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

FLEMMING S. JØRGENSEN* and TOVE THOMSEN

Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

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 C₄ 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⁻⁻³ A three-atom chain constrains the resulting six-membered ring (I) 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 form ⁴ 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.

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(bromo-methyl)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 MMP1ⁱ⁰) and the C₂ conformation with the cyclohexanone ring folded is energetically favoured compared to the planar C₂ᵥ 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⁺⁻¹ 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 C₂ᵥ 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.\textsuperscript{11–13} Comparison of the ionization energies of 1,8-dimethylnaphthalene (8)\textsuperscript{11,12} 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\textsuperscript{-1}) similar to that found for naphthalene\textsuperscript{12} and 1,8-dimethylnaphthalene (8).\textsuperscript{11,12} By bridging the peri-substituents with the carbonyl group (8 → 2), the π levels are stabilized by 0.3–0.4 eV, which is similar to the stabilization of the π\textsubscript{CC} level from cyclopentene to cyclopenta-3-one,\textsuperscript{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\textsubscript{C=O}).\textsuperscript{15}

To support the above assignment we have performed an MNDO molecular orbital calculation\textsuperscript{16} of 2 based on the MMP1 optimized ground state (C\textsubscript{2}) structure. The highest occupied orbitals are the naphthalene π\textsubscript{1} (ε = −8.76 eV) and π\textsubscript{2} (ε = −9.41 eV) orbitals followed by two nearly degenerate orbitals, i.e. the naphthalene π\textsubscript{3} orbital and the carbonyl lone pair, n\textsubscript{C=O} (ε = −10.43 eV and ε = −10.63 eV, respectively). Whereas the naphthalene π orbitals are exclud-

---

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

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 $\sigma$ orbitals of the three carbon bridge.

In conclusion, molecular mechanics calculations indicate 1,3-dihydro-2-phenalenone (2) to prefer a folded conformation with $C_2$ 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-dihydrophenalen-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)naphthalene (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. $^1$H NMR: $\delta$(CDCl3, Me$_2$Si) 1.23 (t, 6H), 3.60 (s, 4H), 4.07 (q, 4H), 7.2–7.7 (m, 6H).

1,3-Dihydrophenalen-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 C$_{15}$H$_{16}$N$_2$O$_2$: C 63.36; H 5.67; N 19.71. Found: C 63.48; H 5.74; N 19.87. $^1$H NMR: $\delta$(DMSO-d$_6$, Me$_2$Si) 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 diiazide 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 hydrosylcar-
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 C_{18}H_{10}O: 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.

Acknowledgements. We are grateful for financial support to FSJ from the Danish Natural Science Research Council and to Dr. N. L. Bauld (University of Texas at Austin) and Dr. A. S. Kende (University of Rochester) for providing experimental details concerning the preparation of 1,3-dihydro-2-phenalenone (2).

REFERENCES

10. Program No. 318, Quantum Chemistry Program Exchange, University of Indiana; See also Allinger, N. L. and Sprague, J. T. J. Am. Chem. Soc. 95 (1973) 3893.

Received April 15, 1983.