

Molecular and crystal structure of 2,3,4,5,6,7,8-heptachloro-2-morpholinocarbonyltricyclo[4.3.0.0^{1,3}]nona- 4,7-dien-9-one

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2,3,4,5,6,7,8-Heptachloro-2-morpholinocarbonyltricyclo[4.3.0.0^{1,3}]nona-4,7-dien-9-one was synthesized by the reaction of the tetrachlorocyclopentadienone dimer with morpholine, and its crystal and molecular structure was established by X-ray diffraction analysis.

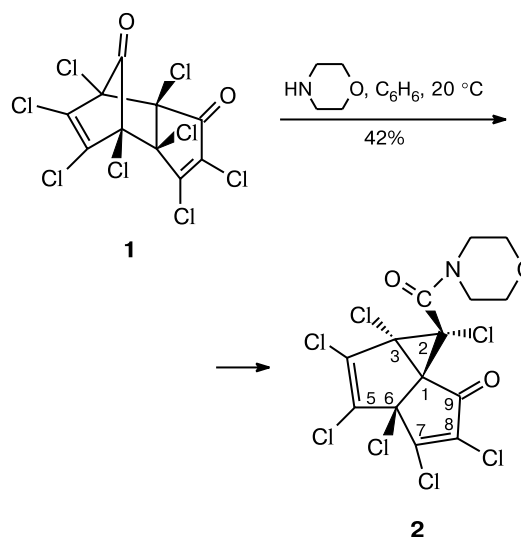
Key words: tetrachlorocyclopentadienone dimer, cyclopropane-containing tricycles, X-ray diffraction analysis.

The readily accessible tetrachlorocyclopentadienone dimer¹ (**1**) attracted our attention as a promising starting compound for constructing unusual structures.^{2,3} The characteristic structural features of this little-studied compound and data on its functionalization suggest a high probability of its unique chemical behavior. Actually, as applied to compound **1**, the *Ad_NE* reaction with amines (HNR¹R²), which proceeds at position 3 and is most typical of 2,3-dichlorocyclopentenones studied by us earlier,⁴ afforded a series of unexpected products containing the amide residue.

Studies by NMR spectroscopy proved to be insufficiently informative to establish the structures of the reaction products, because the core (ring moiety) of the starting compound **1** is devoid of hydrogen atoms. For this reason, we determined the structure of one of the products prepared by the reaction of **1** with morpholine (Scheme 1) by X-ray diffraction analysis.

X-ray diffraction study demonstrated that the reaction gave rise to new tricyclic compound **2**. Its structure is shown in Fig. 1. Molecule **2** involves the bicyclo[3.3.0]octadienone system as the core. This open-book-shaped moiety bears the cyclopropane fragment in the partially triangular junction. Both cyclopentene rings are planar (the average deviations from the C(1)—C(6)—C(5)—C(4)—C(3) (A) and C(1)—C(9)—C(8)—C(7)—C(6) (B) planes are 0.02 and

Scheme 1



0.04 Å, respectively).⁵ The angle between the planes of the rings is 52.2(3)°. The cyclopropane C(1)—C(3)—C(2) fragment bends toward the outer side of the "book" and forms an angle of 117.2(3)° with ring A. The morpholine substituent adopts a usual chair conformation with the N(1) and O(3) atoms deviating from the plane of the ring

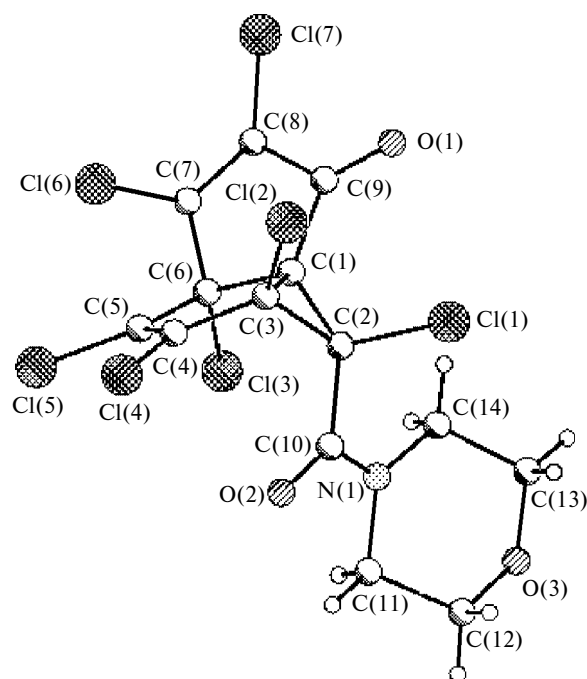


Fig. 1. Molecular structure of **2**.

