Sterically Hindered Alkanes, II
1,1,1,3,3,3-Hexaphenylpropane

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X-ray, Steric Hindrance, C14-Tracer Technique, Triarylmethyl Radical, Diazomethane

The structure of the title compound 3, C6H35C6H5, obtained for the first time by Schlenk and Bornhardt (1912) from triphenylmethyl (1) and diazomethane (2) has been determined by C14-tracer technique, NMR spectroscopy and X-ray analysis. It crystallizes in the monoclinic space group C2/c with Z = 4, a = 9.943(6), b = 19.054(3), c = 14.708(2) Å and β = 101.80(2)°. The structure was solved by direct methods and refined by full-matrix least squares to R = 0.046 for all 2626 reflexions (|F0| > 0). On account of steric repulsions between the phenyl rings at both termini the central propane bond angle φ is stretched to 127.2°, whereas the bond lengths are not much affected. The X-ray results are compared with those of Blount et al. (1982), obtained on a triclinic crystal modification (P1) of 3. A fair agreement of bond lengths and angles is observed, the slopes of the homochiral propellers, however, are different in both modifications. The measurement of the N2-evolution shows that the mechanism of formation of 3 from 1 and 2 is different in the photochemical and dark reaction. A carbene respectively a one-electron transfer mechanism is suggested. In spite of the remarkably normal CC-propane bond lengths homolytic cleavage of these bonds to give 1 is observed at 200–220 °C using the ESR technique.

Historical Background

The crystal structure of the first unclamped hexaarylalkane, [hexakis(2,6-di-tert-butylphenyl)ethane], revealed an unexpectedly short central CC-bond length of 1.47 Å [1]. In order to find the reason for this behavior, we started an X-ray investigation of hindered alkanes [2]. As a second example we selected 1,1,1,3,3,3-hexaphenylpropane [3] for the following reasons:

1. As early as 1912 Schlenk and Bornhardt [3] treated the free radical triphenylmethyl 1 with diazomethane 2 and obtained a compound which analyzed for 3 (1):

\[ 2(C_6H_5)_3C : + CH_2N_2 \rightarrow \]

\[ 1 \quad \text{2 : * = 12} \]

\[ 2a : \ast = 14 \]

\[ (C_6H_5)_3C-CH_2-C(C_6H_5)_3 + N_2 \]

\[ 3 : \ast = 12 \]

\[ 3a : \ast = 14 \]

In connection with our investigations into free radical reactions of diazaalkanes [4] we repeated the experiment of Schlenk and Bornhardt [3] in 1964 and obtained 3 in 46% yield, although the compound showed a lower melting point (214 °C) as compared with the value given by the aforementioned authors (216 °C). Later, it turned out that free radicals of the phenyl-X type, e.g. phenoxy radicals [5], can incorporate two methylene groups originating from the diazaalkanes. Therefore, it seemed worthwhile investigating the structure of 3 with modern facilities.

2. At first glance one is tempted to assume that, owing to the methylene bridge between the triphenylmethyl centers, the steric strain in 3 would be less than in hexaarylalkane. The inspection of models, however, reveals a high strain between the phenyl groups attached to carbons 1 and 3 of the propane chain. Severe repulsive nonbonded interactions between phenyl groups in the bis(triphenylmethyl)oxide or sulfide and between triptycyl groups in bis[9-triptycyl)methane and derivatives as well as in bis[9-triptycyl]ketone are indeed indicated by the X-ray analyses of these compounds showing an extraordinary widening of the central C-C-C bond angle (120–129°) [6–8]. On the other hand, this effect is not restricted to the presence of phenyl groups, as is demonstrated by the X-ray analysis of 2,2,4,4-tetramethylpentane [9]. Therefore, it should operate also in 3, as was predicted by Mislow et al. [8a]. We were also interested in how the steric hindrance in 3 would influence the length of the Csp3-Csp2 bond to the phenyl rings, which...
turned out to be lengthened in hexakis (2,6-di-tert-butyl-biphenyl)ethylene [1].

At about the same time and not independently of us [8b] Blount, Mislow, et al. started an X-ray investigation of 3 in the context of their work on molecular gearing [10–12]. They determined the space group P1 for their crystals [13], whereas our crystals of 3 (see below) showed C2/c. Since Blount, Mislow et al. went ahead with publication of their results [14] without consideration of this fact, the additional burden of looking for the reason for it was laid on our shoulders.

