

All calculations were performed by application of the program packages: *RASA* (Rigaku Co., 1980), *X-STANP* (Taira, 1980), *MULTAN* (Main, Woolfson, Lessinger, Germain, & Declercq, 1974) and *ORTEP* (Johnson, 1965), on a PANAFACOM U1400 mini-computer, an NEC PC9801m2 personal computer at Tokushima Bunri University, and a FACOM-M360 computer at the Computer Center of the University of Tokushima.

**Discussion.** The fractional atomic coordinates and equivalent isotropic temperature factors are given in Table 1.\* The bond distances, bond angles and torsion angles are listed in Table 2. The molecular structure with the numbering scheme is given in Fig. 1. As shown in Fig. 2 and by the torsion angles around the bonds C(2)—S(1) and S(1)—N(13) in Table 2, the benzene and imidazole rings face each other, the dihedral angle between the least-squares planes of the rings being 100.8°. The molecule, except for the nitro group, has a geometry which is nearly symmetrical with respect to the plane through the atoms C(3)—S(1)—N(13), and the bond lengths and angles are distorted by the steric hindrance between the groups overcrowded around the sulfonyl group. In particular the methyl groups at the

*ortho* positions are bent away from the sulfonyl group, similar to the situation found for MSNT (Kuroda, Sanderson, Neidle & Reese, 1982). Although the length of the bond S(1)—C(2) is close to that of MSNT, 1.758 Å, S(1)—N(13) is significantly shorter than the 1.736 Å of MSNT, which is close to the upper limit reported for the S—N bond, 1.616–1.736 Å (Kuroda, Sanderson, Neidle & Reese, 1982). Such a difference in bond length may be caused by the different electronic effects of the imidazole and triazole rings.

#### References

- BOOM, J. H. VAN, BURGERS, P. M. J., VAN DER MAREL, G., VERDEGAAL, C. H. M. & WILLE, G. (1977). *Nucleic Acids Res.* 4(4), 1047–1063.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- ITAKURA, K., KATAGIRI, N., BAHL, C. P., WIGHTMAN, R. H. & NARANG, S. A. (1973). *Can. J. Chem.* 51, 3649–3651.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KURODA, R., SANDERSON, M. R., NEIDLE, S. & REESE, C. B. (1982). *J. Chem. Soc. Perkin Trans. 2*, pp. 617–620.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Rigaku Co. (1980). *RASA. Rigaku Automatic Structure Analysis Programs*. Tokyo, Japan.
- TAIRA, Z. (1980). *X-STANP. X-ray Structure Analysis Programs for a PANAFACOM U1400 Minicomputer and an NEC PC9801 Personal Computer*. Tokushima Bunri Univ., Japan.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51137 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Acta Cryst.* (1988). C44, 2004–2006

## Structure of Bis[2,6-bis(trifluoromethyl)phenyl]diphosphene

BY A. DUBOURG

*Laboratoire de Physique Industrielle Pharmaceutique, Faculté de Pharmacie, avenue Charles Flahaut, 34060 Montpellier, France*

J.-P. DECLERCQ

*Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, place Pasteur 1, B-1348 Louvain-la-Neuve, Belgium*

AND H. RANAIVONJATOVO, J. ESCUDIÉ, C. COURET AND M. LAZRAQ

*Laboratoire de Chimie des Organominéraux, UA 477 du CNRS, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse CEDEX, France*

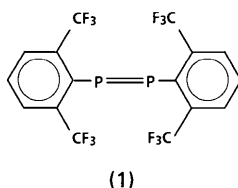
(Received 18 February 1988; accepted 21 June 1988)

**Abstract.** C<sub>16</sub>H<sub>6</sub>F<sub>12</sub>P<sub>2</sub>, *M<sub>r</sub>* = 488.15, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 4.937 (3), *b* = 15.994 (5), *c* = 11.492 (4) Å, β = 93.27 (3)°, *V* = 906.0 (7) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.79 Mg m<sup>-3</sup>, λ(MoKα) = 0.71069 Å, μ = 0.39 mm<sup>-1</sup>, *F*(000) = 480, *T* = 295 K, final *R* = 0.053 for 1415 observed reflections. The title compound

adopts a *trans* configuration with a centre of symmetry at the midpoint of the P=P bond; the two aromatic rings are nearly perpendicular to the C(2)P(1)P(1')C(2') skeleton. The P(1')–P(1)–C(2) angle is the smallest found in diphosphenes. The P=P double-bond length [2.019 (2) Å] lies in the expected range.

