*Journal of Chemical Crystallography, Vol. 28, No. 11, 1998*

# Reaction of 2-methylnaphthalene with hexachlorocyclopentadiene and structural characterization of a new addition-substitution product

**Da-Ming Du,**(1,2) **Feng Xue,**(1) **Henry N. C. Wong,**(1)* **and Thomas C. W. Mak**(1)

*Received December 20, 1996*

2-Methylnaphthalene undergoes Diels-Alder addition and substitution with hexachlorocyclopentadiene to give two products, 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4*a*,4*b*,5,8,8*a*,12*b*-octahydro-10-methyl-1,4;5,8-dimethanotriphenylene **1** and 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4*a*,4*b*,5,8,8*a*,12*b*-octahydro-10-(1′,2′,3′,4′,5′-pentachlorocyclopentadienyl)methyl-1,4;5,8-dimethanotriphenylene **2**. The molecular structure of **2** has been characterized by X-ray crystallography: $C_{26}H_9Cl_{17}$, monoclinic, space group $P2_1/c$, with $a$ = 15.316(3), $b$ = 13.698(3), $c$ = 16.116(3) Å, $\beta$ = 96.113(3)°, and $Z$ = 4.

**KEY WORDS:** 2-Methylnaphthalene; hexachlorocyclopentadiene; crystal structure.

## Introduction

Hexachlorocyclopentadiene shows an unexpected tendency to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20°C and 200°C. It condenses even with simple olefins, which normally do not react with diene, and also with polynuclear aromatic hydrocarbons such as naphthalene and anthracene.[1] The condensation is probably the most extensively investigated reaction of the diene and has furnished a variety of new compounds which are not accessible by other methods.[2]

The diene reactions of hexachlorocyclopentadiene with naphthalene and its derivatives offer a route for a relatively facile synthesis of monosubstituted naphthalenes in the β-position[1] and disubstituted naphthalenes in the 2,3-positions.[3] Look reported[4] that when one mole of 2-methylnaphthalene and two moles of hexachlorocyclopentadiene were heated at 150–155°C for 7 days, the 1:2 adduct 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4*a*,4*b*,5,8,8*a*,12*b*-octahydro-10-methyl-1,4;5,8-dimethanotriphenylene **1** was obtained. The resulting reaction product can be used for further novel synthesis of 3-bromo-2-methylnaphthalene.[3] In the present work, we describe the reaction of 2-methylnaphthalene and hexachlorocyclopentadiene to give the adduct **1** and a new compound 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4*a*,4*b*,5,8,8*a*,12*b*-octahydro-10-(1′,2′,3′,4′,5′-pentachloro-cyclopentadienyl)methyl-1,4;5,8,-dimethanotriphenylene **2**, which was structurally characterized by X-ray crystallography.

## Experimental

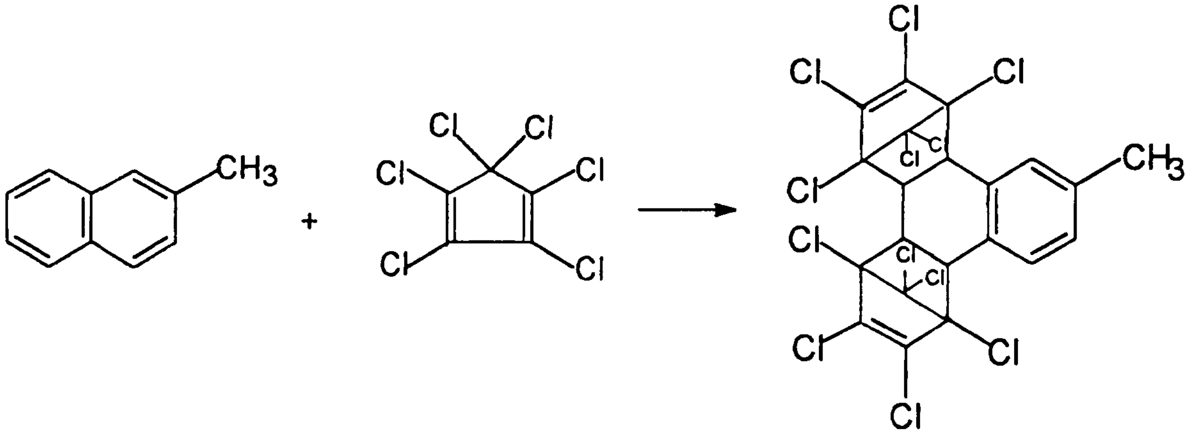
### *Synthesis*

A mixture of 218 g (0.8 mol) hexachlorocyclopentadiene and 57 g (0.4 mol) 2-methylnaphthalene was heated for 7 days at 150–155°C. Excess hexachlorocyclopentadiene and 2-methylnaphthalene were distilled off under vacuum. The mixture was cooled to give a thick oil, which was recrystallized from acetone–methanol (1:1) to give 11.8 g product **2** (yield