**Experimental**

1. **General Methods.** 

   1.1. **H NMR** spectra were taken with Varian A 60 and Bruker WM 400, 13C NMR spectra with Bruker WP 80 spectrometers, TMS as internal standard. IR-spectra were recorded on a Perkin-Elmer 281 spectrometer. Mass spectra were taken with the MAT-711 spectrometer (inlet temperature 180 °C, ionisation energy 20 or 70 eV). ESR investigations were carried out with a Varian E 12 spectrometer (S 122 computer). Radioactivity was determined with a Packard Tricarb Scintillation E 12 spectrometer (S 122 computer). Radioactivity was determined with a Packard Tricarb Scintillation E 12 spectrometer (S 122 computer).

   **Mass Spectra.**

   MS: \([m/e]\) (rel. int.): 500 (ca. 0.07, 70 eV; ca. 0.2, 20 eV) M% = 257 (6); M=-C(3H)5s = 243(100)

   16.4 g (33.7 mmol) of the dimer of 1 were dissolved in 160 ml of benzene (nitrogen atmosphere), subsequently 180 ml of 0.6 M ethereal diazomethane solution (108 mmol) were added. At determined intervals samples of 20 ml of the reaction mixture were removed, rapidly shaken with oxygen until the unreacted 1 was completely consumed, cooled and filtered from the precipitated bis (triphenylmethyl) peroxide. The filtrate was worked up as described in 2a). The yields of 3 (in %) were (reaction times in)

2. **1,1,1,3,3,3-Hexaphenylpropane (3)** [15]

   a) **In the dark:** 4.90 g (10.1 mmol) of the dimer of triphenylmethyl, prepared from chlorotriphenylmethane and zinc dust according to Gomberg [16], were dissolved in 100 ml of benzene (nitrogen atmosphere) and treated with 100 ml of a 0.5 M solution of diazomethane (50 mmol) in ether. After standing for about 7 h at 20 °C in the dark the solvent was evaporated in vacuo. The residue was first re-crystallized from glacial acetic acid, then from ligroine (b.p. 100–140 °C) to give 2.3 g (46%) 3; m.p. 214 °C (lit. [3]: m.p. 216 °C). IR (KBr): 3088, 3052, 3030, 3015, 1492, 1443, 1010, 758, 736, 687 cm⁻¹.

   b) **With light:** 35 ml of a 0.5 N solution of diazomethane (17.5 mmol) in ether were added to 3.90 g (8.01 mmol) of triphenylmethyl (respectively of its dimer) in 140 ml of benzene in an atmosphere of nitrogen. The mixture was illuminated by a Heraeus quartz lamp S 81 (glass condenser jacket) for 1 h. Working up as described under a) led to 1.5 g (37%) 3, m.p. 214 °C; identical (IR spectrum and mixed m.p.) to a sample prepared by method a).

   **C39H32** (500.6) M%, 257 (6) M%=C(3H)5s, 243(100)

   C(3H)5s (500.6)

   **Found** C 93.66 H 6.37.

   **Table I. Counting rates of the radioactive substrates.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Test portion [μmol/l]</th>
<th>Counting rates [impulses/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[14C]Methyl 3-nitrobenzoate</td>
<td>20.43</td>
<td>18113</td>
</tr>
<tr>
<td>3a</td>
<td>6.73</td>
<td>5354</td>
</tr>
<tr>
<td>[14C]Methyl 3-nitrobenzoate</td>
<td>20.43</td>
<td>18113</td>
</tr>
<tr>
<td>3a</td>
<td>6.73</td>
<td>5354</td>
</tr>
</tbody>
</table>

   a) The symbols have the following meaning: A = counting rate measured, B = A minus blank value (natural counting rate without radioactive substance, 58 impulses/min), C = counting rate calculated for 1 μmol substrate, D = mean value of C.

   From these values the number of CH₂-groups in 3a is determined as 811:847 = 0.96 ~ 1.0 relative to [14C]-methyl 3-nitrobenzoate.

