Reactivity of 12π-Electron Arenothiazines: Synthesis and Molecular Structure of Triphenyl[(4,5,6,7-tetrafluoro-1,2$\lambda^4\delta^2$,3-benzodithiazol-2-yl)imino]-λ^5-phosphane

Andrey V. Zibarev,* Yuri V. Gatilov, Irina Yu. Bagryanskaya, Alexander M. Maksimov and Alexey O. Miller
Institute of Organic Chemistry, 630090 Novosibirsk, Russia

5,6,7,8-Tetrafluoro-1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine **1** adds Ph_3P to form triphenyl [(4,5,6,7-tetrafluoro-1,2$\lambda^4\delta^2$,3-benzodithiazol-2-yl)imino]-λ^5-phosphane **2** whose structure has been identified by X-ray structure analysis.

The chemical properties of 12π-electron 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine **3** and its tetrafluoro-derivative **1**[1–3] are unknown except for the reversible cycloaddition of **3** to norbornadiene.[1] However, the antiaromaticity of **1** and **3**, while being essentially weaker, should lead to high and various reactivities.

We have found that the reaction of **1** with Ph_3P proceeds as a 1 : 1 addition of phosphine to form **2**.† This is different from the known reactions of tertiary phosphines and phosphites both with acyclic[4,5] and cyclic[6–9] thiazines; although they also lead to imino-λ^5-phosphanes, they proceed with partial or complete sulfur elimination from the thiazine system (as a rule, in the form of P=S derivatives),[4–8] except for addition of Ph_3P to the heterocyclic compound $PhCN_5S_3$.[9]

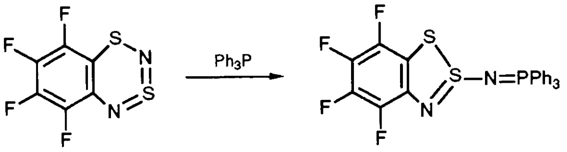
According to X-ray structure analysis (Fig. 1)‡ the hetero-

---

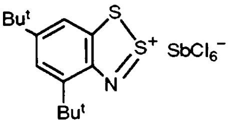
† Ph_3P (0.52 g) in benzene (10 cm^3) was added to **1** (0.48 g) in benzene (10 cm^3) in an argon atmosphere at 20 °C. After 1 h, the solvent was distilled off and the residue was recrystallized three times from hexane. **2**, 0.12 g (12%), transparent orange–brown needles, m.p. 144–145 °C (with decomp.).

Spectroscopic data for **2**: MS *m/z* 502.0362 (M^+; calculated for $C_{24}H_{15}F_4N_2PS_2$ 502.0350). NMR δ (C_6D_6): $^{31}P\{^1H\}$ (external H_3PO_4) 20.9 (s); ^{19}F (internal C_6F_6) 28.9 (ddd, *J* 24, 11, 2 Hz, 1F), 6.2 (ddd, *J* 18, 11, 8 Hz, 1F), −1.1 (ddd, *J* 22, 18, 2 Hz, 1F), −11.6 (ddd, *J* 24, 22, 8 Hz, 1F); ^1H 7.4 (m, 2H), 7.1 (m, 1H), 7.0 (m, 2H). IR ν/cm^{-1} (KBr; vs bands): 1485, 1420, 1410, 1105, 1075, 993, 878, 718, 520. UV (MeCN) λ_{max}/nm (log ε): 513 (2.60).

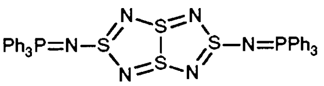
‡ *X-Ray structure data* for **2**: $C_{24}H_{15}F_4N_2PS_2$, $M = 502.48$, monoclinic, $a = 8.895(5)$, $b = 23.80(1)$, $c = 10.669(5)$ Å, $\beta = 95.18(4)°$, $U = 2249(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.484$ g cm^{-3}, μ(Cu-Kα) = 32.37 cm^{-1}, $F(000) = 1024$. Data were measured on a Syntex $P2_1$ diffractometer with graphite monochromated Cu-Kα radiation using θ–2θ scans. An analytical correction for absorption was used. The structure was solved by direct methods and refined in the anisotropic–isotropic approximation to $R = 0.046$ for 1794 independent observed reflections $[|F_o|>3\sigma(|F_o|)]$, $2\theta < 130°$. The parameters of hydrogen atoms were given geometrically and were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Cente. See Notice to Authors, Issue No. 1.



