

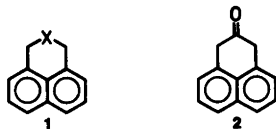
Synthesis and Structural Analysis of the Bridged *peri*-Naphthalene: 1,3-Dihydro-2-phenalenone

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The synthesis of the *peri*-naphthalene, 1,3-dihydro-2-phenalenone is reported in detail. The molecular structure is calculated by molecular mechanics to be a folded C_s conformation with the carbonyl group placed out of the main plane of the molecule. Photoelectron spectroscopy and MNDO molecular orbital calculations indicate the naphthalene and carbonyl moieties to appear as isolated units without appreciable intramolecular interactions in accordance with a folded conformation.

Bridging of the naphthalene framework in the *peri*-positions leads to constrained molecules with conformational properties determined by the length and nature of the bridging chain.^{1–5} A three-atom chain constrains the resulting six-membered ring (1) to a conformation with only the central X-atom out of the main plane of the molecule.^{1,3} We have previously shown the ring inversion to take place through a planar form⁴ and the barrier to depend heavily on the nature of X.⁵ In this paper we report the synthesis of the ketone, 1,3-dihydro-2-phenalenone (2), and a structural analysis by photoelectron (PE) spectroscopy supported by molecular orbital (MNDO) and molecular mechanics (MMP1) calculations.



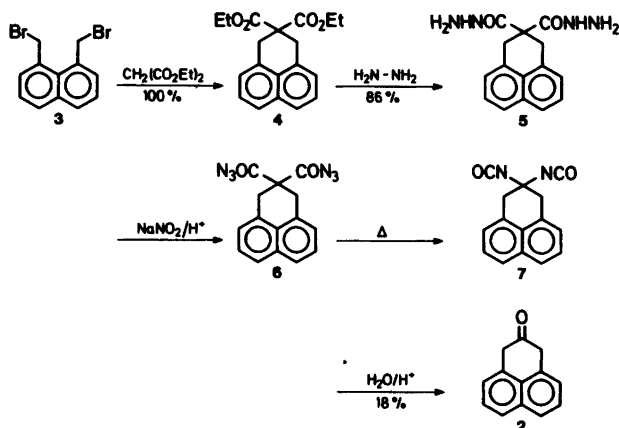
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RESULTS AND DISCUSSION

Two brief reports about the synthesis of 1,3-dihydro-2-phenalenone (2) exist in the literature.^{6,7} The sequence employed here is outlined in Scheme 1 and details collected in the experimental section. The bridging of the *peri*-positions is achieved by a double malonic ester synthesis of the readily available 1,8-bis(bromomethyl)naphthalene (3)⁸ with diethylmalonate. Transformation of the dicarboxylate 4 to the dihydrazide 5, followed by a double Curtius rearrangement,⁹ yields 1,3-dihydro-2-phenalenone (2).

Molecular structures of the ketone 2 with different symmetry have been optimized by the molecular mechanics method (Allinger's MMP1¹⁰) and the C_s conformation with the cyclohexanone ring folded is energetically favoured compared to the planar C_{2v} form. The relatively small puckering angle, *i.e.* the angle between the C–X–C plane and the average plane of the rest of the molecule, of 47.0° reveals 1,3-dihydro-2-phenalenone (2) to be somewhat flatter compared to previously studied C–X–C-bridged *peri*-naphthalenes.^{1,4} The ground state conformation of the ketone 2 being less puckered means that it is closer to the transition state for ring inversion, which is the planar C_{2v} form, and consequently the barrier is smaller. The barrier for ring inversion in 2 has been determined to be lower than 5 kcal/mol by dynamic NMR spectroscopy (F. S. Jørgensen and J. E. Anderson, to be published).

