molbank

Short Note

9,14-Diphenyl-9,9a,10,13,13a,14-hexahydro-9,14:10,13-dimethanobenzo[f]tetraphen-15-one

Brian A. Chalmers, David B. Cordes, Thomas Doig, Yuanyuan Du, Tomas Lebl, Meiyue Liu, Fraser Mealyou, Jasmine Rainer, Siobhan R. Smith, Ryan Walker and Iain A. Smellie *

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews KY16 9ST, UK
* Correspondence: ias10@st-andrews.ac.uk; Tel.: +44-1334-463845

Abstract: X-ray crystallography has been used to characterise the title compound for the first time, ^{1}H NMR, ^{13}C NMR and IR spectroscopic data has also been updated from earlier reports.

Keywords: cycloaddition reactions; X-ray structure; NMR spectra; IR spectrum

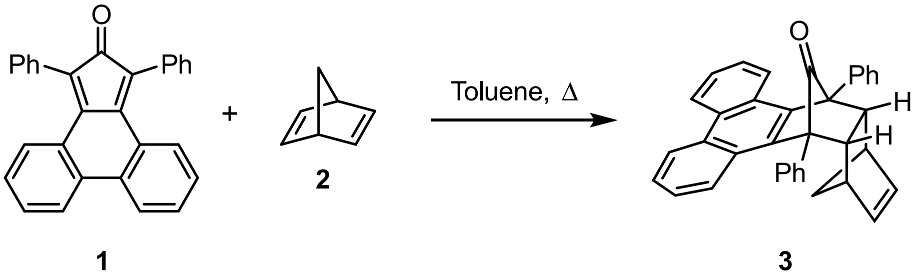
Citation: Chalmers, B.A.; Cordes, D.B.; Doig, T.; Du, Y.; Lebl, T.; Liu, M.; Mealyou, F.; Rainer, J.; Smith, S.R.; Walker, R.; et al. 9,14-Diphenyl-9,9a,10,13,13a,14-hexahydro-9,14:10,13-dimethanobenzo[f]tetraphen-15-one. *Molbank* **2022**, *2022*, M1524. https://doi.org/10.3390/M1524

Academic Editor: Kristof Van Hecke

Received: 20 November 2022
Accepted: 7 December 2022
Published: 10 December 2022

1. Introduction

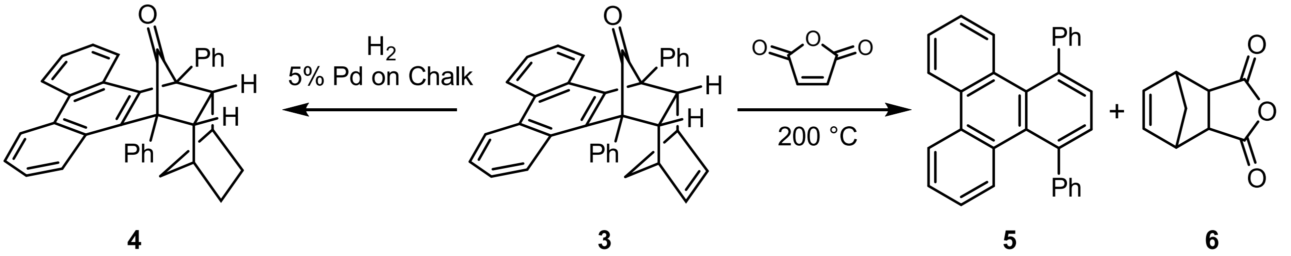
The [4 + 2] cycloaddition reaction of phencyclone **1** and Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) **2** in refluxing chlorobenzene [1,2] or toluene [3,4] affords the cycloadduct **3** as the sole product (Scheme 1).



1 **3**

Scheme 1. Diels-Alder reaction of phencyclone (**1**) with Bicyclo[2.2.1]hepta-2,5-diene (**2**) to form cycloadduct **3**.

