# REACTION OF [2.2]PARACYCLOPHANE WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

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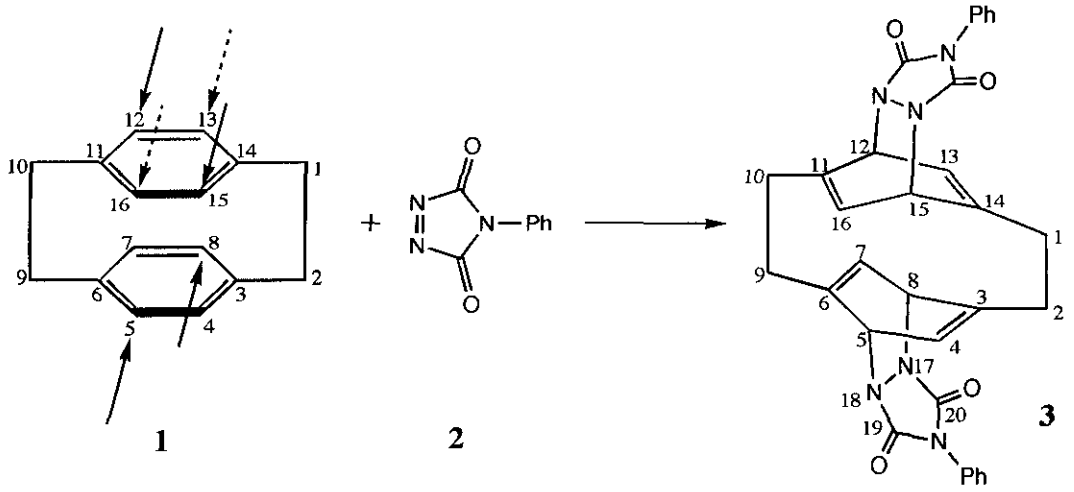
**Abstract**- Diels-Alder reaction of [2.2]paracyclophane with 4-phenyl-1,2,4-triazoline-3,5-dione was reinvestigated. The stereochemistry of the 1:2 adduct was established by the X-ray analysis, the reaction taking place in the sence of 4,7:13,16-cross bridge additions rather than 4,7:12,15-parallel bridge additions.

Non-annelated arenes normally do not participate as diene components in Diels-Alder reactions[1]. To surmount this lack of reactivity, considerable improvements have been realized and still challenged *via* recourse to chemical modification of dienes[2] and dienophiles, catalysis by Lewis acids, and high temperature and high pressure[3] as well. From the diene side, for example, this may be achieved by the incorporation of bridging structural units into arenes. Specifically, when simple aromatic 6π-electron systems, which are extremely sluggish in Diels-Alder additions, are incorporated into a [2n]cyclophane system such as [2.2]paracyclophane (**1**) that is a formal dimer of *p*-xylene, a dramatic increase in the rate of addition is observed in certain cases.[4] Indeed, the super dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) adds to **1** even at 20°C. However, Hoph *et al.* reported the 4,7:12,15-parallel bridge additions between **1** and **2** without any evidence,[4, 5] in disagreement with the X-ray analysis of the 1:2 adduct obtained by Diels-Alder reaction of **1** with *N*-methylmaleimide which arises from 4,7:13,16-cross bridge additions rather than 4,7:12,15-parallel bridge additions[6] (Scheme 1). Therefore, we reinvestigated the title reaction.

A mixture of **1** and **2** in dry benzene was stirred at room temperature overnight. After usual work-up by rapid chromatography on silica gel, a colorless powder was obtained. The product seems to be unstable in solution, reverting to **1** and **2**. Therefore, $^{1}H$ and $^{13}C$ nmr data did not permit us to

determine the structure of the product. Next, the product was recrystallized from acetone/ dichloromethane, giving two kinds of crystals, e.g. prisms and needles, which were separated by hand. The former crystals immediately proved to be **1** from ir spectra. The needle crystal was subjected to the X-ray analysis, proving, however, very difficult to collect good diffraction data. Fortunately, we managed to solve the structure which was established to be **3** (Figure 1). Interestingly, it has proven that the needle crystal constitutes an inclusion complex of **3** with acetone.




