SYNTHESIS AND SOME PROPERTIES OF PHOSPHOIMINO-1-AZAAZULENE DERIVATIVES

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Abstract — 3-Phenyl-8-triphenylphosphoimino- and 2-triphenylphospho-imino-1-azaazulenes were prepared by the reaction of the corresponding 8- and 2-amino-1-azaazulenes with triphenylphosphine dibromide. The structure of 3-phenyl-8-triphenylphosphoimino-1-azaazulene was investigated by X-Ray crystallographic analysis and molecular orbital calculation. The P-atom has trigonal bipiramidal coordination and the intramolecular distance between the N-1 and the P-atom is 2.762(6) Å; the existence of an interaction between N-1 and the P-atom is considered.

Although the chemistry of azaazulenes is of interest for their physical and chemical properties as well as physiological properties,[1] the investigations about azaazulenes containing phosphorus, including in the fused ring or in the side chain, are few.[2—4] Since the resonance stabilization energy in non-alternant conjugation is rather small compared with that of alternant conjugation,[5] the former shows a variety of properties that are noticeably different from the latter. We recently reported that 8-amino-1-azaazulenes (**1**) are interesting non-alternant bidentate ligands and gave 8-diethylborylmethylamino-1-azaazulene (**2**), in which two N—B bond distances are nearly equal.[6] To expand our investigation, we examined the synthesis of 3-phenyl-8-triphenylphosphoimino-1-azaazulene (**3**).

Treatment of 8-amino-3-phenyl-1-azaazulene (**1a**) with triphenylphosphine dibromide in the presence of triethylamine in benzene for 1 d at room temperature gave3-phenyl-8-triphenylphosphoimino-1-azaazulene (**2**) as in 77% yield. For comparison, 2-triphenylphosphoimino-1-azaazulene (**4**)[4,7] and 8-triphenylphosphoiminoquinoline (**5**)[7] were synthesized from corresponding 2-amino-1-azaazulene and 8-aminoquinoline in 52.5% and 69% yields, respectively. The structures of these compounds were decided by their spectroscopic data as well as elemental analyses.[7,8]

In the ^{1}H NMR spectrum of **3**, the seven-membered ring protons appeared at δ 6.88 (dd, J 10.2 and 9.4, H-5), 7.42 (dd, J 10.7 and 9.4, H-6), 7.70 (d, J 10.7, H-7), and 8.12 (d, J 10.2, H-4). The ^{1}H NMR

spectra of **4** and **5** showed the signals of the ring protons at ordinal field.[7]   In the ^{13}C NMR spectrum of **3**, C-2 was observed at δ 143.50 as a broad singlet and C-8 at δ 135.27 (d, J 4.6), whereas, in the ^{13}C NMR spectra of **5**, C-2 was seen at δ 145.51 as a sharp singlet and C-8 at δ 142.22 (d, J 9.5). Moreover, in the ^{13}C NMR spectra, the carbon signals situated at C-7 of **3** (δ 130.69), C-3 of **4** (δ 106.30), and C-7 of **5** (δ 120.25) were coupled with P having coupling constants 2.7, 16.3, and 20.4 Hz, respectively.   These results show that long-range coupling between P and C-2 in **3** exists; the interaction of P and N-1 as shown in **3A** could be considerable.   The ^{31}P NMR of **3** appeared at δ 16.133, and those of **4** and **5** appeared at δ 19.622 and δ 15.955; the ^{31}P NMR data were adequate as a phosphoimine.
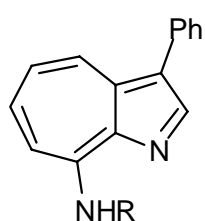
1a : R = H
1b : R = Me
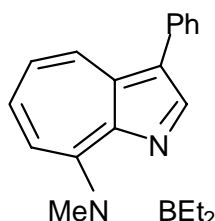
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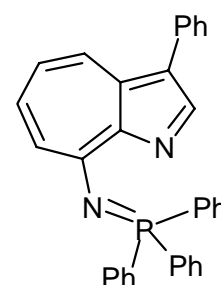
3
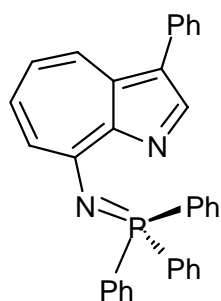
3A
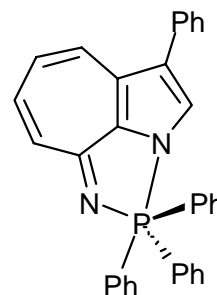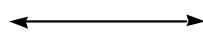
3B