by -0.64 and 0.68 Å, respectively. The bond lengths and bond angles in the morpholinoamide fragment are close to the standard values for this class of compounds. A comparison of the geometry of the tricyclic core with that of structurally similar 6-hydroxy-3-methyl-5-phenyl-tricyclo[4.3.0.0^{1,3}]non-7-en-9-one (**3**)⁶ (Fig. 2) shows that

these compounds differ in the angles between the planes of the cyclic fragments. Thus, the angle between five-membered rings A and B in molecule **3** is $61.5(2)^\circ$ and the angle between the five- and three-membered rings is $107.2(2)^\circ$, *i.e.*, these angles differ from the corresponding angles in compound **2**, on the average, by 10° . This can be attributed to the fact that five-membered ring A in molecule **3** has no double bonds and has a slightly corrugated structure (the average deviation from the plane is 0.12 Å; the C(4) atom deviates from the C(1)—C(6)—C(5)—C(3) plane by -0.36 Å).

In the crystal, molecules **2** are linked by strong intermolecular Cl...Cl interactions, whose lengths (3.53 , 3.48 , 3.44 , and 3.24 Å) are substantially smaller than the sum of the van der Waals radii (3.65 Å⁷).

Experimental

The IR spectrum was recorded on a Specord M-80 spectrophotometer (in Nujol mulls). The NMR spectra were measured on a Bruker AM-300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C) in CDCl_3 . The mass spectrum (EI) was obtained on a Varian MAT CH-5 instrument; the ionizing voltage was 70 eV. The TLC chromatograms were obtained on Silufol UV 254:366 plates (Czechoslovakia); visualization was carried out by burning or with iodine vapor followed by spraying of the plates with water. The reaction products were isolated by column chromatography on L 100/160 μm silica gel (Chemapol, Czechoslovakia) in amounts of 30 – 60 g per gram of the compound; freshly distilled solvents were used as eluents. Morpholine

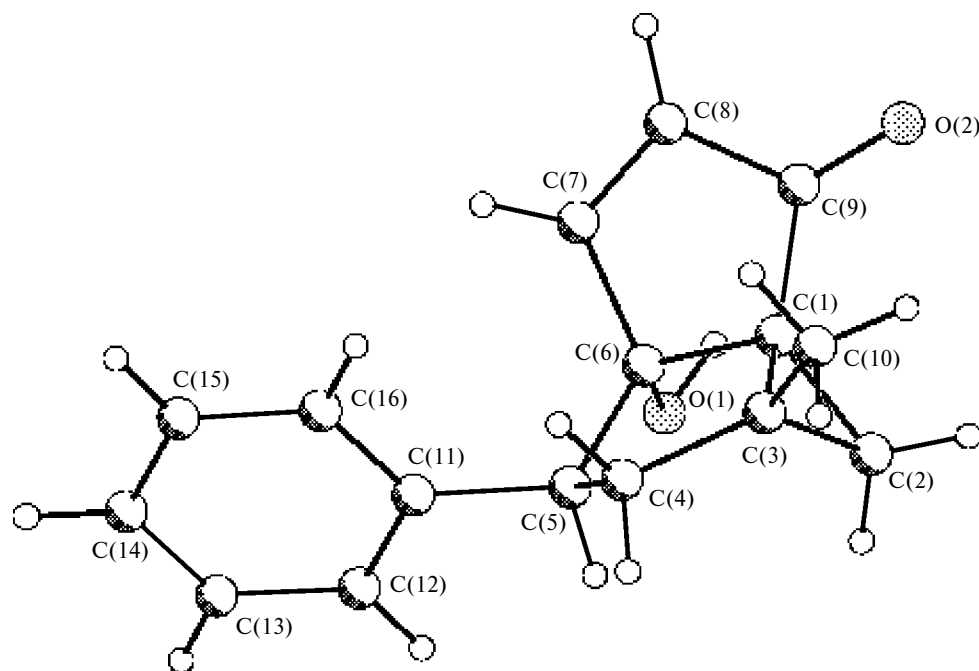


Fig. 2. Molecular structure of **3**.

