

Discussion. Fig. 1 is a thermal-ellipsoid plot of the title compound while Fig. 2 is a stereo drawing. The two six-membered rings are *trans*-fused with the cyclohexenone ring in a 1,2-diplanar conformation slightly distorted towards a half-chair and the cyclohexane ring in a chair conformation. The *trans*-fused lactone is in a half-chair conformation. With the stereochemistry at C(4), C(5), C(6), C(7) and C(10) established by chemical transformations and correlations with santolide C (Rybalko & Dolejs, 1961), the C(11) methyl group can be assigned the α configuration. The bond lengths and angles all fall within the expected range. The only short intramolecular contact is between H(6) and H(14b), 1.99 (4) Å. An intermolecular hydrogen bond is formed between O(12) and O(4) ($2.0-x$, $0.5+y$, $0.5-z$); O(12)···O(4) = 2.967 (3), O(12)···HO(4) = 2.08 (4) Å, O(12)···H—O(4) = 165.7 (6)°.

We thank The Robert A. Welch Foundation (P-074 and F-130) and the TCU/RF for their financial assistance.

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Acta Cryst. (1987). **C43**, 1356–1359

3-(*p*-Cyanophenoxy)quadricyclane and a Redetermination of the Structure of a Hexachloroquadricyclane Dicarboxylate

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(Received 23 October 1986; accepted 24 February 1987)

Abstract. Dimethyl 2,3,3,4,6,7-hexachlorotetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylate (1), C₁₁H₆Cl₆O₄, M_r = 414.88, monoclinic, $P2_1/c$, a = 10.558 (3), b = 12.594 (4), c = 11.732 (3) Å, β = 96.33 (2)°, V = 1550 (1) Å³, Z = 4, D_x = 1.778 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 11.23 cm⁻¹, $F(000)$ = 824, T = 300 K, R = 0.052 for 1909 unique reflections. 3-(Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptyl)oxybenzonitrile (2), C₁₄H₁₁NO, M_r = 209.25, triclinic, $P\bar{1}$, a = 6.034 (2), b = 9.322 (3), c =

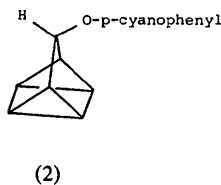
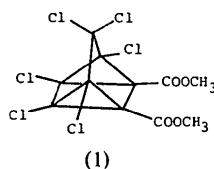
9.458 (3) Å, α = 92.89 (2), β = 93.67 (2), γ = 101.83 (2)°, V = 518.5 (2) Å³, Z = 2, D_x = 1.340 g cm⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.54178 Å, μ = 6.34 cm⁻¹, $F(000)$ = 220, T = 300 K, R = 0.052 for 1312 unique reflections. The two three-membered rings of the quadricyclane (2) form statistically equivalent equilateral triangles with sides and angles averaging 1.495 (3), 1.486 (4) Å, 60.0 (2) and 60.0 (3)°. The four-membered ring forming the base of the quadricyclane is a rectangle with sides of 1.492 (3) and 1.543 (3) Å. Owing to the chloro substitution in (1), the distances around the three-membered rings are

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lengthened and are statistically nonequivalent, 1.518 (6) to 1.547 (6) Å; however, chemically equivalent bonds are statistically equivalent. The four-membered ring of the base is a rectangle with sides averaging 1.534 (4) and 1.560 (6) Å.

Introduction. The first single-crystal X-ray structure of a substituted quadricyclane (1) was reported recently (Matijašić, Ugozzoli, Bocelli, Vancik & Sunko, 1986). Surprisingly, two C—C bond lengths in (1) which symmetry considerations suggest should be identical are reported to be nonequivalent [C(1)—C(7) 1.579 (9) and C(5)—C(6) 1.533 (8) Å; see Fig. 1]. It was suggested that 'repulsive nonbonded interactions' between the carbonyl oxygen atom in the C(1) ester group and the adjacent carbon—chlorine bond, C(7)—Cl, might be responsible for this result. The structure has been redetermined and, in fact, the chemically equivalent bonds are statistically equivalent.

