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Acid-catalyzed transformation of rubrene to indenonaphthacene and its paired interacting orbital (PIO) analysis

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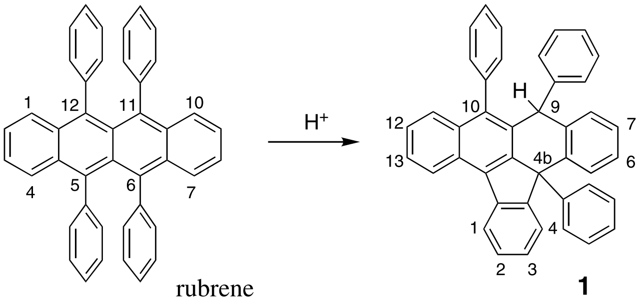
Abstract—Treatment of rubrene (5,6,11,12-tetraphenylnaphthacene) with trifluoroacetic acid in dichloromethane gives 4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]naphthacene (**1**) as the sole isolable product. Paired interacting orbital (PIO) analysis indicates that the reaction is initiated by preferential attack of H^+ at C(11) position of rubrene. © 2003 Elsevier Science Ltd. All rights reserved.

Although the molecule of rubrene (5,6,11,12-tetraphenylnaphthacene) has attracted attention in the field of material science such as a dopant in organic thin-film electroluminescent (EL),[1] its organic transformations have been scarcely reported.[2] In such a background, we have found that a skeletal rearrangement of rubrene to 4b,9,10-triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]naphthacene **1** (Scheme 1) is induced by trifluoroacetic acid. This observation is unprecedented, and of importance because it is referred to as one of fundamental organic reactions of rubrene. We have also found that the initial stage of this reaction can be visually and comprehensively elucidated by paired interacting orbital (PIO) analysis.



Scheme 1.

Since rubrene has been known to be readily converted to its transannular peroxide by irradiating its solution with light in the presence of air,[2a] the following reaction should be carried out by avoiding air and light. Thus, a solution of rubrene (0.5 mmol) in CH_2Cl_2 (3.4 mL) in the presence of CF_3COOH (1.5 mL) was stirred at room temperature under argon in the dark for 3 h. Usual work-up gave triphenyldihydroindenonaphthacene **1**[3] in 63% yield which was purified by TLC ($R_f = 0.5$; hexane/EtOAc = 8/1, SiO_2). Recrystallization from a mixed solvent of benzene, EtOAc, and ether afforded pale yellow crystals (mp 185–188°C) suitable for X-ray analysis.[4] Elemental analysis of the crystal showed the molecular formula of $C_{42}H_{28}\cdot 0.5H_2O$, indicating that it contains water which must come from wet solvent. The space group of this crystal was $P\bar{1}$, and two molecules of **1** are located in a unit cell. The oxygen atom of H_2O included is situated in a general position quite close to the origin, while its occupancy is 0.5. This indicates that only one water molecule is included in a unit cell. The ORTEP presentation of **1** (Fig. 1) shows that the five-membered ring is constructed as an indene structure, and that two newly formed sp^3 carbons are located in C(8) and C(15). The two peripheral phenyl groups at C(8) and C(15) stick out toward the pseudo axial direction, facing each other. The planes defined by C(1)–C(2)–C(3)–C(4)–C(5)–C(6)–C(7)–C(8)–C(15)–C(16)–C(17)–C(18) and by C(8)–C(9)–C(10)–C(11)–C(12)–C(13)–C(14)–C(15) are planar within 0.2 and 0.05 Å, respectively. The angle between the two planes is 121.35(6)°, constructing the bent structure of the molecule. The configuration of two phenyl groups at C(8) and C(15) is

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Keywords: rubrene; indenonaphthacene; paired interacting orbitals; rearrangement.