**Introduction.** The isolation of the first diphosphene, a compound with a phosphorus–phosphorus double bond, occurred in 1981 (Yoshifuji, Shima, Inamoto, Hirotsu & Higuchi, 1981). Since that date, some other compounds of this type have been synthesized and stabilized by use of various bulky groups [tris(trimethylsilyl)methyl, bis(trimethylsilyl)methyl, pentamethylcyclopentadienyl, bis(silyl)amino, transition metals *etc.*] (Cowley & Norman, 1986).

By using the bis(2,6-trifluoromethyl)phenyl group, which presents both steric and electronic effects, we have recently been able to synthesize the new diphosphene (1) (Escudié, Couret, Ranaivonjatovo, Lazraq & Satgé, 1987).



The physicochemical behaviour of (1) was completely unexpected and very different from that previously reported for other diphosphenes: such derivatives generally react with many electrophiles, nucleophiles or transition metals (Cowley & Norman, 1986). However, no addition reactions on the P=P double bond of (1) could be observed with various electrophiles (hydrochloric or hydrofluoric acids, sulfur *etc.*) or nucleophiles (lithio compounds, Grignard reagents); the only reaction observed was sometimes the cleavage of the C–CF<sub>3</sub> bonds.

The reason for this lack of reactivity of the double bond was not clear, and it seemed to us important to know if it arose only from strong electronic effects due to the bis(2,6-trifluoromethyl)phenyl groups, which may result in a short P=P double-bond length, or steric crowding around this bond. Clearly an X-ray structure determination could give interesting information about this steric hindrance and also about the geometry of this new stabilizing group.

**Experimental.** Compound (1) obtained by crystallization from pentane; light-yellow crystals 0.2 × 0.3 × 0.4 mm. Syntex P2<sub>1</sub> diffractometer, room temperature, graphite-monochromatized Mo K $\alpha$  radiation,  $\omega$ –2 $\theta$  scan. Lattice parameters refined using 15 reflections in the range 9 ≤ 2 $\theta$  ≤ 21°. Standard reflection (004) checked every

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for C, F and P atoms, ( $\times 10^3$ ) for H atoms with *e.s.d.*'s in parentheses and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{\text{eq}} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
P(1)	3777 (2)	270 (1)	566 (1)	3.57 (4)
C(2)	6458 (6)	759 (2)	1550 (3)	3.27 (12)
C(3)	7365 (7)	1576 (2)	1378 (3)	3.95 (14)
C(4)	9299 (9)	1943 (3)	2141 (4)	5.45 (20)
C(5)	10358 (9)	1517 (3)	3092 (4)	6.33 (24)
C(6)	9479 (9)	718 (3)	3295 (4)	5.66 (21)
C(7)	7534 (7)	344 (2)	2547 (3)	4.19 (15)
C(8)	6353 (9)	2088 (2)	347 (4)	5.15 (19)
F(9)	7343 (5)	1830 (2)	–645 (2)	6.47 (13)
F(10)	3657 (5)	2058 (2)	144 (3)	7.87 (16)
F(11)	7033 (7)	2887 (2)	449 (3)	8.63 (18)
C(12)	6717 (10)	–523 (3)	2861 (4)	5.50 (20)
F(13)	4078 (6)	–660 (2)	2728 (3)	7.45 (15)
F(14)	7527 (8)	–747 (2)	3924 (3)	10.64 (22)
F(15)	7788 (7)	–1103 (2)	2173 (3)	7.89 (16)
H(C4)	973 (8)	249 (3)	197 (4)	6.4 (10)
H(C5)	1162 (10)	179 (3)	359 (4)	8.8 (13)
H(C6)	1025 (9)	49 (3)	399 (4)	6.7 (11)

50 reflections: no significant deviation; no absorption correction. 2 $\theta_{\text{max}}$  = 55°. Index range *h* –6/6, *k* 0/20, *l* 0/14. 2092 independent reflections, 1415 observed with *I* ≥ 2.5 $\sigma$ (*I*). A part of the structures was solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Complete resolution by use of DIRDIF81 program (Beurskens *et al.*, 1981). Least-squares refinement based on *F* using SHELX76 (Sheldrick, 1976).