Table 1. Bond lengths (*d*), bond angles (ω), and torsion angles (τ) in molecule **2**

Bond	<i>d</i> /Å	Angle	ω /deg	Angle	τ /deg
C(1)—C(9)	1.510(3)	C(8)—C(9)—C(1)	104.68(17)	C(9)—C(1)—C(3)—C(4)	127.12(18)
C(9)—C(8)	1.481(3)	C(7)—C(8)—C(9)	112.19(18)	C(9)—C(1)—C(6)—C(7)	−11.12(16)
C(8)—C(7)	1.329(3)	C(6)—C(7)—C(8)	111.97(18)	C(3)—C(1)—C(6)—C(5)	−1.21(18)
C(7)—C(6)	1.516(3)	C(7)—C(6)—C(5)	117.41(15)	C(9)—C(1)—C(3)—C(2)	−118.0(2)
C(6)—C(5)	1.518(3)	C(4)—C(5)—C(6)	112.10(18)	C(4)—C(3)—C(2)—C(10)	−21.0(3)
C(5)—C(4)	1.322(3)	C(5)—C(4)—C(3)	112.60(16)	C(9)—C(1)—C(2)—Cl(1)	3.2(2)
C(4)—C(3)	1.474(3)	C(4)—C(3)—C(1)	105.09(16)	C(1)—C(9)—C(8)—C(7)	−4.4(2)
C(3)—C(2)	1.500(2)	C(9)—C(1)—C(3)	122.20(16)	C(9)—C(8)—C(7)—C(6)	−3.0(2)
C(1)—C(6)	1.536(3)	C(9)—C(1)—C(2)	128.08(17)	C(8)—C(7)—C(6)—C(5)	121.5(2)
C(2)—C(10)	1.536(3)	C(9)—C(1)—C(6)	107.50(16)	C(7)—C(6)—C(5)—C(4)	−113.7(2)
C(1)—C(3)	1.539(2)	O(1)—C(9)—C(1)	128.25(19)	C(6)—C(5)—C(4)—C(3)	4.1(2)
C(1)—C(2)	1.525(3)	C(9)—C(8)—Cl(7)	120.60(17)	C(5)—C(4)—C(3)—C(1)	−4.7(2)
O(1)—C(9)	1.198(3)	C(8)—C(7)—Cl(6)	126.27(16)		
Cl(7)—C(8)	1.700(2)	C(5)—C(6)—Cl(5)	107.54(13)		
Cl(6)—C(7)	1.696(2)	C(6)—C(5)—Cl(4)	122.32(15)		
Cl(5)—C(5)	1.706(2)	C(5)—C(4)—Cl(3)	126.61(16)		
Cl(4)—C(4)	1.702(2)	C(4)—C(3)—Cl(2)	116.09(12)		
Cl(2)—C(3)	1.739(2)	C(1)—C(2)—Cl(1)	117.90(14)		
Cl(1)—C(2)	1.755(2)				
Cl(3)—C(6)	1.784(2)				

was purified by drying over finely dispersed KOH and distillation.