3. **Kinetic Investigations**

   a) **Time dependence of the yields of 3**

   16.4 g (33.7 mmol) of the dimer of 1 were dissolved in 160 ml of benzene (nitrogen atmosphere), subsequently 180 ml of 0.6 M ethereal diazomethane solution (108 mmol) were added. At determined intervals samples of 20 ml of the reaction mixture were removed, rapidly shaken with oxygen until the unreacted 1 was completely consumed, cooled and filtered from the precipitated bis (triphenylmethyl) peroxide. The filtrate was worked up as described in 2a). The yields of 3 (in %) were (reaction times in...
min are given in brackets): 4(8), 4(15), 8.2(24), 13.8(137), 25.0(60), 26.2(80), 32.2(135), 34.3(210), 38.1(300), 38.8(420).

b) Measurement of the $\text{N}_2$-evolution

The apparatus of Fig. 1 was used. Reaction vessel A was kept under nitrogen (cock C open). Through joint D (cock C closed) either water-free cyclohexane (for the blank test) or triphenylmethyl (1) in cyclohexane was added, in each case followed by diazomethane (2) in cyclohexane. Afterwards, joint D was rapidly closed and the developed amount of nitrogen determined in the gas burette G (cocks E and F open) as a function of time, either in the dark (lamp B out) or under illumination (lamp B on). During this operation the mixture was magnetically stirred with a constant number of revolutions; the temperature was kept at 21 °C throughout.

Experiment 1. 90 ml of cyclohexane + 15 ml of 0.21 N solution of 2 (3.15 mmol) in cyclohexane (dark).

Experiment 2. 700 mg (1.44 mmol) of 1 in 85 ml of cyclohexane + 18.5 ml of 0.17 N solution of 2 (3.14 mmol) in cyclohexane (dark).

Experiment 3. 80 ml of cyclohexane + 21.5 ml of 0.15 N solution of 2 (3.23 mmol) in cyclohexane (light).

Experiment 4. 700 mg (1.44 mmol) of 1 in 75 ml of cyclohexane + 27 ml of 0.12 N solution of 2 (3.24 mmol) in cyclohexane (light).

Fig. 2 shows the plot of the observed ml $\text{N}_2$ vs reaction time $t$. No corrections were made for small
amounts of other gases (e.g., ethene [18], and, in the light reaction, for N₂-evolution by the dark process.

4. ESR Measurements

A sample of 3 was sealed in vacuo in a glass tube and put into the preheated cavity (200 °C) of the ESR spectrometer. It showed no ESR signal at 200 °C, however, at 220 °C the sample (which had only partially melted) revealed a slightly yellow colour, and a strong ESR signal appeared. The moderately resolved hyperfine structure and the overall width indicated the presence of 1. At about 230 °C the melted sample was deep yellow and the ESR signal of increased intensity consisted of a single broad line. The experiment was repeated in solution: 2.5 × 10⁻² M solutions of 3 in toluene or trans-decaline were prepared at ambient temperature. After data reduction, 2625 independent reflexions with I ≥ 2σ(I) were used for further calculations. The structure could be solved by direct methods [19] and refinement by full-matrix least squares showed that the correct space group was C2/c with Z = 4.

All hydrogen atoms were located in difference Fourier maps and refined with isotropic temperature factors (anisotropic thermal parameters were used for the nonhydrogen atoms). With all 2625 reflexions and 241 variables, final R and Rₚ indices of 0.046 and 0.040 could be obtained. A final difference Fourier synthesis revealed only spurious peaks with densities <0.18 e Å⁻³.

Scattering factors were taken from Cromer and Mann [20] and all calculations were performed on PDP 11/60, Telefunken TR 440 and UNIVAC 1100/80 computers with the programs SDP (ENRAF-NONIUS), SHELX (G. Sheldrick), XANADU (J. Roberts and G. Sheldrick) and PLUTO (S. Motherwell). Final fractional coordinates, interatomic distances and angles are given in Tables II-IV*.