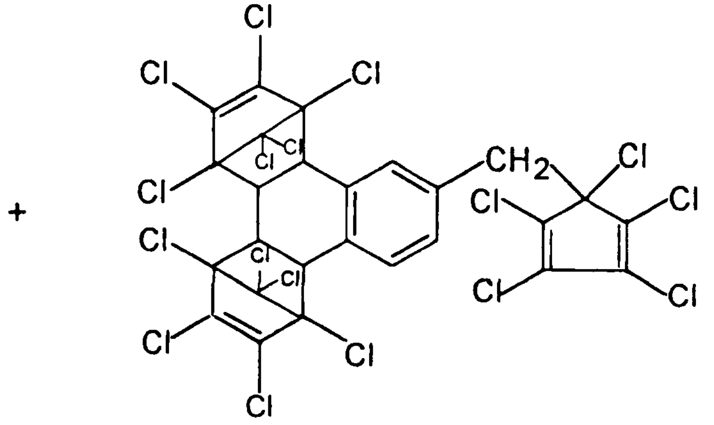
---

(1) Department of Chemistry, The Chinese University of Hong Kong Shatin, New Territories, Hong Kong, P.R. China.
(2) On sabbatical leave from Chemistry Department of Shandong University, Jinan, P.R. China.

* To whom correspondence should be addressed.



Scheme 1.



Scheme 2.

8%): m.p. 232–234°C; IR(KBr) 1603, 1503, 1437, 1254, 1075, 915, 850, 782 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 250MHz) δ3.41(s, 2H), 3.50(d, $J$ = 9.1Hz, 2H), 3.90(t, $J$ = 9.1Hz, 2H), 7.13(d, $J$ = 8.3Hz, 1H), 7.50(s, 1H), 7.63(d, $J$ = 8.3Hz, 1H); mass spectram, *m/e*(%) $M^+$ 924(0.44), 378(16), 237(13), 141(100). Anal. Calcd for $C_{26}H_9Cl_{17}$: C, 33.80; H, 0.98; Cl, 65.22. Found: C, 33.94; H, 1.10; Cl, 65.12.

The mother liquor was chromatographed on silica gel with hexane eluate to give **1**, which was recrystallized from hexane-methanol to give 33 g of pure product **1** (yield 30%): m.p. 154–156°C (lit.[4] 155–158°C); $^{1}$H NMR ($CDCl_3$, 250MHz) δ2.35(s, 3H), 3.50 (d, $J$ = 9.3 Hz, 2H), 3.94 (t, $J$ = 9.3 Hz, 2H), 7.08 (d, $J$ = 8.1 Hz, 1H), 7.51 (s, 1H), 7.58 (d, $J$ = 8.1Hz, 1H).

## *Crystal data of compound 2*

Information concerning crystallographic data and structure determination of compound **2** is summarized in Table 1. Diffraction intensities were collected at 294 K on a Rigaku AFC7R diffractometer using Mo*K*α radiation (λ = 0.71073 Å) in the variable ω-scan mode.[5] The raw data were processed with a learned-profile procedure, and empirical absorption correction based on ω-scan data was also applied.[6]

All the hydrogen atoms were located from difference Fourier maps, assigned isotropic thermal parameters, held stationary, and included in structure-factor calculations in the last stage of full-matrix least-squares refinement. All calculations were performed on a PC 486 computer with the SHELXTL/PC program package.[7,8] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[9]

## Results and discussion

The thermal reaction of hexachlorocyclopentadiene and 2-methylnaphthalene gave the known 2:1