In an early study [1], Mackenzie reported the synthesis of bicyclo[2.2.1]heptene **3** and provided combustion analysis and infrared (IR) spectroscopy data in support of the putative structure. Further evidence in support of the proposed structure was that bicyclo[2.2.1]heptane **4** was isolated after catalytic hydrogenation of **3** (Scheme 2). Furthermore, compound **3** was found to undergo a thermal decomposition sequence that included a retro Diels-Alder reaction, and consecutive thermal cheletropic extrusion of carbon monoxide, to afford 1,4-diphenyltriphenylene (**5**). Mackenzie was able to trap the cyclopentadiene released from the Diels-Alder reaction as cycloadduct **6** (Scheme 2), this was achieved by allowing the gases released to react with maleic anhydride [1]. Further investigations using ^{1}H NMR spectroscopy [2–4] have confirmed that bicyclo[2.2.1]heptene **3** is obtained from the [4 + 2] cycloaddition reaction of phencyclone with norbornadiene. NMR studies demonstrate that the cycloadduct can be readily identified as the *endo-exo* isomer, this is because the norbornyl "bridgehead" CH_2 protons are not magnetically equivalent. Both CH_2 protons have unexpectedly low chemical shift values due to phenanthrene ring current effects.



Scheme 2. Reduction and thermal decomposition reactions of compound **3**.

2. Results

Phencyclone **1** readily reacts with norbornadiene **2** in refluxing chlorobenzene or toluene, however, toluene was found most convenient for this work. The reaction is usually complete within 30–40 min, reaction progress can be readily monitored by observing the colour of the reaction mixture. Phencyclone initially forms a dark green solution when dissolved in toluene, this colour progressively fades to yellow as the starting material is consumed. Material that was suitable for study by X-ray crystallography was obtained by dissolving a sample of compound **3** (0.1 g) in ethyl acetate (5 mL) and then allowing 40–60 light petrol vapour to slowly diffuse into the sample solution. The sample was sealed and stored for 2–3 weeks, until suitable crystals formed and isolated. The crystal structure of **3** (Figure 1) confirms the results from earlier studies that that the compound is isolated as the *endo-exo* isomer [2,3].

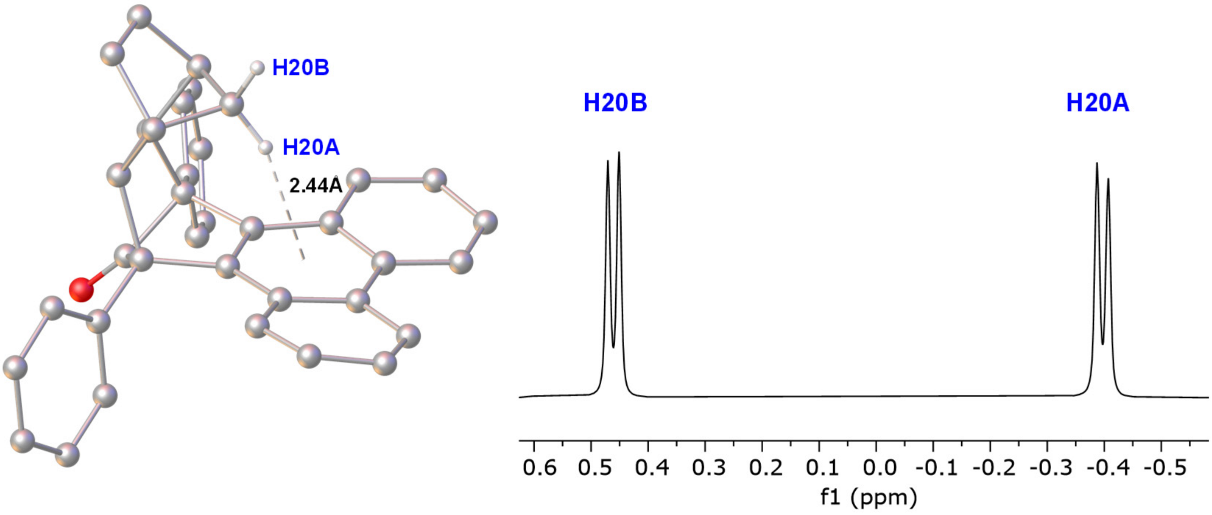


Figure 1. ^{1}H NMR spectrum expansion showing the norbornyl bridgehead CH_2 signals of bicyclo[2.2.1]heptene **3**. The X-ray crystal structure has been superimposed and the distance between H20A and the phenanthrene ring system (2.44 Å) is highlighted.