Table II. Positional parameters with e.s.d.'s in parentheses; the numbering scheme refers to Fig. 3.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>0.0000(0)</td>
<td>0.03372(11)</td>
<td>0.7500(0)</td>
<td>H1</td>
<td>0.013(1)</td>
<td>0.0017(8)</td>
<td>0.6966(9)</td>
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<td>C2</td>
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<td>0.07030(8)</td>
<td>0.7866(1)</td>
<td>H4</td>
<td>0.074(2)</td>
<td>0.2072(8)</td>
<td>0.8172(11)</td>
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<td>C3</td>
<td>0.1349(1)</td>
<td>0.11173(8)</td>
<td>0.8757(1)</td>
<td>H5</td>
<td>0.052(2)</td>
<td>0.2637(10)</td>
<td>0.9514(12)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0922(2)</td>
<td>0.18127(9)</td>
<td>0.9557(1)</td>
<td>H6</td>
<td>0.098(2)</td>
<td>0.2063(10)</td>
<td>0.9871(13)</td>
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<tr>
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<td>0.1070(2)</td>
<td>0.18118(9)</td>
<td>1.0395(1)</td>
<td>H7</td>
<td>0.170(2)</td>
<td>0.0846(10)</td>
<td>0.1019(13)</td>
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<tr>
<td>C6</td>
<td>0.1046(2)</td>
<td>0.11227(11)</td>
<td>1.0423(1)</td>
<td>H8</td>
<td>0.388(2)</td>
<td>0.2483(10)</td>
<td>0.8733(13)</td>
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<tr>
<td>C7</td>
<td>0.1630(2)</td>
<td>0.07799(9)</td>
<td>0.9613(1)</td>
<td>H9</td>
<td>0.292(2)</td>
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<td>C8</td>
<td>0.1603(2)</td>
<td>0.11291(8)</td>
<td>0.7996(1)</td>
<td>H10</td>
<td>0.355(2)</td>
<td>0.2034(10)</td>
<td>0.5296(13)</td>
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<tr>
<td>C9</td>
<td>0.1370(1)</td>
<td>0.11291(8)</td>
<td>0.7996(1)</td>
<td>H11</td>
<td>0.355(2)</td>
<td>0.2034(10)</td>
<td>0.5296(13)</td>
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<tr>
<td>C10</td>
<td>0.3324(2)</td>
<td>0.20357(10)</td>
<td>0.6061(1)</td>
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<td>0.322(2)</td>
<td>0.0993(10)</td>
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<td>C11</td>
<td>0.1795(2)</td>
<td>0.08659(9)</td>
<td>0.6223(1)</td>
<td>H13</td>
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<td>0.0431(8)</td>
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<tr>
<td>C12</td>
<td>0.2158(2)</td>
<td>0.01103(8)</td>
<td>0.8124(1)</td>
<td>H14</td>
<td>0.136(2)</td>
<td>-0.0772(9)</td>
<td>0.7755(11)</td>
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<tr>
<td>C13</td>
<td>0.2370(2)</td>
<td>0.17978(9)</td>
<td>0.7331(1)</td>
<td>H15</td>
<td>0.370(2)</td>
<td>-0.1574(10)</td>
<td>0.8109(12)</td>
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<tr>
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<td>0.08659(9)</td>
<td>0.6223(1)</td>
<td>H16</td>
<td>0.534(2)</td>
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<tr>
<td>C15</td>
<td>0.2158(1)</td>
<td>0.01103(8)</td>
<td>0.8124(1)</td>
<td>H17</td>
<td>0.582(2)</td>
<td>-0.0916(11)</td>
<td>0.9018(14)</td>
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<td>C16</td>
<td>0.2266(2)</td>
<td>-0.03828(9)</td>
<td>0.7966(1)</td>
<td>H18</td>
<td>0.409(2)</td>
<td>0.0809(10)</td>
<td>0.8636(13)</td>
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<tr>
<td>C17</td>
<td>0.3324(2)</td>
<td>-0.10921(10)</td>
<td>0.8253(1)</td>
<td>H19</td>
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<tr>
<td>C18</td>
<td>0.4621(2)</td>
<td>-0.08817(11)</td>
<td>0.8808(1)</td>
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<td>0.409(2)</td>
<td>0.0809(10)</td>
<td>0.8636(13)</td>
</tr>
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</table>