**Table 1.** Crystallographic Data and Structure Refinement of Compound **2**

| | |
|---|---|
| Molecular formula | $C_{26}H_9Cl_{17}$ |
| Formula weight | 924.06 |
| Color/Shape | Colorless needles |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | $a$ = 15.316(3) Å |
| | $b$ = 13.698(3) Å β = 96.113(3)° |
| | $c$ = 16.116(3) Å |
| Volume | 3362(2) $Å^3$ |
| $Z$ | 4 |
| Density (calculated) | 1.826 mg/$m^3$ |
| Absorption coefficient | 1.408 $mm^{-1}$ |
| $F(000)$ | 1816 |
| Crystal size | 0.10 × 0.15 × 0.40 $mm^3$ |
| θ range for data collection | 2.0 to 25.0° |
| Index ranges | $0 \leq h \leq 18, 0 \leq k \leq 16, -19 \leq l \leq 19$ |
| Reflections collected | 6139 |
| Independent reflections | 5904 ($R_{int}$ = 0.0301) |
| Observed reflections | 3111 [$I > 2\sigma(I)$] |
| Absorption correction | Empirical |
| Transmission factors | 0.949 to 1.000 |
| Refinement method | Full-matrix least-squares on $F$ |
| Program used | Siemens SHELXTL PLUS (PC version) |
| Goodness-of-fit on $F^2$ | 1.33 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0437, $wR2$ = 0.0451 |
| $R$ indices (all data) | $R1$ = 0.1126, $wR2$ = 0.0506 |
| Extinction coefficient | 0.00002(2) |
| Largest diff. peak and hole | 0.44 and −0.40 e $Å^{-3}$ |

**Table 2.** Atomic Coordinates (× $10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × $10^3$)

| | $x/a$ | $y/b$ | $z/c$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cl(1) | 3485(1) | 1212(1) | 4389(1) | 45(1) |
| Cl(2) | 1489(1) | 1502(1) | 4952(1) | 56(1) |
| Cl(3) | 923(1) | −567(2) | 5947(1) | 67(1) |
| Cl(4) | 2504(1) | −2198(1) | 5832(1) | 60(1) |
| Cl(5) | 2558(1) | −1002(1) | 3975(1) | 52(1) |
| Cl(6) | 4232(1) | −1095(1) | 4931(1) | 53(1) |
| Cl(7) | 4096(2) | −2097(1) | 7860(1) | 74(1) |
| Cl(8) | 5418(1) | −231(2) | 7557(1) | 87(1) |
| Cl(9) | 4645(1) | 1776(1) | 8494(1) | 69(1) |
| Cl(10) | 2834(1) | 1185(1) | 9289(1) | 54(1) |
| Cl(11) | 2344(1) | −1253(1) | 8856(1) | 57(1) |
| Cl(12) | 4043(1) | −865(1) | 9691(1) | 69(1) |
| Cl(13) | 650(1) | 5219(1) | 7496(1) | 55(1) |
| Cl(14) | 1800(1) | 5361(1) | 5799(1) | 71(1) |
| Cl(15) | 496(1) | 3827(2) | 4546(1) | 86(1) |
| Cl(16) | −515(1) | 2310(2) | 5757(2) | 99(1) |
| Cl(17) | 124(2) | 2817(1) | 7780(1) | 81(1) |
| C(1) | 3567(4) | 514(4) | 6057(3) | 29(2) |
| C(2) | 3347(4) | −503(4) | 6417(3) | 33(2) |
| C(3) | 3016(4) | −558(4) | 7282(3) | 35(2) |
| C(4) | 2651(4) | 386(4) | 7654(3) | 30(2) |
| C(5) | 2317(4) | 2139(4) | 7446(3) | 36(2) |
| C(6) | 2446(4) | 3064(4) | 7123(3) | 37(2) |
| C(7) | 3008(4) | 3138(4) | 6510(3) | 38(2) |
| C(8) | 3389(4) | 2332(4) | 6194(3) | 36(2) |
| C(9) | 3241(3) | 1398(4) | 6501(3) | 29(2) |
| C(10) | 2727(4) | 1316(4) | 7161(3) | 32(2) |
| C(11) | 3089(4) | 443(4) | 5131(3) | 31(2) |
| C(12) | 2113(4) | 509(4) | 5220(3) | 34(2) |
| C(13) | 1891(4) | −298(4) | 5585(3) | 38(2) |
| C(14) | 2703(4) | −950(4) | 5717(3) | 37(2) |
| C(15) | 3150(4) | −659(4) | 4932(3) | 38(2) |
| C(16) | 3744(4) | −891(4) | 7961(4) | 43(2) |
| C(17) | 4461(4) | −120(5) | 7992(4) | 48(2) |
| C(18) | 4163(4) | 662(5) | 8345(4) | 41(2) |
| C(19) | 3234(4) | 450(4) | 8526(3) | 35(2) |
| C(20) | 3345(4) | −650(4) | 8766(4) | 44(2) |
| C(21) | 2001(4) | 3944(4) | 7484(4) | 45(2) |
| C(22) | 1114(4) | 4187(4) | 6994(3) | 37(2) |
| C(23) | 1161(4) | 4432(4) | 6090(4) | 43(2) |
| C(24) | 655(4) | 3830(5) | 5610(4) | 51(3) |
| C(25) | 220(4) | 3174(5) | 6136(5) | 53(3) |
| C(26) | 465(4) | 3371(4) | 6933(4) | 47(2) |