Scheme 1

The theoretical explanation based upon molecular orbital calculations regarding the crossbridge selectivity will be a subject of future communications.

## EXPERIMENTAL SECTION

Melting points were taken on a Yanagimoto micro melting point apparatus and were uncorrected. The $^{1}H$ nmr spectra were measured either on a Hitachi R40 (90 MHz) or on a JEOL JNM-EX270 (270 MHz), or JNM-ALPHA500 (500 MHz) instrument. $^{13}C$ nmr spectra were recorded either on a JEOL JNM- FX90Q or JNM-EX270 or JNM-ALPHA500 pulsed Fourier-transform spectrometer operating at 22.49 MHz, 67.80 Hz, and 125.65 Hz, respectively. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Preparative medium pressure liquid chromatography was carried out using a column (25 x 310 mm) prepacked with silica gel (Lobar, LiChroprep Si60, Merck).

**Reaction of [2.2]paracyclophane (1) with 4-phenyl-1,2,4-triazoline-3,5-dione (2)** ; A mixture

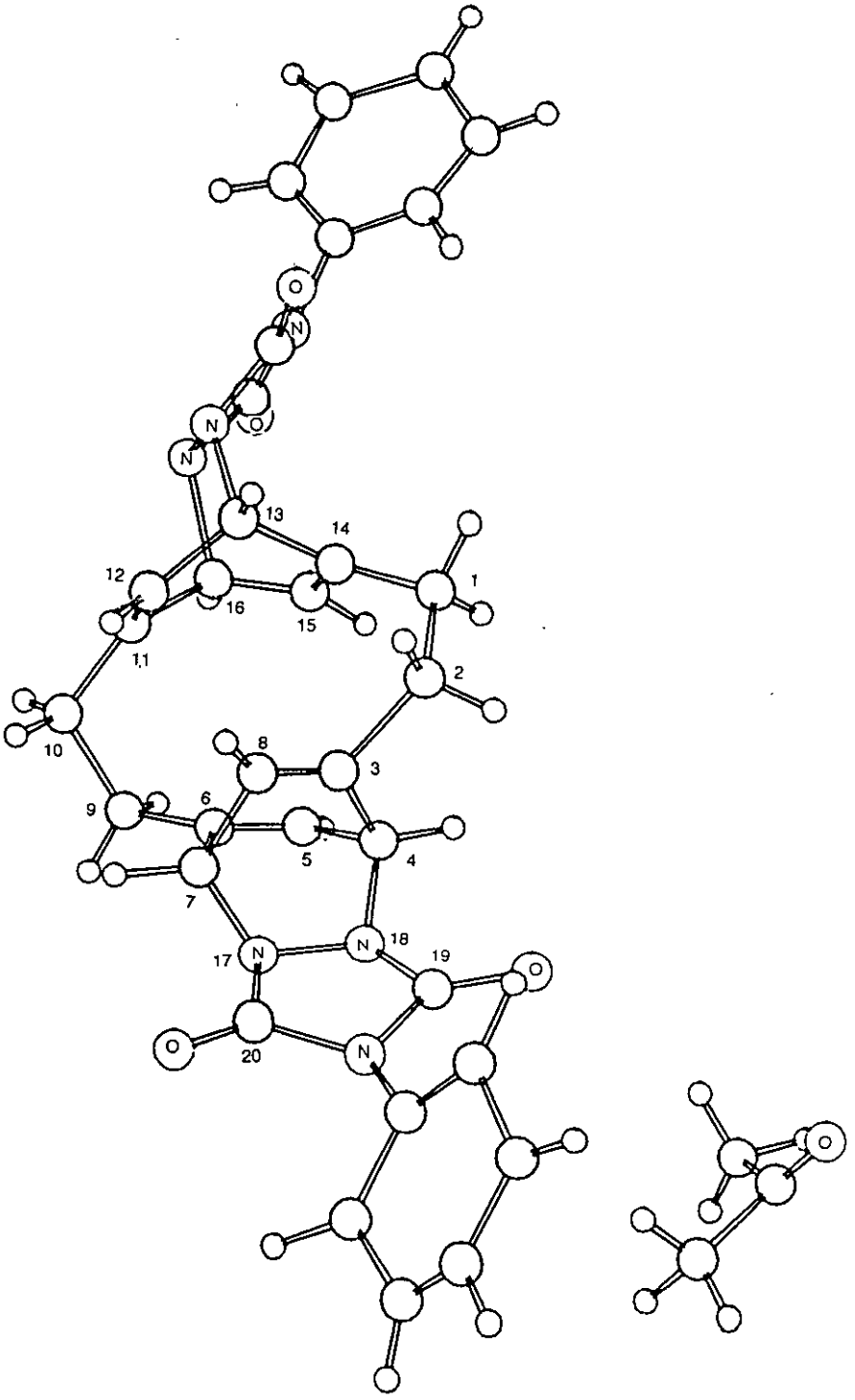



Figure 1. X-ray structure of **3**

Table 1 Crystal data for **3**

| | |
|---|---|
| Formula | $C_{32}H_{26}N_6O_4$ |
| M (a.m.u.) | 58.60 |
| Crystal system | monoclinic |
| Space group | Cc(#9) |
| a /Å | 8.548(4) |
| b /Å | 24.467(4) |
| c /Å | 14.966(2) |
| β / ° | 100.59(2) |
| *U* / Å$^3$ | 3077(1) |
| Z | 4 |
| $D_c$ / g cm$^{-3}$ | 1.206 |
| μ / cm$^{-1}$ | 0.77 |
| *F* (000) | 1168 |
| Radiation | Cu-Kα |
| graphite monochromatized | l=0.71069 Å |
| Diffratometer | Rigaku AFC5R |
| Orienting reflections, range | 25.8, 37.57 <2θ< 41.96° |
| T /°C | 20 |
| Scan method | ω |
| Data collection range | 3.0 <2θ<55.0° |
| No. unique data | 5786 |
| Total $I>3\sigma(I)$ | 818 |
| No. of parameters | 183 |
| $R^a$ | 6.8% |