* Lists of thermal parameters and structure factors may be obtained from one of the authors (W. W.) or from FIZ Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2. The Registry-Nr., CSD 50308, the name of the author, and the reference should be given.
Table III. Bond lengths (Å) with e.s.d.’s in parentheses.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Lengths</th>
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<tbody>
<tr>
<td>C1 - C2</td>
<td>1.566(3)</td>
</tr>
<tr>
<td>C1 - H1</td>
<td>1.03 (2)</td>
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<tr>
<td>C2 - C3</td>
<td>1.544(3)</td>
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<td>C2 - C9</td>
<td>1.546(3)</td>
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<tr>
<td>C2 - C15</td>
<td>1.564(3)</td>
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<tr>
<td>C3 - C4</td>
<td>1.390(3)</td>
</tr>
<tr>
<td>C3 - C8</td>
<td>1.390(3)</td>
</tr>
<tr>
<td>C4 - C5</td>
<td>1.373(4)</td>
</tr>
<tr>
<td>C5 - C6</td>
<td>1.375(4)</td>
</tr>
<tr>
<td>C6 - C7</td>
<td>1.375(4)</td>
</tr>
<tr>
<td>C7 - C8</td>
<td>1.389(4)</td>
</tr>
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Table IV. Selected bond angles (°) with e.s.d.’s in parentheses.

<table>
<thead>
<tr>
<th>Bond Angles</th>
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<tbody>
<tr>
<td>C2 - C1 - C2A</td>
<td>127.2(2)</td>
</tr>
<tr>
<td>C2 - C1 - H1</td>
<td>106 (1)</td>
</tr>
<tr>
<td>C1 - C1 - H1A</td>
<td>107 (2)</td>
</tr>
<tr>
<td>C1 - C2 - C3</td>
<td>100.0(2)</td>
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<td>C1 - C2 - C9</td>
<td>114.6(2)</td>
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<td>C1 - C2 - C15</td>
<td>107.3(2)</td>
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<tr>
<td>C2 - C3 - C4</td>
<td>123.0(2)</td>
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<td>C2 - C3 - C8</td>
<td>119.8(2)</td>
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<tr>
<td>C4 - C3 - C8</td>
<td>117.1(2)</td>
</tr>
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</table>

Results and Discussion

General structural investigations on 3

Apart from an elementary analysis of medium quality performed in 1912 [3] apparently no structural determination has been undertaken on 3. The reaction of 1 and 2 can, in principle, lead to a combination of one or more methylene groups with two radicals 1. Indeed, we could show that phenoxy radicals, other examples of phenyl-X type radicals, are able to react with two equivalents of 2 [5]. Moreover, attack in the para (and/or ortho) position of the phenyl rings of 1 has also to be considered. Besides 3, structures 4 and 5 are therefore the most reasonable candidates.

Both of the latter compounds are described in the literature, and their reported melting points (4: 287 °C [21]; 5: 177 °C [22]) are different from that of our sample (214 °C). Since in 1964, when we first repeated the experiment of Schlenk and Bornhardt, no high-resolution physical methods were available to us, we performed the reactions of 1 with 14C-labeled diazomethane 2a; a part of the same solution of 2a was used to transform 3-nitrobenzoic acid into [14C]-methyl 3-nitrobenzoate. The radioactivities of the obtained products from 1 and from methyl 3-nitrobenzoate were measured with a scintillation counter (see experimental section). The measured activity (reduced to equal molar amounts) is expected to be the same for 3 and 5, and twice for 4 with respect to that found for 3-nitrobenzoate. The experimental value 0.96 (taken from Table I) clearly excludes 4 and all other structures resulting from the insertion of more than one methylene group. This is further supported by the mass spectrum of 3, showing a very small molecular peak of m/e = 500 [2(C6H5)3C + CH2]+. For the interesting fragmentation pattern vide infra.

The distinction between structures 3 and 5 is easily achieved in favour of 3 by 1H and 13C NMR spectroscopy. The 1H NMR spectrum (60 MHz) shows two singlets for the aromatic and aliphatic protons each (intensity relation 1:15). In the 400 MHz spectrum the aromatic protons reveal two multiplets; a detailed assignment was not intended. The 13C NMR spectrum (coupled and broad-band decoupled) allowed for a straightforward assignment (see experimental section). It is only for the signals of C-2', 6' and C-3', 5' that there remains some uncertainty. The coupling constant J_C-2/H-2 of 127.5 Hz is indicative of an enlarged angle ϕ (C-1/C-2/C-3), which had been pointed out already by Baum et al. [23] (vide infra). Dynamic processes are not evident in the 13C NMR spectrum of 3 at ambient temperatures.