The structures of few quadricyclanes have been elucidated by X-ray techniques, and we propose to provide additional insight into the bonding and geometry of these strained ring systems. As an initial study we report the structure of the symmetric quadricyclane (2) which is substituted only at the methano bridge. Quadricyclane (2) should provide a reference point for the discussion of the more highly substituted derivatives.



Experimental. Compound (1) was prepared by irradiation of a diethyl ether solution of dimethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate. Transparent crystal 0.3 × 0.4 × 0.5 mm; Nicolet R3m/μ update of a P2₁ diffractometer; data collected in the Wyckoff mode (2θ fixed, ω varied, 3 ≤ 2θ ≤ 45°), graphite-monochromated Mo Kα radiation; P2₁/c, Laue class 2/m, unit-cell dimensions from Matijašić, Ugozzoli, Bocelli, Vancik & Sunko (1986); monitored reflections ($\bar{2}1\bar{2}$ and $\bar{5}02$) showed about 10% decay during data collection, 2264 unique reflections of which 1909 had intensities greater than 3σ(I) (0 ≤ h ≤ 13, 0 ≤ k ≤ 14, -13 ≤ l ≤ 13); Lorentz-polarization corrections, ψ scan empirical absorption correction (transmission factors 0.440 to 0.474); direct methods revealed the positions of all Cl atoms, remainder found in subsequent difference Fourier maps, block-cascade least-squares refinement with riding model for H atoms, final R = 0.0501, wR = 0.0563, 192 parameters, S = 2.10, (Δ/σ)_{max}

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for compound (1)

	x	y	z	U_{eq}^*
Cl(1)	7547 (1)	7862 (1)	5414 (1)	56 (1)
Cl(2)	9239 (1)	7443 (1)	8012 (1)	55 (1)
Cl(3)	10083 (1)	6187 (1)	6159 (1)	59 (1)
Cl(4)	9390 (1)	4775 (1)	8522 (1)	52 (1)
Cl(5)	6238 (1)	5096 (1)	8779 (1)	48 (1)
Cl(6)	5130 (1)	7107 (1)	6883 (1)	55 (1)
C(1)	6925 (4)	5715 (4)	5776 (4)	38 (1)
C(2)	7631 (4)	6729 (3)	6241 (4)	38 (1)
C(3)	8804 (4)	6441 (4)	6973 (3)	37 (1)
C(4)	8377 (4)	5433 (4)	7511 (4)	37 (1)
C(5)	7426 (4)	4833 (3)	6653 (3)	36 (1)
C(6)	6961 (4)	5494 (3)	7627 (3)	34 (1)
C(7)	6443 (4)	6355 (4)	6750 (4)	39 (1)
C(8)	6434 (4)	5608 (4)	4551 (4)	42 (2)
C(9)	7076 (5)	5156 (4)	2757 (4)	55 (2)
C(10)	7410 (4)	3661 (4)	6544 (3)	36 (1)
O(1)	7373 (3)	5299 (3)	3959 (3)	49 (1)
C(11)	7436 (6)	2225 (4)	5256 (4)	60 (2)
O(2)	5381 (3)	5812 (4)	4149 (3)	33 (1)
O(3)	7495 (3)	3365 (3)	5466 (2)	51 (1)
O(4)	7337 (3)	3071 (3)	7334 (3)	51 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

= 0.07, (Δ/σ)_{mean} = 0.012; largest peaks in final difference Fourier map +0.41 (adjacent to a Cl atom) and -0.21 e Å⁻³; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.00128F_o^2]^{-1}$. Atomic positional parameters are given in Table 1 while selected bond distances and valence angles are presented in Tables 3 and 4. All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections contained in the program package (*International Tables for X-ray Crystallography*, 1974).