| $R_W{}^b$ | 6.6% |
| Largest shift/esd, final cycle | 0.87 |
| Largest positive peak(e/Å$^3$) | 0.26 |
| Largest negative peak(e/Å$^3$) | -0.25 |

[a] $R=[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R_W=\{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{1/2}$ ; $w= 4F_o^2/[\sigma^2 F_o^2]$

of **1** (106.5 mg, 0.51 mmol) and **2** (202.4 mg, 1.16 mmol) was stirred in dry benzene (10 ml) under argon and allowed to stand overnight. The sightly brown precipitates were collected by filtration. The mother solution was concentrated in vacuum. The residue, combined with the above precipitates, was dissolved in acetone and was chromatographed on silica gel using dichloromethane and acetone as eluent to give **3** as colorless powder (248.7 mg, 87%) whose tlc showed only one spot. The parts of these crystals were recrystallized from acetone/dichloromethane to give two kinds of crystals, needles (**2**) and prisms (**1**) which were separated by hand for an X-ray analysis. **3**: mp 331°C (decomp.); Anal. Calcd for $C_{32}H_{26}N_6O_4 \cdot C_3H_6O$: C, 68.17; H, 5.23; N, 13.63. Found: C, 68.03; H, 5.21; N, 13.76.

**Crystal Structure Determination.**

Summary of the crystal data and structure refinement details is given in Table 1. The structure was solved by a direct method,[7] and refined by full matrix least squares. The atoms other than hydrogen were refined anisotropically. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for atoms other than hydrogen were taken from the literature.[8-10] All calculations were performed using the TEXSAN [11] crystallographic software package of the Molecular Structure Corporation.

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