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Synthesis and Structure of 1,7-Dichlorodibenzo[*ef,kl*]heptalene-4,10-dione, a Saddle-Shaped Polycyclic Aromatic Compound

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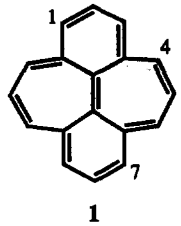
Key words: Strained aromatic compounds; nonplanar aromatic compounds

Abstract: *We describe the synthesis and X-ray crystal structure of the title compound, which is the first fully unsaturated derivative of dibenzo[ef,kl]heptalene to be prepared. The X-ray structure reveals a saddle-shaped molecule possessing approximate* C_2 *symmetry.*

Dibenzo[*ef,kl*]heptalene (**1**) has not been prepared, nor has any derivative which remains fully unsaturated.[1] The related tetracyclic compounds pyrene (**2**) and azupyrene[2] (**3**, dicyclopenta[*ef,kl*]heptalene) have a long history, but these are stable planar aromatic molecules. However, any planar geometry for compound **1** would require several abnormal bond angles (or bond lengths), and it is very likely that the ring system would deform from planarity to relieve such angle strain. Our interest in nonplanar polycyclic aromatic systems[3] has led us to prepare 1,7-dichlorodibenzo[*ef,kl*]-heptalene-4,10-dione (**4**) and to characterize its structure by X-ray crystallography.



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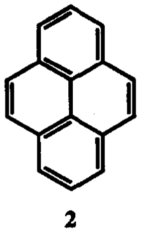

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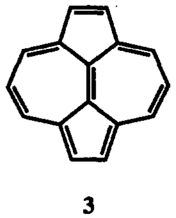

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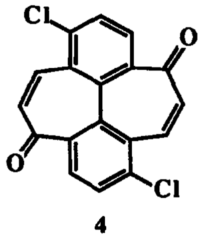

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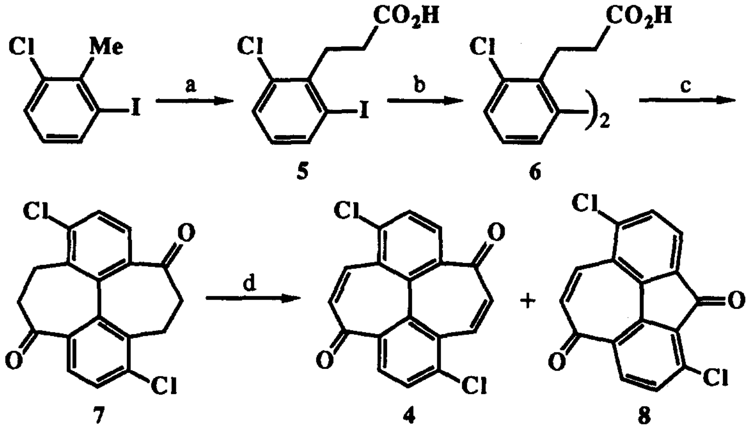
Most of the synthesis of **4** was classical and straightforward (Scheme 1). 2-Iodo-6-chlorotoluene[4] was brominated and carried through a standard malonic ester synthesis to yield the phenylpropanoic acid **5** (77% overall yield).[5] This material was esterified, subjected to an Ullmann coupling, and hydrolyzed to give the biphenyl diacid **6** (20% overall).[6] The tetracyclic ring system was formed by double Friedel-Crafts acylation. The chlorine atoms prevent reaction ortho to the propionic acid groups (which would yield five-membered rings); the only remaining possibilities for intramolecular acylation give the desired seven-membered rings. When compound **6** was heated in polyphosphoric acid at temperatures lower than 160 °C, only a single cyclization occurred, but after heating at 200-220 °C for one hour, compound **7**[7] was isolated in 40% yield by silica gel chromatography (CH_2Cl_2).