2,3,4,5,6,7,8-Heptachloro-2-morpholinocarbonyltri-cyclo[4.3.0.0^{1,3}]nona-4,7-dien-9-one (2). A solution of morpholine (3–4 equiv.) in benzene (3 mL) was added to a solution of diketone **1** (0.5 g, 0.57 mmol) in benzene (5 mL). The reaction mixture was stirred at −20 °C until the starting compound disappeared (TLC, a 1 : 5 EtOAc—light petroleum mixture as the eluent), diluted with CHCl₃, washed with a saturated NaCl solution, dried with MgSO₄, and evaporated. The residue was purified by column chromatography on SiO₂ (1 : 10 EtOAc—light petroleum mixture as the eluent). After evaporation of the solvents, the product was triturated with a 1 : 10 EtOAc—light petroleum mixture and recrystallized once again. Compound **2** was obtained as colorless crystals, m.p. 208–210 °C (from a 1 : 10 EtOAc—light petroleum mixture), the yield was 42%. Found (%): C, 33.98; H, 1.40; Cl, 50.31; N, 2.50. C₁₄H₈Cl₇NO₃. Calculated (%): C, 34.57; H, 1.66; Cl, 51.02; N, 2.88. IR, ν /cm^{−1}: 1580, 1608 (C=C), 1664 (C=O of amide), 1708 (C=O). ¹H NMR, δ : 3.30 (m, 1 H, CH₂N); 3.40 (m, 1 H, CH₂N); 3.63 (dt, 1 H, CH₂N, ³J = 8.8 Hz, ²J = 2.8 Hz); 3.70–3.90 (m, 5 H, NCH₂, 2 CH₂O). ¹³C NMR, δ : 43.3 (NCH₂); 46.3 (NCH₂); 49.3 (C(1)); 59.3 (C(2)); 60.3 (C(3)); 65.5, 66.1 (OCH₂); 76.3 (C(6)); 127.9 (C(8)); 136.5, 136.9 (C(5), C(4)); 157.2 (C(7)); 158.6 (C=O of amide); 179.3 (C(9)). MS, *m/z*: 491, 489, 487, 485, 483 [M]⁺ (100%), 442, 444, 446, 448 [M − Cl]⁺ (30%).

X-ray diffraction analysis. Colorless needle-like crystals of **2** (C₁₄H₈NO₃Cl₇, *M* = 486.36), monoclinic, at 293(2) K, *a* = 20.645(3), *b* = 15.912(3), *c* = 13.875(2) Å, β = 125.955(3)°, *V* = 3689(1) Å³, *Z* = 8, μ = 1.090 mm^{−1}, *d*_{calc} = 1.751 g cm^{−3}, space group C2/c, single-crystal dimensions were 0.40×0.15×0.10 mm.

X-ray diffraction data were collected on a Bruker SMART CCD 1000 diffractometer at room temperature (293 K). A total

of 23204 reflections were measured. Merging of equivalent reflections gave 3958 independent reflections (*R*_{int} = 0.0310). Absorption corrections were applied using the SADABS program⁹ (transmission (max/min) for **2** was 0.952/0.726). The X-ray data were processed and merged using the SAINT Plus⁸ and SADABS⁹ program packages.

The structure was solved by direct methods with the use of successive electron density syntheses. All nonhydrogen atoms were located from difference electron density syntheses. The refinement was carried out against *F*²_{hkl} with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms in **2** were calculated geometrically and refined using the riding model with *U*_{iso}(H) = 1.2*U*_{eq}(C), where *U*_{eq}(C) are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bound.

The final reliability factors for **2** were as follows: *R*₁ = 0.0524 (for 3158 reflections with *I* > $\sigma(I)$), *wR*₂ = 0.1518 (based on *F*²_{hkl} for all 3958 reflections); 226 parameters were refined.

All calculations were carried out using the SHELXTL program package (version 5.10).¹⁰

The selected geometric parameters of molecule **2** are given in Table 1. The atomic coordinates were deposited with the Cambridge Structural Database.

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References

1. J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, 1949, **71**, 946.

2. E. D. Weil and J. Linder, *J. Org. Chem.*, 1963, **28**, 2218.
3. P. E. Eaton, D. Tang, and R. Gilardi, *Tetrahedron Lett.*, 2002, **43**, 3.
4. R. R. Akhmetvaleev, F. A. Akbutina, N. A. Ivanova, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1417 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1489].
5. F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, 51.
6. A. G. Griesbeck, T. Deufel, K. Peters, E.-M. Peters, and H. G. von Schnering, *J. Org. Chem.*, 1995, **60**, 1952.
7. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1995, **64**, 446 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
8. Bruker SMART. Bruker Molecular Analysis Research Tool, version 5.059. Bruker AXS, Madison, Wisconsin, USA, 1998.
9. G. M. Sheldrick, SADABS, version 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.
10. G. M. Sheldrick, SHELXTL, version 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.

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