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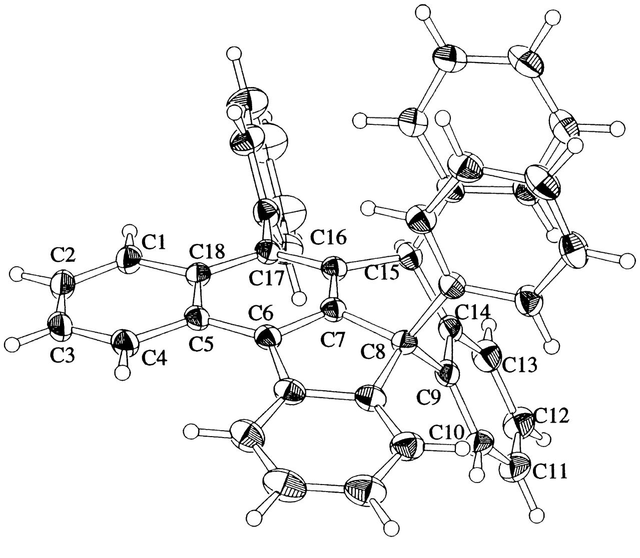
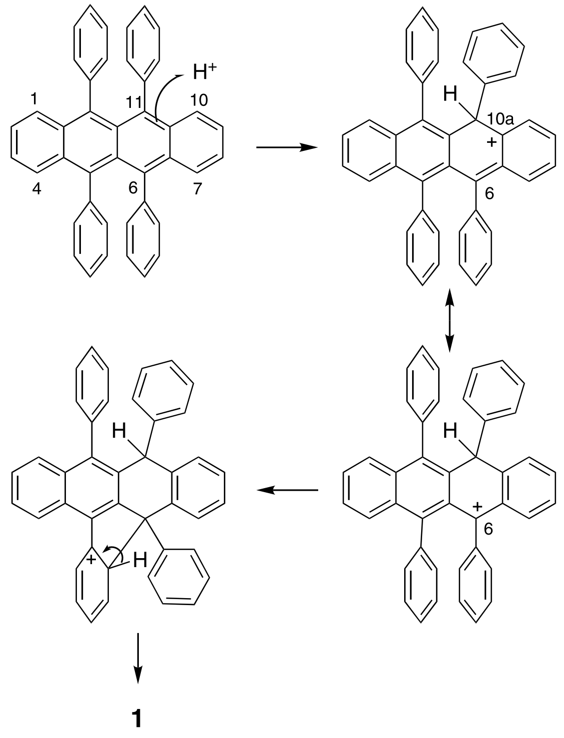


Figure 1. ORTEP drawing of **1** with 30% probability thermal ellipsoids. Water molecule was omitted for clarity.

cis. A simple MOPAC calculation showed that the corresponding *trans* isomer is less stable by ~5 kcal/mol.

The formation of **1** from rubrene can be schematically represented by the pathways shown in Scheme 2. Thus, proton attacks C(11) of rubrene to produce the cationic center at C(10a) which is in allylic conjugation. The resulting cation at C(6) undergoes cyclization via attack at the *ortho* carbon of phenyl ring in the adjacent position. Although the pathway is depicted by a stepwise manner, it may proceed via electrocyclic reaction, because the cation is in the π-conjugation. The initial H^+ attack at C(11) is demonstrated by ^{1}H NMR of deuterated 4b,9-dihydroindenonaphthacene **1** obtained by using CF_3COOD, where no C(9) proton of **1** appeared at δ 5.22 was observed.



Scheme 2.

To understand the reason why proton preferentially attacks C(11) of rubrene, we have carried out PIO analysis.[5] Given in Figure 2(a) is a contour map of PIO where H^+ approaches C(11) position of rubrene. The PIO of H^+ part (indicated by solid lines) is nicely in-phase with the bonding lobe on C(11) of rubrene