As highlighted in the introduction, there are useful chemical shift features in the ^{1}H NMR spectrum of compound **3** that allow the identification of the isomer formed in the cycloaddition reaction. Earlier work used lower field spectrometers in NMR studies, in this case ^{1}H NMR spectra have been acquired at 500 MHz (see the Supplementary Materials). In this study, NMR and X-ray crystallography data have been used to account for the usually low chemical shifts of the norbornyl protons H20A and H20B. (Figure 1). The crystal structure clearly illustrates the close proximity of H20A to the phenanthrene aromatic ring system (H···centroid distance is 2.44 Å, Figure 1), this orientation is also reflected in the ^{1}H NMR spectrum since H20A is strongly shielded by the phenanthrene ring (CH-π interaction) and is observed as an apparent doublet at −0.40 ppm. H20B is also affected, but to a lesser extent, the corresponding signal is observed at 0.46 ppm.

The ^{1}H NMR spectrum of compound **3** indicates that the bridgehead phenyl groups exhibit restricted rotation around the C(sp^2)-C(sp^3) bond. Slow C-C rotation on the NMR timescale would be expected to lead to the observation of 5 chemical shift environments associated with the phenyl groups. As expected, 5 signals in the ^{1}H NMR spectrum can be assigned to the phenyl ring protons. Detailed NMR studies of [4 + 2] cycloadducts obtained from phencyclone and maleimides have been published [5]. Recently we have also observed this effect in the cycloadduct obtained from the reaction of phencyclone with maleic anhydride [6]. Work to date suggests that steric interactions between the *ortho*-hydrogen atoms of the phenyl ring and hydrogen atoms in close proximity from the adjacent phenanthrene ring (Figure 2) responsible for restricted rotation of phenyl groups in substituted bicyclo[2.2.1]heptenes [5]. In this work, EXSY (Exchange SpectroscopY) NMR spectra have been acquired that allow the phenyl protons that undergo slow exchange to be identified, the associated spectra are provided in the Supplementary Materials document.

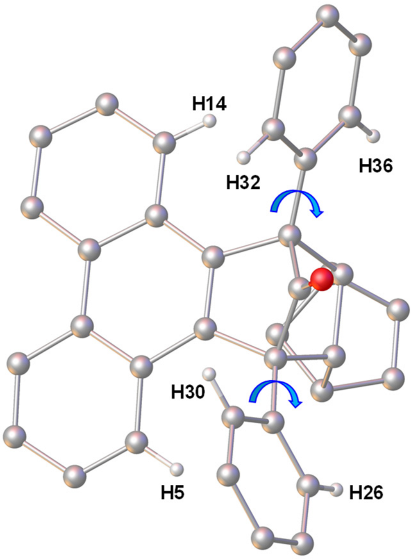
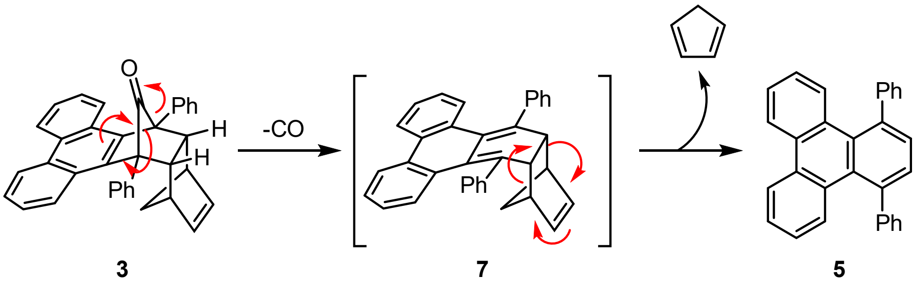


Figure 2. Illustration of phenanthrene and phenyl hydrogen atoms associated with steric interactions that result in restricted rotation of bridgehead phenyl groups.