4

5

6
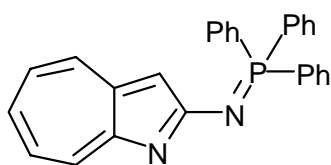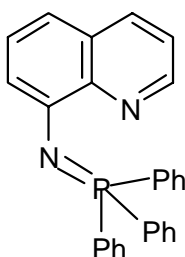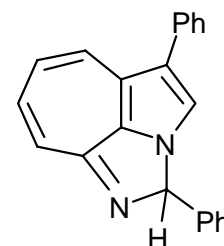
To clarify the structure of **3**, X-Ray crystallographic analysis and molecular orbital calculation (Gaussian 98, RHF/6-31G*) were performed. Results were shown at Figure 1 and Figure 2. From the X-Ray structure analysis,[9,10] the bond distance between N(2) and P(1) is 2.762(6) Å, which is rather short from the value of van der Waals radii (3.4 Å), and the bond distance between C(28) and P(1) is 1.814(2) Å, which is slightly longer than other P—C(phenyl) distances [1.804(2) and 1.811(2) Å]. The intramolecular bond angle of C(28)—P(1)—N(2) is 175.2(2)°. The results show that P(1)-atom has trigonal bipyramidal coordination. The bond distance between N(1) and P(1) is 1.597(2) Å and the bond distance between N(1) and C(1) is 1.350(2) Å; these are to be considered as medium value between single bonds and double bonds. The distinct bond-alternation of seven-membered ring was not observed. Fromthese results, the existence of the resonance between the formulae **3A** and **3B** could be considered. The molecular orbital calculation is comparable to the result of the X-Ray crystallographic analysis.
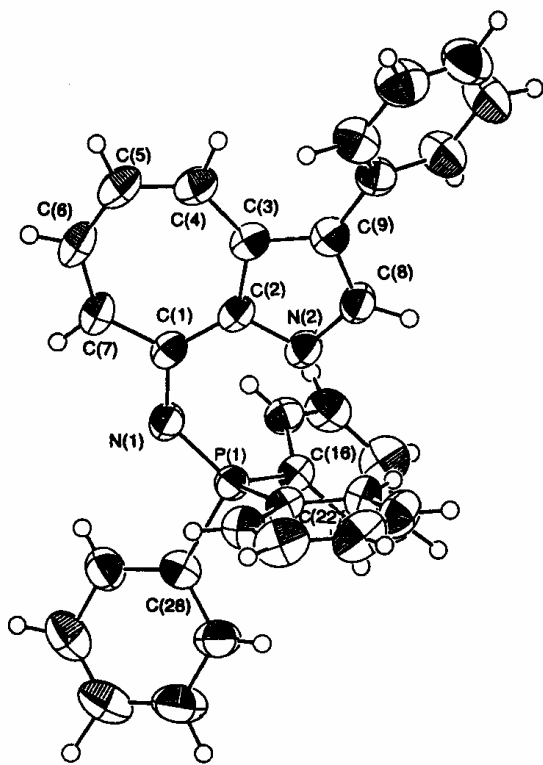

Figure 1. An ORTEP drawing of **3** with thermal ellipsoids (50% probability).
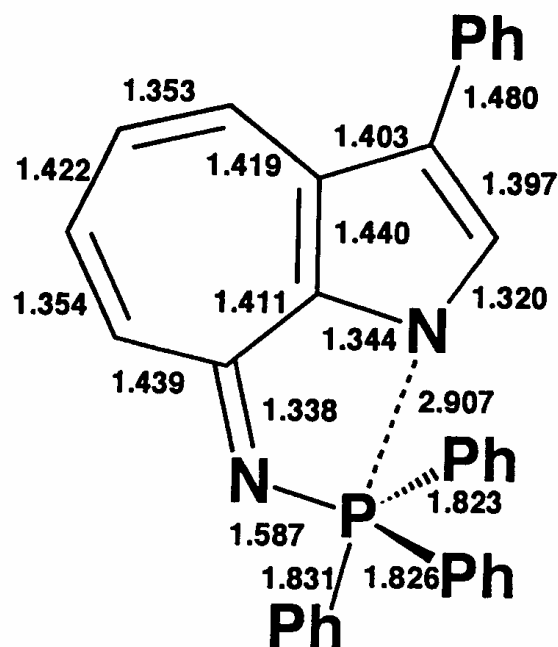
Figure 2. Calculated bondlengths (Å) of **3**.