X-ray analysis

The structure 3 was finally proved by X-ray analysis*, which also provided an answer to other

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* In the discussion of the X-ray analysis the atomic numbering given in Fig. 3 is used for practical reasons.
problems formulated in the introduction to this paper. As has already been mentioned, Blount et al. [14] have very recently determined the crystal structure of 3 in a triclinic modification. With the cell dimensions given by these authors, it is not possible to transform the triclinic into the monoclinic C-centered cell found by us. Obviously, the authors have not overlooked a hidden monoclinic symmetry, as occasionally happens for the space groups P1¢-C2/c [24]. We have tried hard to find the conditions, under which either triclinic or monoclinic crystals are formed, but a dozen further crystals investigated all showed monoclinic diffraction symmetry with identical cell dimensions. These crystals included species, which had been gained by crystallization from acetic acid and then from petroleum ether (130–150 °C) or heptane. Therefore, our first suspicion that the monoclinic and triclinic crystals represent “low-temperature” – and “high-temperature” – modifications could not be confirmed. For the moment, we cannot give any explanation for our unsuccessful search for the triclinic 3. Perhaps there is only a very small abundance of this modification, and Blount et al. [14] selected a triclinic crystal by chance.

In the monoclinic modification 3 has a crystallographically imposed C2-symmetry, as depicted in Fig. 3. According to the rules of Kitaigorodski [25], this result is not surprising: one of the most suitable space groups for crystals with molecules of C2-symmetry is C2/c, because in this case optimal packing is guaranteed. The volume of the triclinic cell found by Blount et al. [14] (1398.1 Å³, calculated using the published cell dimensions) is indeed higher by ca. 35 Å³ than the volume of our monoclinic cell (2727.4:2 = 1363.7 Å³).

It is of interest to compare the molecular structures of hexaphenylpropane in the triclinic and the monoclinic packing arrangement with respect to bond lengths, bond angles and torsional angles. First of all, we have calculated the deviations of the triclinic form from ideal C2-symmetry using the coordinates published by Blount et al. [14]: pseudo-equivalent bond lengths and angles are identical within 2 σ in the central part of the molecule [26] and become slightly larger in the “outer sphere”, obviously a result of the higher thermal motion of these atoms. However, the angles around the benzene carbon atoms C3 and C3A (Fig. 3) respectively C21 and C51 (Blount et al. [14]) differ significantly up to 2.8°. The largest deviations from C2-symmetry are found in the torsional angles of the triclinic hexaphenylpropane; especially at those torsional angles which describe the slope of the phenyl propellers. Here, differences between 10 and 16° are found, whereas the differences in the stag-
gered "propane part" are only between 1 and 3.5° (see below, Table VI).

When we compare this nearly C₂-symmetrical triclinic hexaphenylpropane with our monoclinic one of perfect C₂-symmetry, we can detect no significant differences in bond lengths and angles for the central propane part. In Table V, a summary of the corresponding bond lengths and angles in both modifications is given.

Table V. Comparison of "equivalent" bond lengths (Å) and angles (°) in triclinic and monoclinic 3.

<table>
<thead>
<tr>
<th>Bond Lengths and Angles</th>
<th>Monoclinic modification</th>
<th>Corresponding pair of bond lengths and angles in the triclinic modification [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>1.546</td>
<td>1.571 1.567</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.544</td>
<td>1.541 1.543</td>
</tr>
<tr>
<td>C2-C9</td>
<td>1.546</td>
<td>1.548 1.549</td>
</tr>
<tr>
<td>C2-C15</td>
<td>1.560</td>
<td>1.562 1.562</td>
</tr>
<tr>
<td>C2-C1-C2A</td>
<td>127.2</td>
<td>128.0</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>109.0</td>
<td>108.6 109.0</td>
</tr>
<tr>
<td>C1-C2-C9</td>
<td>114.0</td>
<td>114.6 114.7</td>
</tr>
<tr>
<td>C1-C2-C15</td>
<td>107.3</td>
<td>106.8 107.1</td>
</tr>
</tbody>
</table>

As expected, a similarly large angle ϕ at C1 (carbon 2 in the IUPAC nomenclature) is found and even small deviations of bond lengths and angles within each modification are found in both forms, e.g. the elongated C2-C15 bond, the enlarged C1-C2-C9 angle and the slightly depressed C1-C2-C15 angle.