Compound (2) was prepared (Marchand & Dave, 1987) *via* reaction of 3-hydroxyquadricyclane (Story & Fahrenholtz, 1964) with *p*-cyanophenol and diethylazodicarboxylate in the presence of triphenylphosphine; transparent crystal of dimensions 0.45 × 0.30 × 0.15 mm; data collected in the Wyckoff mode (4 ≤ 2θ ≤ 120°), graphite-monochromated Cu Kα radiation; lattice parameters from a least-squares refinement of 25 reflections (4.0 ≤ 2θ ≤ 29.30°), angles measured by a centering routine associated with the diffractometer; no systematic absences, space group $P\bar{1}$, Laue class $\bar{1}$; monitored reflections (010 and 00 $\bar{1}$) showed no significant changes in intensities; 1584 independent reflections measured (0 ≤ h ≤ 7, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11), 1312 with intensities greater than 3σ(I); Lorentz-polarization corrections, ψ scan empirical absorption correction (transmission factors 0.663 to 0.801); direct methods revealed the positions of all non-hydrogen atoms, block-cascade least-squares refinement with riding model for H atoms, final R = 0.052, wR = 0.071, 146 parameters, S = 2.15,

$(\Delta/\sigma)_{\max} = 0.031$, $(\Delta/\sigma)_{\text{mean}} = 0.005$; largest peaks in the final difference Fourier map of $+0.24$ and $-0.23 \text{ e } \text{\AA}^{-3}$; $w = [\sigma^2(F_o) + 0.0050F_o^2]^{-1}$. Other details as for (1). Atomic positional parameters are listed in Table 2 while selected bond lengths and angles are presented in Tables 3 and 4.*

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters for compounds (1) and (2) and additional bond lengths and angles for compound (1) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43818 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for compound (2)

	x	y	z	U_{eq}^*
C(1)	5705 (4)	1866 (3)	3584 (3)	61 (1)
C(2)	3897 (4)	1637 (3)	2395 (2)	55 (1)
C(3)	2389 (4)	2702 (2)	2541 (2)	50 (1)
C(4)	2522 (4)	2922 (3)	4129 (2)	57 (1)
C(5)	4754 (4)	2740 (3)	4751 (3)	66 (1)
C(6)	2728 (4)	1524 (3)	4769 (2)	63 (1)
C(7)	3663 (4)	650 (3)	3603 (2)	59 (1)
C(8)	2079 (3)	5082 (2)	1741 (2)	45 (1)
C(9)	3023 (4)	6291 (3)	1015 (2)	50 (1)
C(10)	1969 (4)	7450 (3)	889 (2)	52 (1)
C(11)	-98 (4)	7417 (2)	1480 (2)	48 (1)
C(12)	-1074 (4)	6206 (3)	2181 (2)	51 (1)
C(13)	-6 (4)	5041 (3)	2314 (2)	52 (1)
C(14)	-1237 (4)	8633 (3)	1373 (2)	53 (1)
O(1)	3303 (2)	4019 (2)	1836 (2)	54 (1)
N(1)	-2162 (4)	9580 (2)	1297 (2)	70 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (\AA)

	(2)	(1)	(1)*	6-31G†	ED‡
C(1)–C(2)	1.491 (3)	1.547 (6)	1.530 (9)	1.519	1.51 (2)
C(1)–C(5)	1.547 (4)	1.566 (6)	1.553 (9)	1.549	1.565 (2)
C(1)–C(7)	1.495 (3)	1.530 (6)	1.579 (9)	1.519	1.515 (2)
C(2)–C(3)	1.485 (4)	1.473 (6)	1.524 (9)	1.514	1.54 (2)
C(2)–C(7)	1.499 (3)	1.522 (6)	1.479 (9)	1.519	
C(3)–C(4)	1.501 (3)	1.509 (6)	1.512 (10)	1.514	
C(3)–O(1)	1.452 (3)				
C(4)–C(5)	1.480 (4)	1.539 (6)	1.502 (10)	1.519	
C(4)–C(6)	1.489 (4)	1.518 (6)	1.480 (9)	1.519	
C(5)–C(6)	1.489 (3)	1.538 (6)	1.533 (8)	1.519	
C(6)–C(7)	1.540 (4)	1.553 (6)	1.552 (9)	1.549	
C(1)–C(8)	1.355 (3)				
C(8)–C(9)	1.390 (3)				
C(8)–C(13)	1.396 (3)				
C(9)–C(10)	1.368 (3)				
C(10)–C(11)	1.394 (3)				
C(11)–C(12)	1.384 (3)				
C(11)–C(14)	1.446 (3)				
C(12)–C(13)	1.378 (3)				
C(14)–N(1)	1.140 (3)				
C(2)–Cl(1)		1.722 (4)			
C(4)–Cl(4)		1.719 (4)			
C(3)–Cl(2)		1.780 (4)			
C(3)–Cl(3)		1.767 (5)			
C(6)–Cl(5)		1.699 (4)			
C(7)–Cl(6)		1.701 (5)			

* Matijašić, Ugozzoli, Bocelli, Vancik & Sunko (1986).