Since compound (**3**) has a phosphimino moiety, it is considered that **3** could act upon aza-Wittig reaction. Thus, compound (**3**) reacted with benzaldehyde under reflux in toluene for 6 d to give 2,4-diphenyl-1,2a-diaza-2,2a-dihydrocyclopent[*cd*]azulene (**6**)[7, 8] in 10% yield, but did not react with paraformaldehyde or 3-pentanone.

REFERENCES AND NOTES

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7 **3**: δ_H = 6.88 (1H, dd, *J* 10.2 and 9.4), 7.19—7.23 (1H, m), 7.32—7.40 (13H, m), 7.42 (1H, dd, *J* 10.7 and 9.4), 7.64 (1H, s), 7.70 (1H, d, *J* 10.7), 7.82—7.88 (6H, m), and 8.12 (1H, d, *J* 10.2).
4: δ_H = 6.49 (1H, s), 7.09 (1H, dd, *J* 10.1 and 9.7), 7.18 (1H, dd, *J* 10.3 and 9.6), 7.32 (1H, dd, *J* 10.3 and 9.7), 7.44—7.48 (5H, m), 7.53—7.57 (3H, m), 7.66—7.69 (1H, m), 7.71 (1H, d, *J* 10.1), 7.75 (1H, d, *J* 9.6), and 7.82—7.89 (6H, m).   **5**: δ_H = 7.32—7.35(2H, m), 7.47—7.49 (1H, m), 7.53—7.55 (1H, m), 7.61—7.72 (9H, m), 7.98—8.03 (6H, m), 8.25 (1H, dd, *J* 8.3 and 8.2), and 8.30 (1H, m). **6**: δ_H = 5.29 (1H, s), 5.69 (1H, dd, *J* 11.9 and 8.5), 5.96 (1H, dd, *J* 11.9 and 8.5), 6.01 (1H, d, *J* 11.9), 6.62 (1H, d, *J* 11.9), 7.10—7.19 (1H, m), 7.19 (1H, s), 7.28—7.35 (5H, m), 7.40 (2H, t, *J* 7.3), ahd 7.79 (2H, d, *J* 7.3).

8 All new compounds gave satisfactory elemental analyses in accord with the assigned structures.

9 **Crystal data for 3**: Orange prism, $C_{34}H_{25}N_2P \cdot CHCl_3$, *M*=599.92, triclinic, space group P-1, *a*=9.4400(9), *b*=12.0000(7), *c*=12.711(1) Å, α=91.426(5)°, β=96.067(4)°, γ=102.332(6)°, *V*=1431.4(7) Å^3, *Z*=2, D_{calcd}=1.530 g/cm^3, crystal dimensions 0.35 x 0.20 x 0.15 mm.   Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation.   A total 6382 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°.   The structure was solved by direct methods and refined by a full-matrix least-squares method using Crystan structure analysis software (Mac Science),   using 460 variables and 5154 observed reflections ($I > 2\sigma(I)$).   The non-hydrogen atoms were refined anisotropically.   The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses.   The final *R* and *Rw* values were 0.061 and 0.083.   The maximum peak and the minimum peak in final difference map were 3.33 e$^-$/Å^3 and –1.30 e$^-$/Å^3.

10 Selective data: C(1)—C(2) 1.409(3), C(1)—C(7) 1.430(3), C(2)—C(3) 1.459(3), C(3)—C(4) 1.408(3), C(4)—C(5) 1.380, C(5)—C(6) 1.397(3), C(6)—C(7) 1.370(3), C(3)—C(9) 1.415(3), C(8)—C(9) 1.392(3), N(2)—C(2) 1.348(3), N(2)—C(8) 1.349(3); ∠C(28)—P(1)—N(2) 175.2(2)°, ∠C(16)—P(1)—N(1) 115.6(1)°, ∠C(22)—P(1)—N(1) 118.4(1)°, ∠C(28)—P(1)—N(1) 103.0(1)°, ∠C(22)—P(1)—N(1) 118.4(1)°, ∠C(16)—P(1)—C(22) 110.5(1)°, ∠C(16)—P(1)—C(28) 103.7(1)°, ∠C(16)—P(1)—C(28) 103.4(1)°, ∠P(1)—N(1)—C(1) 129.8(2)°.