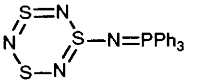
1 **2**



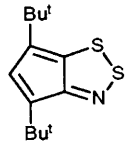
4



5



6



7

cyclic fragment of **2** resembles the 1,2,3-arenodithiazolyl cation **4**[10] but as opposed to **4**, the five-membered ring of **2** is non-planar [the S(1) atom (Fig. 1) deviates from the plane of the other four atoms by 0.396(2) Å], and the chemical bonds in it [except C(1)–C(2)] are longer by 0.024–0.164 Å. The P=N bond of the molecule **2** is shorter than the same bonds in compounds **5**[7] and **6**[6] by 0.098 and 0.151 Å, respectively. The stacking interaction between the polyfluorinated ring and the phenyl group C(19)–C(24) of the molecule **2** is characterized by a distance of 3.39 Å and an angle of 3.8(2)° between their planes. This is very close to the values of the structural parameters of the 1 : 1 complex of hexafluorobenzene and hexamethylbenzene: the angle between the molecular planes of arene and of polyfluoroarene is 3.6°, the distance is 3.43 Å.[11] There is no intermolecular charge transfer in the 1 : 1 arene–polyfluoroarene complexes,[11,12] nor does it seem to occur in **2**.

Among other properties of **2** we note a weak long-wave band in the UV–VIS spectrum lying in the same range as the long-wave bands of pseudoazulene derivatives of 1,2,3-dithiazole,[13,14] for example, **7**.[13]

We thank the International Foundation–Cultural Initiative for financial support of this work as a part of the Gnosis Project.

Received, 19th October 1992; Com. 2/05566J

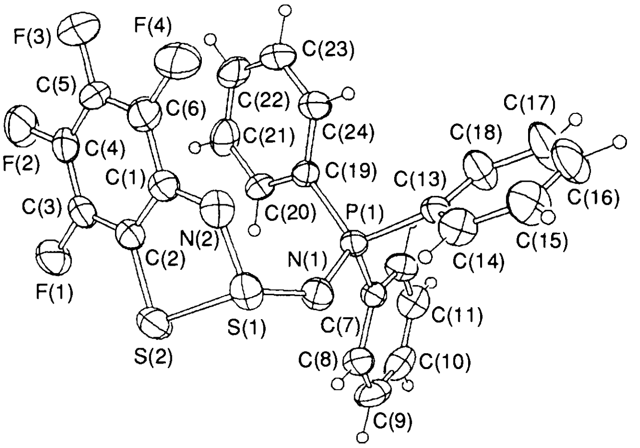


Fig. 1 The structure of molecule **2**. Selected bond lengths (Å) and bond angles (°): S(1)–S(2) 2.186(2), S(1)–N(1) 1.574(5), S(1)–N(2) 1.595(5), S(2)–C(2) 1.745(6), C(1)–C(2) 1.399(7), N(2)–C(1) 1.382(7), P(1)–N(1) 1.494(5), P(1)–C 1.799(5), C–F 1.350(7); S(1)–S(2)–C(2) 89.9(2), S(2)–S(1)–N(1) 107.9(2), S(2)–S(1)–N(2) 96.2(2), N(1)–S(1)–N(2) 114.1(2), S(1)–N(2)–C(1) 115.6(4), S(1)–N(1)–P(1) 136.2(3), S(2)–C(2)–C(1) 114.6(4), N(2)–C(1)–C(2) 119.9(5), N(1)–P(1)–C(19) 119.3(2).

References

1 A. W. Cordes, M. Hojo, H. Koenig, M. C. Noble, R. T. Oakley and W. T. Pennington, *Inorg. Chem.*, 1986, **25**, 1137.

2 A. P. Hitchcock, R. S. DeWitte, J. M. Van Esbroeck, P. Aebi, C. L. French, R. T. Oakley and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 1991, **57**, 165.

3 A. V. Zibarev, Yu. V. Gatilov and A. O. Miller, *Polyhedron*, 1992, **11**, 1137.

4 E. S. Levchenko and B. N. Ugarov, *Zh. Org. Khim.*, 1968, **4**, 1413.

5 T. Minami, H. Miki, H. Matsumoto, Y. Ohshiro and T. Agawa, *Tetrahedron Lett.*, 1968, 3049.

6 E. M. Holt and S. L. Holt, *J. Chem. Soc., Dalton Trans.*, 1974, 1990.

7 J. Bojes, T. Chivers, A. W. Cordes, G. MacLean and R. T. Oakley, *Inorg. Chem.*, 1981, **20**, 16.

8 T. Chivers, *Chem. Rev.*, 1985, **85**, 341.

9 R. T. Boere, A. W. Cordes and R. T. Oakley, *J. Am. Chem. Soc.*, 1987, **109**, 7781.

10 J. W. Bats, H. Fuess, K. L. Weber and H. W. Roesky, *Chem. Ber.*, 1983, **116**, 1751.

11 T. Dahl, *Acta Chem. Scand.*, 1973, **27**, 995.

12 J. S. Brennan, N. M. D. Brown and F. L. Swinton, *J. Chem. Soc., Faraday Trans. 1*, 1974, 1965.

13 K. Hafner, B. Stowasser and V. Sturm, *Tetrahedron Lett.*, 1985, **26**, 189.

14 M. J. Plater and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1991, 311.