Cycloadduct **3** can be stored for several years without significant decomposition, however, as is the case with closely related analogues [1,4,6], it is not stable if heated to the melting point. At high temperature, decomposition of **3** to form intermediate **7**, and then 1,4-diphenyltriphenylene (**5**) will occur via the sequence illustrated in Scheme 3. On heating to the melting point, vigorous release of carbon monoxide bubbles is observed, the gas can also be detected using a domestic CO alarm [4]. Thermal cheletropic CO extrusion reactions of are known to occur in other phencyclone cycloadducts and this process has been subject of several studies [1,3,4,7]



Scheme 3. Thermal decomposition of compound **3** via cheletropic extrusion of carbon monoxide and retro Diels-Alder reaction.

Crystallographic techniques have found to be useful for probing cheletropic decarbonylation reactions of bicyclo[2.2.1]heptenes. It has been proposed that the C=O and highlighted C–C bond distances (Figure 3) in bridged cyclopentenone compounds (such as **3**) can be indicators of the potential for cheletropic decarbonylation to take place [7]. A previous survey of bridged cyclopentenone structures has indicated that C-C bonds broken during the cheletropic reaction are typically longer than those expected for the associated cyclopentanone. This study also suggests, the C=O bond is shorter than would be expected in the corresponding bridged cyclopentanone [7]. Our own recent work on the X-ray structures of cycloadducts derived from phencyclone with norbornene [5] and maleic anhydride [6] are in agreement with the original survey [7]. The crystal structure of **3** has allowed key bond distances to be measured and compared with those expected. In this case, the C1–O1 bond distance is 1.1989(19) Å, the C1–C2 bond distance is 1.555(2) Å and the C1–C17 bond distance is 1.553(2) Å. These data are consistent with similar structures that we have obtained [5,6] and those previously reported in the literature [7]; for comparison, the relevant C–C and C=O bond distances in bridged cyclopentanones are typically 1.519 Å and 1.207 Å, respectively [7].

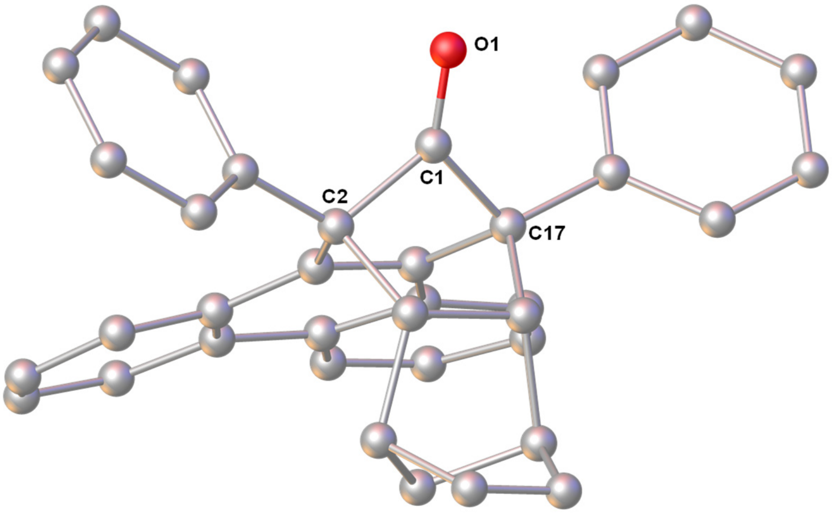


Figure 3. Crystal structure of **3** with key atoms highlighted and hydrogen atoms omitted.

In summary, the first X-ray crystal structure of **3** has been obtained and this confirms the findings of previous studies that *endo-exo* cycloadduct **3** is the product from the [4 + 2] cycloaddition reaction of phencyclone **1** with norbornadiene **2**. The crystallographic data provides useful insight into observed NMR spectroscopy phenomena and thermal decomposition behavior of the title compound.