However, the differences in molecular packing cause marked deviations of the torsional angles in both forms, especially of the phenyl-propeller slope torsional angles, as shown in Table VI.

Mechanistic aspects

Although the main goal of this work was the structural determination of 3, a few results on the formation and redissociation of this propane will be discussed in this chapter.

The formation of 3. A rough determination of the reaction time via the isolated yields of 3 showed that, in the dark, 80–90% of the final conversion was achieved after about 5 h (Schlenk and Bornhardt [3] used 24 h with several additions of 2, they did not give, however, any yields). A more exact pursuit of the reaction is possible by measuring the volume of the evolved nitrogen with time. Since apparative effects hard to control are known to determine the decomposition of 2 [18], a rigorous kinetic investigation was not undertaken. In order to keep the number of artefacts as small as possible, the apparatus used (Fig. 1) was the same for all reactions, i.e. for photochemical and dark reactions with and without 1 as substrate.

There is a characteristic difference between the light and the dark reaction (Fig. 2). To a first approximation, the N₂ development in the light reaction (and hence the decomposition of 2) is the same whether triphenylmethyl is present in the reaction mixture or not, and not strictly follows first-order kinetics.

Photolysis (and thermolysis, see below) of diazoalkanes is assumed to be the only method which produces free carbenes [18, 27, 28]. According to [27], illumination of 2 should produce an electronically excited species via n → π* excitation (2). The excited molecule then decomposes in the photochemical primary process into N₂ and :CH₂ in the singlet state (S₁). Methylene :CH₂ exists only as an intermediate and reacts further with the substrates present. By intercombination in inert solvents or gases triplet methylene (T₁) may be produced by intersystem crossing [29].
\[
\begin{align*}
\text{CH}_2\text{N}_2 & \xrightarrow{h\nu} \text{CH}_2\text{N}_2^* \xrightarrow{\text{N}_2} \text{(2)} \\
\text{ISC} & \xrightarrow{\cdot} \text{CH}_2 \\
(C_6\text{H}_5)_3\text{C}^- & + \text{CH}_2 \rightarrow (C_6\text{H}_5)_3\text{C}-\text{CH}_2. & \text{(3)} \\
(C_6\text{H}_5)_3\text{C}-\text{CH}_2^- & + (C_6\text{H}_5)_3\text{C}^- \rightarrow (4) \\
(C_6\text{H}_5)_3\text{C}-\text{CH}_2^- & + (C_6\text{H}_5)_3\text{C}^- \rightarrow (5) \\
1 & + \cdot\text{CH}_2\text{N}_2^\circ \rightarrow (C_6\text{H}_5)_3\text{C}-\text{CH}_2\text{N}_2^\circ. & \text{(6)} \\
N_2 & + (C_6\text{H}_5)_3\text{C}-\text{CH}_2 & \rightarrow (C_6\text{H}_5)_3\text{C}-\text{CH}_2^- & + (C_6\text{H}_5)_3\text{C}^- \rightarrow 3. & \text{(7)}
\end{align*}
\]

The originating step (5) would be a one electron transfer from 2, which is known to occur e.g. in the anodic [31-33] or chemical [34] oxidation of diazokanes. An induced or chain process seems also to be possible [32]. The sequences (6) and (7) are less evident; a deprotonation of \((C_6\text{H}_5)_3\text{C}-\text{CH}_2\text{N}_2^\circ\) by trityl anion formed in step (5) and further connected reactions have also to be considered.