For the final dehydrogenation, DDQ oxidation was unsuccessful, but treatment of 7 with benzeneselenenic anhydride[8] gave significant amounts of compound 4 (10-20% yield), always accompanied, however, by at least six other byproducts under the variety of conditions tried (solvents toluene and chlorobenzene; temperatures 90-130 °C; reaction times 0.5-4 h). Compound 4[9] was purified from these mixtures by preparative TLC (4:1 benzene-hexanes), and among the isolated byproducts was compound 8,[10] a planar compound which results from the remarkable loss of two carbons during the oxidation.[11]



Scheme 1. Conditions: (a) $Br_2/h\nu/CCl_4$/reflux; diethyl malonate/Na/EtOH; $HCl/H_2O/HOAc$/reflux; (b) $EtOH/H^+$/reflux; Cu/240 °C; $HCl/H_2O/HOAc$/reflux; (c) PPA/220 °C; (d) $(PhSeO)_2O/PhCl$/100 °C.

Single crystals of compound 4 were obtained from benzene, and an X-ray crystallographic analysis[12] yielded the structure illustrated in Figure 1. The molecule adopts a conformation with approximate C_2 symmetry, and its overall saddle shape is clearly evident in the figure. The torsion angle between the two six-membered rings is approximately 46°.

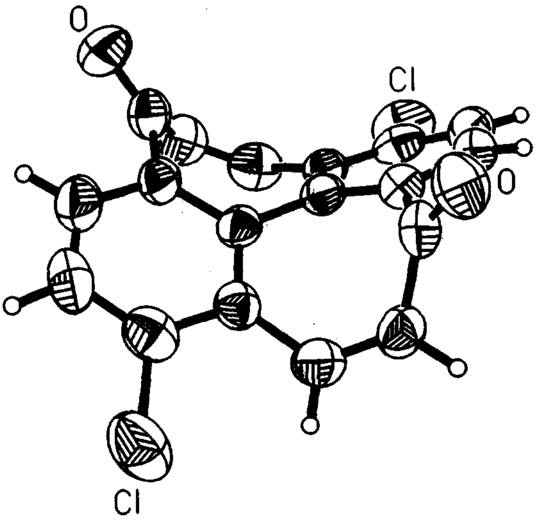
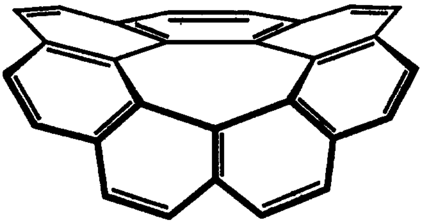


Figure 1. Computer generated perspective drawing of the crystal structure of compound 4 (thermal ellipsoids at 50%).

The degree of distortion in compound **4** is such that the average deviation of its carbon atoms from the mean plane of the C_{18} tetracyclic nucleus is 0.47 Å, and C-6 and C-12 deviate from the mean plane by 0.95 Å and 0.89 Å, respectively. For comparison, in the saddle-shaped hydrocarbon [7]circulene[13] (**9**) the average and maximal deviations from its mean plane (calculated in the same way) are 0.51 Å and 1.07 Å, respectively, but the distortion is spread over a much larger molecule than **4**.



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It may be possible to reduce compound **4** to the parent hydrocarbon **1**, but the low yield of the present synthesis (0.5-1% overall) renders the exploration of such chemistry impractical at this time.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-9106903.