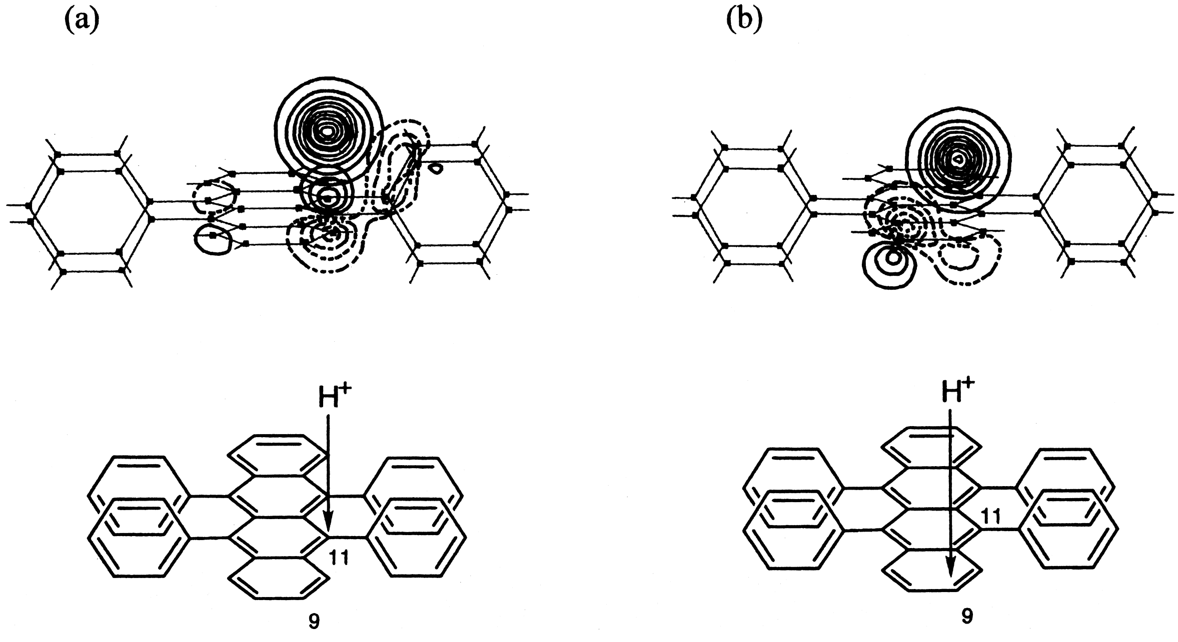


Figure 2. PIO contour maps where H+ approaches either C(11) (a) or C(9) (b) of rubrene.

(also indicated by solid lines), and the bonding lobe of C(11) vertically expands toward H^+ orbital. Therefore, the H^+ attack at C(11) is favorable. A contour map of PIO where H^+ approaches C(9) of rubrene is given in Figure 2(b). Obviously, the PIO of H^+ part shown by solid lines is not in-phase with the PIO lobe on C(9) (indicated by dotted lines). Thus, the H^+ attack at C(9) is not preferable. The same was also the case in the attack at C(10) or (10a) position.

In summary, the transformation of rubrene to triphenyldihydroindenonaphthacene **1** induced by acid is initiated by the attack of H^+ toward C(11) position of rubrene. Such a fundamental fact must be a useful information on the organic transformations of rubrene.

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3. 4b,9,10-Triphenyl-4b,9-dihydroindeno[1,2,3-*fg*]naphthacene (**1**): Some characteristic NMR values δ_H (400 MHz, $CDCl_3$) 8.87 (d, $J=8.3$ Hz, 1H), 8.46 (d, $J=7.7$ Hz, 1H), 8.05 (m, 1H), 5.22 (s, 1H, C-9); δ_C (100 MHz, $CDCl_3$) 152.8, 149.3, 143.2, 60.7 (C-4b), 50.2 (C-9); ν_{max} (KBr) 1594, 1492, 1377, 762, 749, 705, 649, 670; MS (FAB): *m*/*z* 532 (M^+). The yield was determined by NMR.
4. Crystallographic data for **1**: $C_{42}H_{28}\cdot 0.5H_2O$, $M=541.69$, triclinic, $P\bar{1}$, $a=11.979(2)$, $b=12.421(2)$, $c=11.467(2)$ Å, $\alpha=109.33(1)$, $\beta=105.28(1)$, $\gamma=89.09(1)°$, $V=1548.3(4)$ Å^3, $Z=2$, $D_{calcd}=1.162$ g cm^{-3}, μ (Mo Kα) $=0.67$ cm^{-1}, $F(000)=507.00$, $2\theta_{max}=55°$, Mo Kα radiation, of 7454 reflections measured, 7099 were unique. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares method. The final R_1 and Rw factors were 0.065 for $I>2.0\sigma(I)$ data, and 0.243 for all unique reflections, respectively.
5. The PIO analysis, proposed by Fujimoto et al. (Fujimoto, H. *Acc. Chem. Res.* **1987**, *20*, 448 and Fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157–6161), is a method for unequivocally determining the orbitals which should play dominant roles in chemical interactions between two systems, [A] and [B]. In this study, [A] is rubrene and [B] is H^+. An interacting system of rubrene/H^+ (combined system [C]) was constructed by putting H^+ 2.000 Å above a carbon atom of naphthacene ring. The geometrical structure of rubrene was obtained by using following parameters; bond lengths of C–C = 1.390 Å and C–H = 1.080 Å, bond angles of $\angle CCH = \angle CCC = 120.0°$, and an angle between naphthacene ring and phenyl ring is 90.0°. The MOs of [A], [B] and [C] were calculated by the extended Hückel method (EH parameters; H: 1s 1.300-13.60 eV, C: 2s 1.625-21.40 eV, 2p 1.625-11.40 eV). PIOs were obtained by applying the procedure developed by Fujimoto et al. Since the proton [H^+] has only one orbital, only one PIO, namely PIO-1, is constructed. The PIO-1 contains all orbital interactions corresponding to electron delocalization interaction and overlap repulsion. Both of the interactions, that is, in-phase interaction and out of phase interaction are graphically illustrated in Figure 2(a), whereas only the repulsive out of phase interaction can be seen in Figure 2(b). Thus, construction of PIOs allows us to easily extract all interactions which are spread over canonical MOs. The PIO analysis presented here was done by using a software called 'LUMMOX™' (Least Unified Meta-Molecular Orbital Calculation System) recently developed by Sumitomo Chemical Co., Ltd in Japan.