Coefficients of scattering factors used given by *International Tables for X-ray Crystallography* (1974). H atoms from difference Fourier synthesis. In last refinement, anisotropic for P, C and F (parameters refined: *x*, *y*, *z* and *U*<sub>*ij*</sub>) and isotropic for H (*x*, *y*, *z* and *U*), final *R* = 0.053, *wR* = 0.060, weight for every observed structure factor calculated according to  $w = 1/[\sigma^2(F) + 0.00154F^2]$ . ( $\Delta/\sigma$ )<sub>max</sub> = 0.16; *S* = 1.43; –0.30 ≤  $\Delta\rho$  ≤ 0.46 e Å<sup>–3</sup>. Fractional atomic coordinates and bond distances and angles are displayed in Tables 1 and 2 respectively.\* Torsion angles (Table 3) calculated according to Klyne & Prelog (1960) convention. Molecular structure (Fig. 1) drawn with PLUTO (Motherwell & Clegg, 1978).

**Discussion.** As for other diphosphenes, the molecule adopts a *trans* configuration, which is the most favourable. The two P atoms and the two *ipso* carbons of the aromatic rings are in a plane (centre of symmetry

\* Lists of structure factors, anisotropic thermal parameters, atomic coordinates, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51169 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

P(1)—P(1')	2.019 (2)	F(9)—C(8)	1.332 (4)
C(2)—P(1)	1.863 (3)	F(10)—C(8)	1.339 (5)
C(3)—C(2)	1.399 (4)	F(11)—C(8)	1.324 (4)
C(7)—C(2)	1.402 (4)	F(13)—C(12)	1.321 (5)
C(4)—C(3)	1.389 (5)	F(14)—C(12)	1.313 (5)
C(8)—C(3)	1.503 (5)	F(15)—C(12)	1.346 (5)
C(5)—C(4)	1.366 (7)	H(C4)—C(4)	0.92 (4)
C(6)—C(5)	1.373 (7)	H(C5)—C(5)	0.93 (5)
C(7)—C(6)	1.387 (5)	H(C6)—C(6)	0.93 (5)
C(12)—C(7)	1.495 (5)		
C(2)—P(1)—P(1')	98.0 (1)	F(11)—C(8)—C(3)	112.6 (3)
C(3)—C(2)—P(1)	121.9 (2)	F(11)—C(8)—F(9)	105.8 (3)
C(7)—C(2)—P(1)	121.4 (2)	F(11)—C(8)—F(10)	107.1 (3)
C(7)—C(2)—C(3)	116.6 (3)	F(13)—C(12)—C(7)	113.8 (3)
C(4)—C(3)—C(2)	121.3 (4)	F(14)—C(12)—C(7)	113.8 (3)
C(8)—C(3)—C(2)	121.7 (3)	F(14)—C(12)—F(13)	108.0 (4)
C(8)—C(3)—C(4)	116.9 (3)	F(15)—C(12)—C(7)	112.2 (4)
C(5)—C(4)—C(3)	120.8 (4)	F(15)—C(12)—F(13)	103.7 (4)
C(6)—C(5)—C(4)	119.3 (4)	F(15)—C(12)—F(14)	104.5 (4)
C(6)—C(5)—C(6)	120.6 (4)	H(C4)—C(4)—C(3)	115 (3)
C(6)—C(7)—C(2)	121.3 (4)	C(5)—C(4)—H(C4)	124 (3)
C(12)—C(7)—C(2)	122.7 (3)	H(C5)—C(5)—C(4)	119 (3)
C(12)—C(7)—C(6)	115.9 (3)	C(6)—C(5)—H(C5)	123 (3)
F(9)—C(8)—C(3)	112.6 (3)	H(C6)—C(6)—C(5)	113 (3)
F(10)—C(8)—C(3)	113.6 (3)	C(7)—C(6)—H(C6)	126 (3)
F(10)—C(8)—F(9)	104.4 (3)		