3. Experimental Section

Melting points were recorded on an SMP3 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum Two instrument (Bruker, Billerica, MA, USA) with DTGS detector and diamond ATR attachment. NMR spectra were obtained for ^{1}H at 500 MHz and for ^{13}C at 125 MHz using a Bruker AVIII 500 instrument (Bruker, Billerica, MA, USA). Spectra were run at 25 °C in $CDCl_3$. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are reported in Hz.

9,14-Diphenyl-9,9a,10,13,13a,14-hexahydro-9,14:10,13-dimethanobenzo[f]tetraphen-15-one (**3**). A solution of phencyclone **1** (0.5 g, 1.3 mmol) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) **2** (0.32 g, 3.25 mmol) in toluene (10 mL) was heated under reflux for 30–40 min (until the green colour due to dissolved phencylone was no longer visible). Upon cooling to room temperature, methanol (5 mL) was added to the reaction flask and the resulting mixture was cooled in an ice bath for 15 min. A colourless solid was formed, this was filtered off and washed with ice-cold methanol (3 × 5 mL) to afford product **3** (0.33 g, 54%) as a colourless solid, mp 228–230 °C (lit. [1] 224–226 °C). IR (ATR) 3029 (ArCH), 1782 (C=O), 1605, 1498, 1448 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$); 8.73 (2H, d, *J* = 8.2 Hz, ArH), 7.87 (2H, apparent d, *J* = 7.5 Hz, PhH), 7.67 (2H, apparent t, *J* = 7.5 Hz, PhH), 7.54 (2H, apparent t, *J* = 7.6 Hz, ArH), 7.50 (2H, apparent t, *J* = 7.3 Hz, PhH), 7.43 (2H, apparent t, *J* = 7.5 Hz, PhH), 7.27–7.21 (4H, m, overlapping ArH and PhH), 7.12 (2H, apparent d, *J* = 8.3 Hz, ArH), 6.46 (2H, s, Alkene CH), 3.07–3.04 (4H, m, overlapping alkyl CH), 0.46 (1H, d, *J* = 9.8 Hz, CH_2-Hb), −0.40 (1H, d, *J* = 9.8 Hz, CH_2-Ha); ^{13}C NMR (125 MHz, $CDCl_3$) 198.9 (C=O), 140.9 (Alkene CH), 137.2 (ArCq), 135.1 (ArCq), 131.6 (ArCH) 130.9 (ArCq), 129.1 (ArCH), 128.8 (ArCH), 128.0 (ArCq), 127.8 (overlapping, 2 × ArCH), 126.3 (overlapping, 2 × ArCH), 125.3 (ArCH), 123.4 (ArCH), 63.4 ($\underline{C}$-Ph), 44.6 (CH), 44.4 (CH), 40.9 (CH_2).

Colourless X-ray quality crystals of **3** were grown by slow diffusion of 40–60 light petrol into a solution of **3** in ethyl acetate. X-ray diffraction data for compound **3** were collected at 173 K using a Rigaku SCXmini CCD diffractometer (Tokyo, Japan) with a SHINE curved graphite monochromator [Mo Kα radiation (λ = 0.71073 Å)]. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data were collected using CrystalClear [8] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro [9]. The structure was solved by dual-space methods (SHELXT) [10] and refined by full-matrix least-squares against F^2 (SHELXL-2018/3) [11]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the Olex2 [12] interface. CCDC 2219492 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures, accessed on 1 November 2022.

Crystal data for $C_{36}H_{26}O$ (M = 474.57): triclinic, space group $P2_1/c$ (no. 14), a = 16.6032(8), b = 10.1889(4), c = 14.8829(7) Å, β = 99.394(4) °, V = 2484.0(2) $Å^3$, Z = 4, T = 173 K, μ (Mo Kα) = 0.075, ρ (calc) = 1.269 g/cm^3, 32121 reflections measured ($5.308° \leq 2\theta \leq 65.646°$), 8772 unique ($R_{int}$ = 0.0965, R_{sigma} = 0.1251), which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0781 and wR_2 (all data) was 0.1457.