The PE spectrum of 1,3-dihydro-2-phenalenone (2) (Fig. 1) exhibits four well resolved



peaks below 10 eV, and three of these can be attributed to ionizations from the highest occupied naphthalene π orbitals.^{1,11-13} Comparison of the ionization energies of 1,8-dimethylnaphthalene (8)^{1,12} and 1,3-dihydro-2-phenalenone (2) (cf. Fig. 2) allows us to assign the first (7.97 eV), second (8.96 eV) and fourth (9.93 eV) ionizations to the π orbitals of the naphthalene moiety. The first peak shows a vibrational fine structure (1400–1450 cm^{-1}) similar to that found for naphthalene¹³ and 1,8-dimethylnaphthalene (8).^{1,12} By bridging the *peri*-substituents with the carbonyl group (8 \rightarrow 2), the π levels are stabilized by 0.3–0.4 eV, which is similar to the stabilization of the π_{CC} level from cyclopentene to

cyclopenten-3-one,¹⁴ due to the electronegative character of the carbonyl group. Thus, the remaining low energy ionization (the third, 9.51 eV) can be assigned to the oxygen lone pair of the carbonyl group ($n_{\text{C=O}}$).¹⁵

To support the above assignment we have performed an MNDO molecular orbital calculation¹⁶ of 2 based on the MMP1 optimized ground state (C_2) structure. The highest occupied orbitals are the naphthalene π_1 ($\epsilon = -8.76$ eV) and π_2 ($\epsilon = -9.41$ eV) orbitals followed by two nearly degenerate orbitals, *i.e.* the naphthalene π_3 orbital and the carbonyl lone pair, $n_{\text{C=O}}$ ($\epsilon = -10.43$ eV and $\epsilon = -10.63$ eV, respectively). Whereas the naphthalene π orbitals are exclu-

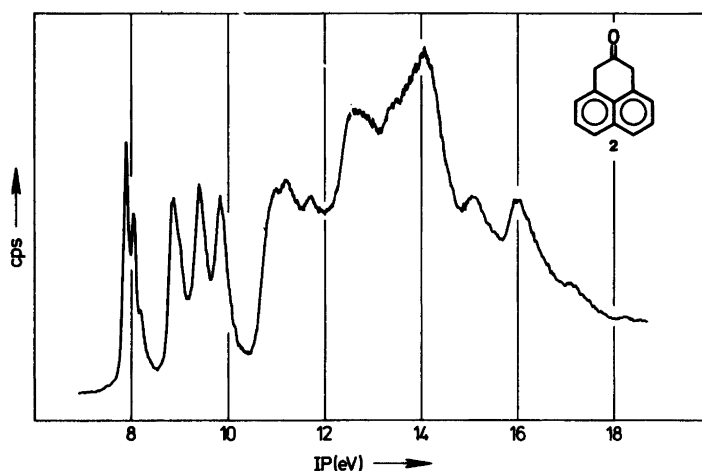


Fig. 1. Photoelectron spectrum of 1,3-dihydro-2-phenalenone (2).

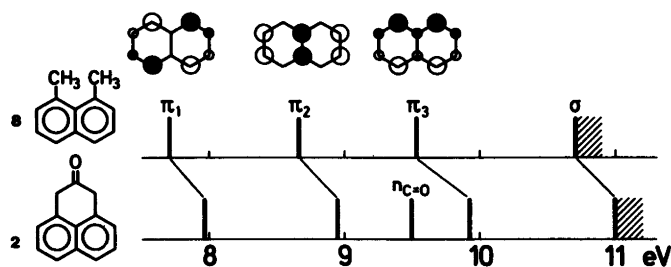


Fig. 2. Correlation diagram for the highest occupied orbitals in 1,8-dimethylnaphthalene (8) and 1,3-dihydro-2-phenalenone (2) based on observed ionization energies.

sively localized on the naphthalene moiety, the $n_{C=O}$ lone pair is localized on the C-CO-C bridge. The latter orbital contains a considerable contribution from the σ orbitals of the three carbon bridge.

In conclusion, molecular mechanics calculations indicate 1,3-dihydro-2-phenalenone (2) to prefer a folded conformation with C_s symmetry, and accordingly interpretation of the PE spectrum suggests intramolecular interactions between the naphthalene and carbonyl moieties to be nearly absent, a property being shown to be characteristic for a folded conformation by the MNDO calculations.