Table 3. Selected torsion angles (°) ( $\bar{\sigma} = 0.7^\circ$ )

P(1')—P(1)—C(2)—C(3)	91.8	C(4)—C(3)—C(8)—F(11)	-13.7
P(1')—P(1)—C(2)—C(7)	-92.6	C(2)—C(7)—C(12)—F(13)	-43.3
C(2)—C(3)—C(8)—F(9)	-72.6	C(2)—C(7)—C(12)—F(14)	-167.7
C(2)—C(3)—C(8)—F(10)	45.9	C(2)—C(7)—C(12)—F(15)	73.9
C(2)—C(3)—C(8)—F(11)	167.9	C(6)—C(7)—C(12)—F(13)	137.8
C(4)—C(3)—C(8)—F(9)	105.8	C(6)—C(7)—C(12)—F(14)	13.5
C(4)—C(3)—C(8)—F(10)	-135.7	C(6)—C(7)—C(12)—F(15)	-104.9

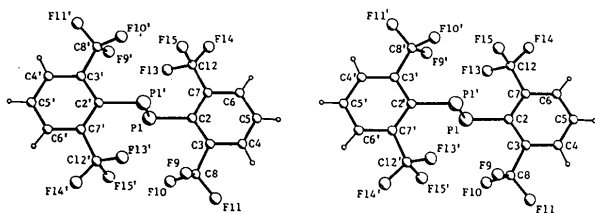


Fig. 1. Stereoscopic view of the title molecule.

110°) have also been observed with a very bulky group such as tris(trimethylsilyl)methyl (Escudié, Couret, Ranaivonjatovo, Satgé & Jaud, 1983) or a transition metal (Weber & Reizig, 1985).

The P=P double-bond length [2.019 (2) Å] lies in the normal range: the shortening in relation to the standard P—P single bond is about 10%. A normal value [1.863 (3) Å] is also observed for P(1)—C(2). Very short contacts are observed between fluorine and phosphorus: F(10)—P(1) = 2.901 (3) and F(13)—P(1) = 2.891 (3) Å. Short distances are also observed between phosphorus P(1') and the fluorines F(9) or F(15) bound to the other aromatic ring: P(1')—F(9) = 3.406 (3), P(1')—F(15) = 3.465 (3) Å. So it appears that this diphosphene is particularly crowded, probably among the most crowded of the diphosphenes so far reported.

Nevertheless this large steric hindrance round the —P=P— bond could not explain alone the lack of reactivity of this diphosphene; so it is likely that electronic effects have an important contribution, even if P=P and P—C bond lengths have standard values; in support of this hypothesis, we note the ipsochromic shifts observed in the UV spectrum (Escudié *et al.*, 1987) for  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions (about 70 nm).

## References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH., PRICK, P. A., NOORDIK, J. H., BEURSKENS, G. & PARTHASARATHI, V. (1981). *DIRDIF81. An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- COWLEY, A. H. & NORMAN, N. C. (1986). *Prog. Inorg. Chem.* **34**, 1–63.
- ESCUDIÉ, J., COURET, C., RANAIVONJATOVO, H., LAZRAQ, M. & SATGÉ, J. (1987). *Phosphorus Sulfur*, **32**, 27–31.
- ESCUDIÉ, J., COURET, C., RANAIVONJATOVO, H., SATGÉ, J. & JAUD, J. (1983). *Phosphorus Sulfur*, **17**, 221–235.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JUTZI, P., MEYER, U., KREBS, B. & DARTMANN, M. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 919–921.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WEBER, L. & REIZIG, K. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 865–866.
- YOSHIFUJI, M., SHIMA, I., INAMOTO, N., HIROTSU, K. & HIGUCHI, T. (1981). *J. Am. Chem. Soc.* **103**, 4587–4589.