† Raghavachari, Haddon & Roth (1983).

‡ Mizuno, Fukuyama & Kuchitsu (1972); electron diffraction uncertainties estimated from series of calculations fixing different bond lengths.

Discussion. Figs. 1 and 2 are drawings of compounds (1) and (2). In (2) the phenoxy group is extended away from the quadricyclane moiety and should have a minimal steric effect upon bond lengths and geometry. STO-3G and 6-31G *ab initio* calculations have been reported for quadricyclane (Raghavachari, Haddon &

Table 4. Selected valence angles ($^\circ$)

	(2)	(1)	(1)	6-31G	ED
C(2)C(1)C(5)	103.5 (2)	104.2 (3)	104.0 (5)		
C(2)C(1)C(7)	60.3 (1)	59.0 (3)	56.8 (4)		
C(5)C(1)C(7)	89.3 (2)	90.4 (3)	89.6 (5)		
C(1)C(2)C(3)	111.4 (2)	110.3 (4)	108.9 (5)		
C(1)C(2)C(7)	60.0 (2)	59.9 (3)	63.3 (5)	60.0	
C(3)C(2)C(7)	109.7 (2)	112.1 (4)	110.8 (6)		
C(2)C(3)C(4)	99.6 (2)	99.9 (4)	97.8 (6)	99.0	98.5 (2)
C(2)C(3)O(1)	109.6 (2)				
C(4)C(3)O(1)	114.0 (2)				
C(3)C(4)C(5)	110.5 (2)	110.7 (4)	110.7 (6)		
C(3)C(4)C(6)	109.4 (2)	110.5 (4)	112.1 (5)		
C(5)C(4)C(6)	60.2 (2)	60.6 (3)	61.9 (4)		
C(1)C(5)C(4)	105.1 (2)	102.5 (4)	104.1 (5)		
C(1)C(5)C(6)	90.4 (2)	89.5 (3)	90.3 (5)		
C(4)C(5)C(6)	60.2 (2)	58.7 (3)	58.4 (4)		
C(4)C(6)C(5)	59.6 (2)	60.7 (3)	59.8 (4)		
C(4)C(6)C(7)	104.6 (2)	103.8 (4)	103.9 (6)		
C(5)C(6)C(7)	89.8 (2)	89.7 (3)	91.3 (5)		
C(1)C(7)C(2)	59.7 (2)	61.1 (3)	59.9 (4)		
C(1)C(7)C(6)	90.4 (2)	90.3 (3)	88.7 (4)		
C(2)C(7)C(6)	104.1 (2)	103.4 (4)	104.9 (5)		
C(3)O(1)C(8)	119. (2)				
C(10)C(11)C(14)	120.9 (2)				
C(12)C(11)C(14)	119.5 (2)				
C(11)C(14)N(14)	179.0 (2)				

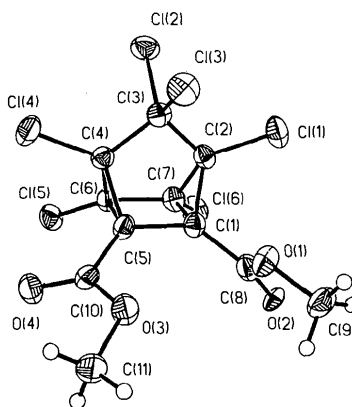


Fig. 1. Drawing of compound (1). Thermal ellipsoids are drawn at the 35% probability level. H atoms are shown as spheres of arbitrary size.