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized $U_{ij}$ tensors.

adduct **1** and a new addition-substitution product **2**. Compound **2** is probably generated in the present reaction by formation of cyclopentadienyl and naphthalenemethyl radicals and their combination, or by naphthalenemethyl radical attack on hexachlorocyclopentadiene with elimination of a Cl atom.[10] The molecular structure of compound **2** is consistent with its NMR, MS, IR spectrum and elemental analysis.

The fractional atomic coordinates and equivalent isotropic temperature factors for the crystal structure of compound **2**, along with their estimated standard deviations, are presented in Table 2. The selected bond lengths and bond angles are listed in Table 3.

The molecular structure of compound **2** is shown in Fig. 1. The two addition moieties of hexachlorocyclopentadiene are fused to the central ring in the expected *trans* conformation, which reduces steric hindrance. The average bond length of the C−Cl bonds on the unsaturated C atoms is significantly shorter than that of C−Cl bonds on the saturated C atoms, and the average ΔC−Cl value is 0.065 Å. The longest C−Cl bond is Cl(13)−C(22) at 1.812 Å. It is noted that the bond length of Cl(13)−C(22)is significantly longer than the average length (1.757 Å) of other C−Cl bonds on the saturated C atoms, which is probably caused by repulsion exerted by the neighboring Cl(14) and Cl(17) atoms.

**Table 3.** Selected bond lengths (Å) and bond angles (°) of compound **2**

| | | | |
|---|---|---|---|
| Bond lengths (Å) | | | |
| Cl(1)–C(11) | 1.750(6) | C(3)–C(4) | 1.554(8) |
| Cl(2)–C(12) | 1.692(6) | C(3)–C(16) | 1.545(8) |
| Cl(3)–C(13) | 1.691(6) | C(4)–C(10) | 1.513(7) |
| Cl(4)–C(14) | 1.749(6) | C(4)–C(19) | 1.584(7) |
| Cl(5)–C(15) | 1.768(6) | C(6)–C(21) | 1.529(8) |
| Cl(6)–C(15) | 1.763(6) | C(11)–C(12) | 1.519(8) |
| Cl(7)–C(16) | 1.749(6) | C(11)–C(15) | 1.547(8) |
| Cl(8)–C(17) | 1.698(7) | C(12)–C(13) | 1.314(8) |
| Cl(9)–C(18) | 1.701(7) | C(13)–C(14) | 1.527(8) |
| Cl(10)–C(19) | 1.750(6) | C(14)–C(15) | 1.553(8) |
| Cl(11)–C(20) | 1.761(7) | C(16)–C(17) | 1.520(9) |
| Cl(12)–C(20) | 1.764(6) | C(16)–C(20) | 1.530(9) |
| Cl(13)–C(22) | 1.812(6) | C(17)–C(18) | 1.317(9) |
| Cl(14)–C(23) | 1.703(7) | C(18)–C(19) | 1.510(9) |
| Cl(15)–C(24) | 1.707(6) | C(19)–C(20) | 1.560(8) |
| Cl(16)–C(25) | 1.701(7) | C(21)–C(22) | 1.534(8) |
| Cl(17)–C(26) | 1.693(7) | C(22)–C(23) | 1.505(9) |
| C(1)–C(2) | 1.560(7) | C(22)–C(26) | 1.491(9) |
| C(1)–C(9) | 1.518(7) | C(23)–C(24) | 1.322(9) |
| C(1)–C(11) | 1.593(7) | C(24)–(25) | 1.446(10) |
| C(2)–C(3) | 1.536(8) | C(25)–C(26) | 1.326(10) |
| C(2)–C(14) | 1.544(8) | | |
| Bond angles (°) | | | |
| C(2)–C(1)–C(9) | 116.3(5) | C(12)–C(11)–C(15) | 99.2(4) |
| C(2)–C(1)–C(11) | 101.4(4) | C(11)–C(12)–C(13) | 107.3(5) |
| C(9)–C(1)–C(11) | 110.4(4) | C(12)–C(13)–C(14) | 108.0(5) |
| C(1)–C(2)–C(3) | 119.2(4) | C(13)–C(14)–C(15) | 99.1(4) |
| C(1)–C(2)–C(14) | 103.2(4) | C(11)–C(15)–C(14) | 92.3(4) |
| C(2)–C(3)–C(4) | 118.5(4) | C(3)–C(16)–C(20) | 102.3(5) |
| C(4)–C(3)–C(16) | 103.6(4) | C(17)–C(16)–C(20) | 100.0(5) |
| C(3)–C(4)–C(10) | 116.5(5) | C(16)–C(17)–C(18) | 107.3(6) |
| C(3)–C(4)–C(19) | 101.3(4) | C(17)–C(18)–C(19) | 107.7(5) |
| C(6)–C(5)–C(10) | 121.8(6) | C(4)–C(19)–C(20) | 101.7(4) |
| C(5)–C(6)–C(7) | 117.3(5) | C(18)–C(19)–C(20) | 98.9(5) |
| C(6)–C(7)–C(8) | 121.8(5) | C(16)–C(20)–C(19) | 92.3(4) |
| C(7)–C(8)–C(9) | 121.0(6) | C(6)–C(21)–C(22) | 112.4(5) |
| C(1)–C(9)–C(10) | 122.4(5) | C(23)–C(22)–C(26) | 101.7(5) |
| C(8)–C(9)–C(10) | 118.0(5) | C(22)–C(23)–C(24) | 110.0(6) |
| C(4)–C(10)–C(9) | 123.4(5) | C(23)–C(24)–C(25) | 108.9(6) |
| C(5)–C(10)–C(9) | 119.8(5) | C(24)–C(25)–C(26) | 109.8(6) |
| C(1)–C(11)–C(12) | 105.4(4) | C(22)–C(26)–C(25) | 109.6(6) |
| C(1)–C(11)–C(15) | 102.8(4) | | |