References and Notes

1. Several derivatives of **1** in which the seven-membered rings are partially saturated have been synthesized: Mislow, K.; Glass, M. A. W.; Hopps, H. B.; Simon, E.; Wahl, G. H., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1710-1733.
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5. 3-(2-Iodo-6-chlorophenyl)propionic acid (**5**): mp 131-133 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.63 (m, 2H), 3.33 (m, 2H), 6.65 (t, J = 8 Hz, 1H), 7.36 (dd, J = 8, 1 Hz, 1H), 7.74 (dd, J = 8, 1 Hz, 1H); MS, *m/z* 310 (M^+, 3), 275 (M - Cl, 4), 251 (M - CH_2CO_2H, 23), 183 (M - I, 100). Exact mass 309.9278, calcd for $C_9H_8{}^{35}ClO_2I$ 309.9259.
6. 2,2'-Bis(2-carboxyethyl)-3,3'-dichlorobiphenyl (**6**): mp behavior: ~200 °C, partly melts and resolidifies; 222-223 °C, melts sharply. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.28 (m, 2H), 2.53 (m, 4H), 2.98 (m, 2H), 6.99 (dd, J = 8, 1 Hz, 2H), 7.18 (t, J = 8 Hz, 2H), 7.38 (dd, J = 8, 1 Hz, 2H); MS, *m/z* 366 (M^+, 2), 348 (M - H_2O, 17), 320 (M-H_2O-CO, 14), 247 (M - CH_2CO_2H - CH_3CO_2H, 100). Exact mass 366.0436, calcd for $C_{18}H_{16}{}^{35}Cl_2O_4$ 366.0426.

7. 1,7-Dichloro-5,6,11,12-tetrahydrodibenzo[*ef,kl*]heptalene-4,10-dione (**7**): mp 231-233 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.92 (m, 6H), 3.50 (dt, J = 13, 3 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 7.51 (d, J = 8 Hz, 2H); MS, *m/z* 330 (M^+, 92), 302 (M - CO, 100), 273 (M - CO - HCO, 34), 267 (M - CO - Cl, 47), 239 (M - 2CO - Cl, 85). Exact mass 330.0221, calcd for $C_{18}H_{12}{}^{35}Cl_2O_2$ 330.0214.
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9. 1,7-Dichlorodibenzo[*ef,kl*]heptalene-4,10-dione (**4**): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.75 (d, J = 12 Hz, 2H), 7.48 (d, J = 8 Hz, 2H), 7.64 (d, J = 12 Hz, 2H), 7.67 (d, J = 8 Hz, 2H); MS, *m/z* 326 (M^+, 1.4), 298 (M - CO, 16), 270 (M - 2CO, 100), 235 (M - 2CO - Cl, 15), 200 (M - 2CO - 2Cl, 49). Exact mass 325.9910, calcd for $C_{18}H_{8}{}^{35}Cl_2O_2$ 325.9901.
10. 1,5-Dichlorocyclohepta[*def*]fluorene-4,8-dione (**8**): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.99 (d, J = 13 Hz, 1H), 7.58 (d, J = 9 Hz, 1H), 7.68 (d, J = 8 Hz, 1H), 7.84 (d, J = 8 Hz, 1H), 8.03 (d, J = 13 Hz, 1H), 8.42 (d, J = 9 Hz, 1H); MS, *m/z* 300 (M^+, 37), 272 (M - CO, 100), 244 (M - 2CO, 13), 209 (M - 2CO - Cl, 21), 174 (M - 2CO - 2Cl, 44). Exact mass 299.9756, calcd for $C_{16}H_{6}{}^{35}Cl_2O_2$ 299.9745.
11. A reasonable mechanism for carbon excision and ring contraction, which is often observed in such oxidations, is outlined by Barton et al.[8]
12. A crystal of **4** measuring 0.12 mm x 0.22 mm x 0.38 mm was used for X-ray measurements. Crystal data: $C_{18}H_8Cl_2O_2$; monoclinic, space group $P2_1/c$; a = 9.819 (1) Å, b = 8.533 (2) Å, and c = 17.981 (3) Å, β = 110.26 (1)°, V = 1413.4 (4) Å^3, Z = 4, D_{calcd} = 1.537 g/cm^3. Intensity measurements were made with $4° \leq 2\theta \leq 50°$ by using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature on a Nicolet R3m diffractometer. A total of 2484 independent reflections were measured, of which 1251 were considered to be observed [$|F_0| > 3\sigma(F_0)$]. The structure was solved by direct methods and refined by using the SHELXTL PLUS software. Refinement of 231 parameters converged at R = 0.048, wR = 0.047, with goodness-of-fit = 1.06.
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