EXPERIMENTAL

Diethyl 1,3-dihydrophenalene-2,2-dicarboxylate (4). Under a nitrogen atmosphere diethyl malonate (15.3 g, 0.096 mol) was added dropwise to a solution of sodium (4.8 g, 0.21 mol) in absolute ethanol (400 ml). This mixture was added dropwise over 2 h to a slurry of 1,8-bis-(bromomethyl)naphthalene⁸ (3) (30.0 g, 0.096 mol) in absolute ethanol (200 ml) and left overnight with stirring. The reaction mixture was refluxed for 2 h, cooled to room temperature and water (700 ml) and chloroform (700 ml) added. The water phase was separated and washed twice with chloroform (100 ml). The combined chloroform extracts were washed twice with a sodium hydroxide solution (10 %, 200 ml) and water (3×200 ml). Removal of the chloroform leaves the dicarboxylate quantitatively as an oil (30.0 g, 0.096 mol), which was pure by TLC and crystallized on standing. ¹H NMR: δ (CDCl₃, Me₄Si) 1.23 (t, 6H), 3.60 (s, 4H), 4.07 (q, 4H), 7.2–7.7 (m, 6H).

1,3-Dihydrophenalene-2,2-dicarboxylic acid dihydrazide (5). A solution of hydrazine (95 %,

64.3 g, 2.01 mol) in absolute ethanol (100 ml) was heated to reflux and a solution of the dicarboxylate 4 (30.0 g, 0.096 mol) in absolute ethanol (20 ml) was added dropwise over 30 min. The reaction mixture was refluxed for 5 h and then left overnight at room temperature. Addition of ether (250 ml) caused precipitation and after filtration and washing with cold ether the dihydrazide 5 was obtained as a white solid (23.6 g, 0.083 mol, 86 %). Recrystallization from absolute ethanol afforded a pure sample, m.p. 210 °C. Anal. Calc. for C₁₅H₁₆N₄O₂: C 63.36; H 5.67; N 19.71. Found: C 63.48; H 5.74; N 19.87. ¹H NMR: δ (DMSO-d₆, Me₄Si) 3.62 (s, 4H), ~4.7 (broad signal, 6H), 7.3–7.8 (m, 6H).

1,3-Dihydro-2-phenalenone (2). The dihydrazide 5 (5.0 g, 0.018 mol) was suspended in benzene (20 ml) and glacial acetic acid (20 ml). After cooling to about 0 °C sodium nitrite (3.0 g, 0.044 mol) in water (10 ml) was added dropwise over 30 min. The reaction mixture was stirred at 0 °C for 1½ h and after addition of benzene (150 ml), it was poured into a cold solution of sodium carbonate (800 ml 1.5 N in water). After the gas evolution ceased, the water phase was separated and washed with chloroform (3×100 ml). The organic phase and the chloroform extracts were combined, dried and the solvent evaporated to give the diazide 6 as a yellow oil, which crystallized by standing overnight in the cold. The diazide 6 was dissolved in chloroform (100 ml) and heated to reflux for 6 h under a nitrogen atmosphere. During the reflux the reaction mixture turned dark green. Evaporation of the solvent yielded the diisocyanate 7, which was dissolved in benzene (130 ml) and concentrated hydrochloric acid (90 ml) added dropwise over 20 min under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h, then refluxed for 2½ h, and after cooling chloroform (150 ml) was added and excess of acid neutralized with saturated sodium hydrogencar-

bonate. The water phase was separated and washed with chloroform (3×75 ml). The combined chloroform phase was washed with water (2×100 ml), dried and evaporation of the solvent yielded a green solid. Sublimation (100 °C/0.5 mmHg) yielded the ketone 2 as yellow needles, m.p. 100 °C. (0.6 g, 0.003 mol, 18 %). The ketone 2 is sensitive to exposure to air, but can be stored in the freezer in ampoules under argon for several months. Anal: Calc. for C₁₃H₁₀O: C 85.69; H 5.53. Found: C 85.64; H 5.56. ¹H NMR: δ(CDCl₃, Me₄Si) 3.97 (s, 4H), 7.2–7.9 (m, 6H).

Photoelectron spectroscopy. The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) with a He(I) source and calibrated with a mixture of argon and xenon introduced into the target chamber simultaneously with the sample. The spectra were recorded at 80–81 °C with an experimental resolution on 30 meV. The reported ionization energies are averages of four determinations.

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