## Acknowledgment

The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. CUHK 456/95P).

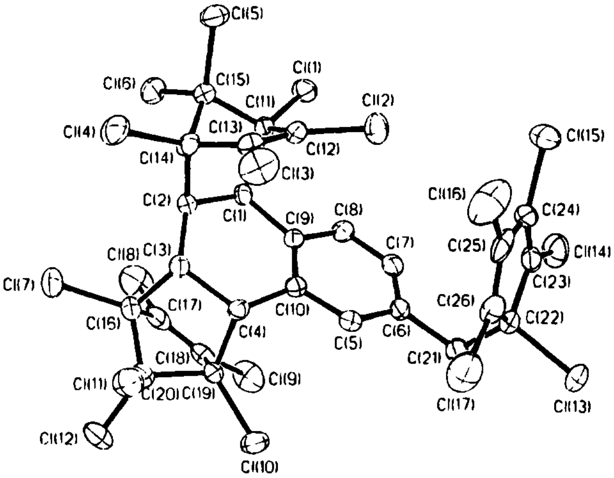


**Fig. 1.** Molecular structure of compound **2** with atom labeling. The thermal ellipsoids are drawn at the 35% probability level.

**Supplementary material.** Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5437. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

## References

1. Danish, A.A.; Silverman, M.; Tajima, Y.A. *J. Am. Chem. Soc.* **1954**, *76*, 6144.
2. Ungnade, H.E.; Mobee, E.T. *Chem. Revs.* **1958**, *58*, 249.
3. Look, M.; Cerrito, E.; Padgett, W.M., II U. S. 3480646 (1969). *Chem. Abstr.* **1965**, *62*, 503b.
4. Look, M. U.S. 3177246 (1965). *Chem. Abstr.* **1965**, *63*, p4227*e*.
5. Sparks, R.A. In *Crystallographic Computing Techniques*; Ahmed, F.R., Ed.; Munksgaard: Copenhagen, 1976; p 452.
6. Kopfmann, G.; Huber, R. *Acta Crystallogr. Sect A* **1968**, *24*, 348.
7. Sheldrick, G.M. In *Computational Crystallography*; Sayre, D., Ed.; Oxford University Press: New York, 1982; p 506.
8. Sheldrick, G.M. In *Crystallographic Computing 3: Data Collection, Structure Determination of Proteins, and Databases*; Sheldrick, G.M.; Kruger, C.; Goddard, R., Eds.; Oxford University Press: New York, 1985; p 175.
9. Ibers, J.A.; Hamilton, W.C. *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press: Birmingham, UK (now attributed by Kluwer Academic Press: Dordrecht, The Netherlands), 1974; pp 55, 99, 149.
10. Freidlina, R.Kh.; Belyavskii, A.B.; Velichko, F.K. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1967**, 407.