Supplementary Materials: The following are available online. Figure S1: IR spectrum of **3**; Figure S2: ^{1}H-NMR spectrum of **3**; Figure S3: ^{1}H-^{1}H COSY 2D H-H correlation NMR spectrum of **3**; Figure S4a–c: EXSY NMR spectra of **3**; Figure S5a,b: ^{13}C DEPTQ NMR spectrum of **3**; Figure S6a,b: ^{1}H-^{13}C HSQC 2D H-C correlation NMR spectrum of **3**; Figure S7: ^{1}H-^{13}C HSQC 2D H-C correlation NMR spectrum of **3**; CIF and checkCIF files for compound **3**.

Author Contributions: This work has been conducted as part of a research project involving honours level undergraduate students (T.D., Y.D., M.L., F.M., J.R. and R.W.), all of the required synthetic steps, crystallisation trials and preliminary analysis have been conducted by this group; D.B.C. collected the x-ray data and solved the structure; S.R.S. and T.L. acquired and analysed the NMR spectroscopy data; I.A.S. and B.A.C. designed the study, analysed the data, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: CCDC 2219492 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures, accessed on 1 November 2022.

Acknowledgments: This work was conducted as part of an undergraduate group research project at the University of St Andrews. The authors express gratitude to the University of St Andrews School of Chemistry for use of their laboratory facilities and provision of materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mackenzie, K. Bicyclo [2.2.1]heptadiene in the Diels-Alder Reaction. *J. Chem. Soc.* **1960**, 473–483. [CrossRef]
2. Sasaki, T.; Kanematsu, K.; Iizuka, K. Molecular design by cycloaddition reactions XXV. High peri- and regiospecificity of phencyclone. *J. Org. Chem.* **1976**, *41*, 1105–1112. [CrossRef]

3. Harrison, E.A. Synthesis of a bicyclo[2.2.1]heptene Diels-Alder adduct: An organic chemistry experiment utilizing NMR spectroscopy to assign endo stereochemistry. *J. Chem. Educ.* **1991**, *68*, 426–427. [CrossRef]
4. Smellie, I.A.; Carpenter-Warren, C.L.; Chalmers, B.A.; Cordes, D.B.; De, A.; Gouy, R.P.F.; Keddie, N.S.; Lebl, T.; Patterson, I.L.J.; Slawin, A.M.Z. Simple and inexpensive method for the detection of carbon monoxide released from thermal cheletropic decarbonylation reactions. *J. Chem. Educ.* **2021**, *98*, 3608–3613. [CrossRef]
5. Callahan, R.; Ramirez, O.; Rosmarion, K.; Rothchild, R.; Bynum, K.C.; Multinuclear, N.M.R. Studies and ab initio structure calculations of hindered phencyclone Diels-Alder adducts from symmetrical cyclic dienophiles: Cyclohexene, vinylene carbonate, vinylene trithiocarbonate and two N-aryl maleimides. *J. Heterocycl. Chem.* **2005**, *42*, 889–898. [CrossRef]
6. Blake, C.; Chalmers, B.A.; Clough, L.A.; Clunie, D.; Cordes, D.B.; Lebl, T.; McDonald, T.R.; Smith, S.R.; Stuart-Morrison, E.; Smellie, I.A. (9R,9aS,12aR,13S)-9,13-Diphenyl-9,9a,12a,13-tetrahydro-9,13-methanotriphenyleno[2,3-c]furan-10,12,14-trione. *Molbank* **2022**, M1435. [CrossRef]
7. Yit Wooi, G.; White, J.M. Structural Manifestations of the Cheletropic Reaction. *Org. Biomol. Chem.* **2005**, *3*, 972–974. [CrossRef] [PubMed]
8. *CrystalClear-SM Expert, v2.1*; Rigaku Americas: The Woodlands, TX, USA; Rigaku Corporation: Tokyo, Japan, 2015.
9. *CrysAlisPro, v1.171.41.93a*; Rigaku Oxford Diffraction; Rigaku Corporation: Oxford, UK, 2020.
10. Sheldrick, G.M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A* **2015**, *71*, 3–8. [CrossRef] [PubMed]
11. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst. Sect. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]
12. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [CrossRef]