It is of great interest in this context, whether reactions (4) and (3) are reversible, i.e. whether the \(\text{C}-1/\text{C}-2\) bond in 3 tends to dissociate thermally. Although Schlenk and Bornhardt [3] stated 3 to be completely stable, the mass spectrum (inlet system 180 °C) shows that the molecular peak is very low. The base peak is caused by a fragment \((C_6\text{H}_5)_3\text{C}^-\) and the second largest fragment peak by \((C_6\text{H}_5)_3\text{C}-\text{CH}_2^\circ\) (or a rearranged ion of the same mass). Furthermore, we observed a bright yellow colour of the melt of 3 when heated slightly above the melting point (220–230 °C), indicative of a radical of type 1. ESR measurements of the melt or of 3 heated to 205–235 °C in toluene or trans-decaline (see experimental section) give ESR spectra which clearly demonstrate the presence of 1. Thus, at temperatures of 200–220 °C, at least equation (4) is reversible, although the radical \(\cdot\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_3\) or the rearranged species \(\text{C}_6\text{H}_5\text{CH}_2(C_6\text{H}_5)_3\text{C}^-\) [35] could not be observed. Further aspects of the thermolysis and the product palette are currently being investigated. Here we should like to point out one consequence: the bond \(\text{C}-1/\text{C}-2\), the length of which has been determined by X-ray analysis to be 1.566 Å, dissociates at about 200–220 °C, whereas the central \(\text{C}-\text{C}\) bond in 6 with a length of 1.567 Å [2] did not show a dissociation into the radicals 7 at 230 °C in 1,3-di-tert-butylbenzene [36] or even at 300 °C in ether [2]. Other examples may be found in Table III of literature [37]. We have no indication of an induced decomposition of 3, a chain
reaction [38] or a secondary production of 1 from 3. Obviously, a direct and quantitative relation between bond lengths in alkanes and their degree of dissociation into radicals does not generally exist, although it has often been held as an argument and is supported by *prima facie* evidence (free activation enthalpies $\Delta G^*$ correlate with calculated strain enthalpies $H_s$, the latter, in turn, with the CC-bond lengths in question [39, 40]). However, homolysis of a bond is not only determined by its length compared to a "standard" bond length [39, 41]. Moreover, X-ray data describe the molecules packed *in the crystal*, while degrees of dissociation are measured *in solution* and calculations refer to an isolated molecule [42]. As a consequence, a short central bond length in hexakis(2,6-di-tert-butylbiphenylyl)ethane does not *a priori* exclude its high degree of dissociation [1].

**Conclusions**

We did not find the modification with space group $\overline{P}1$, reported by Blount *et al.* [14], all crystals of 3 investigated by us so far showed space group $C2/c$, although several of them had been prepared under the same conditions as used by the aforementioned authors.

Triclinic and monoclinic molecules of 3 are very similar with respect to bond lengths and bond angles, but differ in the most flexible part of the molecule: the slopes of the homochiral propellers. The corresponding values of the torsional angles in monoclinic 3 (with crystallographically imposed $C2$-symmetry) lie between the pairs of values in the triclinic modification. Hence, the conclusions drawn from the above mentioned authors [14] with respect to molecular gearing remain valid.

The large central angle $\varphi$ in both modifications is a consequence of the steric hindrance between the phenyl rings $C9$–$C14/C3$–$C8A$ and $C3$–$C8/C9A$–$C14A$, *i.e.* the close contacts of $3.166$, $3.168$, $3.256$, $3.276$ and $3.379$ Å between atoms $C4$–$C9A$, $C3$–$C14A$, $C4$–$C14A$, $C3$–$C9A$ and $C8$–$C14A$ (and the related atoms $C4A$–$C9$, ... *etc.*).

On the other hand, the considerable internal strain of the molecule does not lead to a remarkable stretching of the C–1/C–2 bond (1.566 Å) in 3. Nevertheless, this bond is homolytically cleaved at about $200^\circ C$. This observation indicates that correlation of bond lengths, determined in crystals, with degrees of bond dissociation in solution should be treated with reservation.

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b) A. Moosmayer, Diplomarbeit, University of Tubingen 1965.


b) we have to thank Professor K. Mislow for initiating correspondence and several preprints of his papers.


[12] The one of us (A. R.) thanks Prof. H. Iwamura for many discussions in this field during his stay at the Institute for Molecular Science, Okazaki, Japan, as an Invited Foreign Scholar, September to November 1979.


[15] This experiment was taken from the diploma thesis of A. Moosmayer [4b], performed in the laboratory of Prof. E. Müller (deceased 1976),
Tübingen, under the guidance of E. Müller and A. Ricker.


[19] MULTAN version included in the SDP-program system of ENRAF-NONIUS.


[26] See footnote 7) in ref. [14].


