three times with 50-mL portions of diethyl ether. The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried with Na_2SO_4, and the solvent was removed by evaporation. The almost colorless residue (875 mg) was found to contain some 1,2-diphenylethane, which was removed by Kugelrohr distillation (< 0.01 mbar; 150 °C). A yellow solid residue (775 mg) was obtained that, after purification by chromatography ($CHCl_3$/hexanes, 72:28) and another Kugelrohr distillation, furnished the hydrocarbon **3** (571 mg, 75%) as colorless crystals; m.p. 293 °C (decomp.). − R_f ($CHCl_3$/hexanes, 1:1) = 0.52. − The compound tends to incorporate solvent molecules such as CH_2Cl_2, as shown by ^{1}H-NMR spectroscopy, which could not be removed completely. Combustion analysis gave varying results with deviations for C contents in the range of 1.7−4.0%; closest values for $C_{30}H_{20}$ (380.5): calcd. C 94.70, H 5.30; found C 93.00, H 5.44.

(B) From 9-Benzyltriptindan-9-ol (6):[5] A solution of benzyllithium/TMEDA in toluene was prepared in exactly the same way, from the same amounts of reagents, as described above. At ambient temperature, a solution of 9-benzyltriptindane-9-ol (**6**) (410 mg, 1.02 mmol) in toluene (5.0 mL) was added and the color of the solution changed to deep green. The reaction mixture was heated with stirring at 80 °C for 8 h and then stirred at room temperature overnight. A deep green precipitate had formed on the surface of the reaction flask. Hydrolysis and workup was performed as described above to give a strongly fluorescent solution. Separation and purification of the product by chromatography and Kugelrohr distillation (< 0.002 mbar; 140 °C) gave a pale yellow solid (413 mg). The crude product was purified by crystallization from CH_2Cl_2 and washed with hexanes, yielding colorless crystals that proved to be hydrocarbon **3** (296 mg, 77%) and identical to the product obtained from **1**, by its physical and spectroscopic properties.

(C) From (*Z*)-9-Benzylidenetriptindane (4):[5] A solution of benzyllithium/TMEDA in toluene was prepared in exactly the same way from the same quantities as described above. At ambient temperature, a solution of olefin **4** (300 mg, 0.78 mmol) in 5.0 mL of toluene was added. The color of the solution changed to deep green. The reaction mixture was heated with stirring at 80 °C for 6 h and stirring was continued at ambient temperature for 16 h. The black solution and the deep green precipitate that had formed on the surface of the reaction flask were hydrolyzed by dropwise addition of water to give a clear, colorless, two-phase mixture that again exhibited strong fluorescence under irradiation at 366 nm. Workup as described above, including separation of 1,2-diphenylethane by kugelrohr distillation (< 0.01 mbar; 150 °C), yielded a pale yellow solid (324 mg). This crude product was purified by recrystallization from a small amount of CH_2Cl_2 followed by washing with hexanes, giving colorless crystals of **3** (227 mg, 76%). Again, the product was shown to be identical to those obtained by procedures (A) and (B) described above.

Spectroscopic Data for 3: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.66 (d, 1 H, ^{3}J = 7.6 Hz), 7.64 (d, 1 H, ^{3}J = 7.5 Hz), 7.56 (d, 1 H, ^{3}J = 7.6 Hz), 7.53 (d, 1 H, ^{3}J = 7.5 Hz), 7.42 (d, 1 H, ^{3}J = 7.7 Hz), 7.14−7.30 (m, 9 H), 7.07 (t, 1 H, ^{3}J = 7.4 Hz), 6.96 (d, 1 H, ^{3}J = 7.5 Hz), 6.78 (s, 1 H), 4.26 (s, 1 H), 3.26, 2.88 (AB system, 2 H, ^{2}J = 16.4 Hz). − $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, TMS; DEPT): δ = 148.09 (q), 144.78 (q), 143.83 (q), 143.75 (q), 143.10 (q), 142.77 (q), 139.75 (q), 134.03 (q), 133.32 (q), 130.47 (t), 128.82 (t), 127.66 (t), 127.54 (t), 127.30 (t), 127.21 (t), 127.03 (t), 125.72 (t), 124.44 (t), 124.36 (t), 123.99 (t), 123.81 (t), 121.77 (t), 119.78 (t, olefinic CH), 74.84 (q), 65.32 (q), 51.27 (t, benzhydryl−CH), 38.66 (s). − IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (m), 3040 (m), 3019 (m), 2959 (w), 2910 (w), 2866 (w), 1599 (w), 1481 (m), 1474 (m), 1465 (s), 1432 (m), 1151 (m), 1119 (m), 1019 (m), 937 (m), 868 (m), 855 (m), 757 (s), 749 (s), 742 (s), 734 (s), 722 (s), 705 (s), 645 (m), 621 (w), 613 (s). − MS (EI, 70 eV): *m/z* (%): 380 (100) [M^+], 303 (23), 302 (22), 291 (12), 289 (25), 182 (8), 151 (7), 91 (10). − HR MS: calcd. for $C_{30}H_{20}$ ($M^{+\bullet}$) 380.1565, found 380.1565.

X-ray Structure Analysis of 3: A single crystal of 0.6 × 0.4 × 0.3 mm size was analyzed with a Siemens $P2_1$ diffractometer. Empirical formula: $C_{30}H_{20}$, molecular mass 380.5, crystal system triclinic; space group $P\bar{1}$; lattice parameters: a = 8.978(1) Å, b = 10.645(2) Å, c = 11.874(2) Å, (= 108.40(1)°, β = 94.92(1)°, γ = 109.83 (1)°, V = 989.0 (3) Å^3; $d_{\mathrm{calcd.}}$ = 1.278 g/cm^3; $F(000)$ = 400, μ(Mo-K_α) = 0.072 mm^{-1}; T = 193 K; $2\Theta_{\max}$ = 50°; 3721 data collected; programs used SHELXTL PLUS and SHELXL-93, 271 parameters refined; residual R_F and $wR_F{}^2$ for 2754 data with [I > 2 $\sigma(I)$] 0.043, 0.101; largest peak in final diff. map 0.2e/Å^3; no absorption correction.[27]

Acknowledgments

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[27] Crystallographic data (excluding structure factors) for the structure of **3** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115223. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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