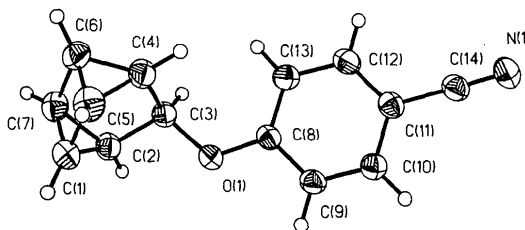


Fig. 2. Drawing of compound (2). Thermal ellipsoids are drawn at the 35% probability level. H atoms are shown as spheres of arbitrary size.

Roth, 1983); however, the only experimental numbers available for this system come from a gas-phase electron diffraction study in which the value of one bond length was assumed in order to allow data analysis (Mizuno, Fukuyama & Kuchitsu, 1972; see Table 3). For comparison purposes the X-ray-determined distances in this discussion have been corrected for thermal motion with the uncorrected values reported in Table 3. The 6-31G calculations (Raghavachari, Haddon & Roth, 1983) predict the sides of the cyclopropane rings to be equal and 1.519 Å in length, which may be compared with our corrected value of 1.496 (3) Å and the gas-phase value of 1.51 (2) Å. The sides of the four-membered ring joining the cyclopropane units, e.g. C(1)–C(5), are 1.549, 1.549 (3) and 1.565 (2) Å for the three sets of data. The C(2)–C(3) distances are 1.514, 1.500 (4) and 1.54 (2) Å while the C(2)C(3)C(4) angles are 99.0, 99.6 (2) and 98.5 (2)°, respectively. The electron diffraction values for the cyclopropane rings agree well with the X-ray and 6-31G values; however, C(1)–C(5) and the related bond are statistically longer. In (2) the interplanar angle between C(2)C(3)C(4) and C(1)–C(2)C(4)C(5) is 3.6 (3)° larger than the corresponding angle with C(2)C(7)C(4)C(6). This small distortion arises because of the phenoxy substituent and may account for the small discrepancy between calculated and observed values for C(2)–C(3).

These data suggest that the current X-ray values for 3-(*p*-cyanophenoxy)quadricyclane should provide an excellent reference structure for the substituted quadricyclanes. While the bond lengths in the quadricyclane (1) (Matijašić, Ugozzoli, Bocelli, Vancik & Sunko, 1986) were expected to be considerably different owing to the electron-withdrawing character of the chloro and

carboxylate substituents, it was difficult to visualize the nonequivalence of chemically identical bonds. The redetermination of the structure shows the C(1)–C(7) [1.530 (6)] and C(5)–C(6) [1.533 (8) Å] bonds to be statistically equivalent as expected and the four-membered ring of the base to be a rectangle. The chemically equivalent C–Cl bonds [e.g. C(2)–Cl(1) and C(4)–Cl(4)] are statistically equivalent in length; however, the chemically nonequivalent sets [e.g. C(2)–Cl(1) and C(7)–Cl(6)] differ in length. Comparison of structures (1) and (2) indicates that the chlorine and carboxylate substituents modify the C–C bonds significantly.

We thank the Robert A. Welch Foundation (WHW P-074, APM B-963), the Air Force Office of Scientific Research (AFOSR-84-0085 to APM), the National Science Foundation (CHE-8514367) and the Texas Christian University and North Texas State University Faculty Research Committees.

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Acta Cryst. (1987). **C43**, 1359–1362

Die Struktur des Diphenhydramin–Thioharnstoff-Komplexes

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(Eingegangen am 9. Juni 1986; angenommen am 27. Februar 1987)

Abstract. 2-Diphenylmethoxy-*N,N*-dimethylethylamine-thiourea (1/3), C₁₇H₂₁NO₃CS(NH₂)₂, *M_r* = 483.7, monoclinic, *Cc*, *a* = 12.129 (4), *b* =

24.380 (8), *c* = 9.668 (3) Å, *β* = 111.74 (2)°, *V* = 2655 Å³, *D_x* = 1.21, *D_m* = 1.21 g cm^{−3}, *Z* = 4, λ(Mo Kα) = 0.7107 Å, *μ* = 2.9075 cm^{−1}, *F*(000) =