The Structure of 1-Phenyl-3-Trifluoromethyl-1,3-Propanedionatobis(triphenylphosphite)Rhodium(I)

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Abstract

The crystal structure of 1-phenyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)-rhodium(I), $[Rh(TFBA)(P(OPh)_3)_2]$ has been determined by means of single crystal X-ray diffraction. The structure was refined to a R value of 0.043. 2719 Independant observed reflections were used. The unit cell is orthorombic, with space group $Pca2_1$, a = 20.761 Å, b = 10.790 Å, c = 19.035 Å and Z = 4. The compound was prepared by substitution of the two carbonyl groups in the Rh(I) complex, 1-phenyl-3-trifluoromethyl-1,3-propanedionatobiscarbonylrhodium(I), $[Rh(TFBA)(CO)_2]$, by triphenylphosphite in methanolic medium. The significant difference between the two Rh–P bond lengths reveals that the oxygen atom nearest to the phenyl group has a larger *trans* influence than the other oxygen atom.

Introduction

It is a well-known fact that triphenylphosphine, PPh_3, substitutes only one carbonyl group in complexes of the type $[Rh(LL')(CO)_2]$, where LL′ = monocharged bidentate ligands like β-diketones [1, 2], tropolone [3] and 8-hydroxyquinoline [4]. This phenomenon was successfully used for the determination of the relative *trans* influence of the bonded atoms in the bidentate ligand.

$[Rh(acac)(P(OPh)_3)_2]$ was synthesized recently by Treciak and Ziólkowski [5] by reacting $[Rh(acac)(CO)_2]$ with triphenylphosphite, $P(OPh)_3$, in a 1:2 ratio in a methanolic medium. A possible explanation for the fact that $P(OPh)_3$ substitutes both CO groups is that $P(OPh)_3$ is a weaker σ-electron donor and a better π-electron acceptor than PPh_3 [6]. The result is that more electron density is drawn from the Rh(I) and therefore weakens the Rh–C bond in $[Rh(LL')(CO)P(OPh)_3]$ relative to $[Rh(LL')(CO)(PPh_3)]$. Another explanation could be found by considering the steric parameter θ, as described by Tolman [7]. The smaller ligand cone angle θ of $P(OPh)_3$ (128°), makes it a better entering ligand than PPh_3, with a cone angle of 145°. Two PPh_3 groups *cis* to one another would therefore experience a much larger steric hindrance than two $P(OPh)_3$ groups *cis* to each other.

A possible way to distinguish between the *trans* influence of the two oxygen atoms of a non-symmetrical β-diketone like TFBA, is to determine the metal–ligand bond lengths of two chemical equivalent bonds *trans* to the oxygen atoms of the β-diketone. The success of the method was illustrated by the structure determination of [Rh(TFBA)(COD)] [8] and [Rh(oxine)(COD)] [9].

The results and conclusion drawn from the crystal structure determination of [Rh(oxine)(COD)] were also confirmed by means of the crystal structure determination of $[Rh(oxine)(CO)(PPh_3)]$ [4], which was synthesized according to the following reaction:

$$[Rh(oxine)(CO)_2] + PPh_3 \longrightarrow [Rh(oxine)(CO)(PPh_3)] + CO$$

It was assumed that the CO group *trans* to the atom of the chelate ring with the largest thermodynamic *trans* influence will be substituted. Although it is possible that the other isomer will also form to some extent during the reaction, it was clear (during the synthesis) that mainly one isomer (the PPh_3 group *trans* to the nitrogen atom of the oxine ligand) was obtained during this reaction.

The crystal and molecular structure of 1-phenyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I), $[Rh(TFBA)(P(OPh)_3)_2]$, was determined as part of a program for the study of the substitution and oxidative addition reactions of rhodium(I) complexes with singly charged bidentate ligands such as β-diketones, oxine, tropolone etc.

It should also be possible to determine the relative *trans* influence of the two oxygen atoms of TFBA from the two Rh–P bond lengths, especially since the Rh–P bond distance would have a much smaller standard deviation than a Rh–C bond length as in the case of the structure determination of [Rh(TFBA)(COD)] [8].

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Experimental

A solution of $[Rh_2Cl_2(CO)_4]$ was prepared by refluxing a solution of $RhCl_3 \cdot 3H_2O$ in dimethyl formamide for approx. 30 min. [10]. An equivalent amount of TFBA (1-phenyl-3-trifluoromethyl-1,3-propanedione) was added to the resulting light yellow solution. The solution was diluted with water and the resulting precipitate was removed by filtration and washed with ether. The $[Rh(TFBA)(CO)_2]$ was recrystallized from methanol.

The title compound $[Rh(TFBA)(P(OPh)_3)_2]$, was prepared by adding 0.048 g $[Rh(TFBA)(CO)_2]$ to a solution of 0.080 g $P(OPh)_3$ (1:2 ratio) in 2 cm^3 methanol. The resulting orange precipitate was filtered, washed with methanol and recrystallized from an acetone-water solution. Well formed needle-like orange crystals suitable for data collection were obtained.

Crystal Data

$RhC_{46}H_{36}O_8F_3P_2$, molecular mass = 938.63, orthorombic space group $Pca2_1$, a = 20.761 Å, b = 10.790 Å, c = 19.035 Å, Z = 4, d = 1.462 g cm^{-3}, $\mu(MoK_\alpha) = 5.12\ cm^{-1}$.

The three dimensional intensity data were collected with a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoK_α radiation (λ = 0.7107 Å) for θ values between 3° and 23°. Three reflections were used as standards and remeasured after every 60 reflections. No decomposition of the crystal was detectable during the data collection. A total of 3345 reflections were measured of which 2719 were considered as observed reflections. The data were corrected for Lorentz and polarization effects. A crystal with dimensions 0.43 X 0.38 X 0.18 mm^3 was used for the data collection.

The structure was solved using the X-ray 72 system of programs on a Univac 1100 computer. The rhodium atom was located from a three dimensional Patterson synthesis. The positional parameters of the other non-hydrogen atoms were deduced from successive Fourier and difference-Fourier synthesis. A full matrix least square refinement using all the observed reflections and anisotropic temperature parameters for all the atoms resulted in the residual factor $R = \Sigma ||F_0| - |F_c|| \div \Sigma |F_0|$ of 4.3%. The atomic scattering factors were those tabulated by Cromer and Waber [11]. The final positional and thermal parameters with their standard deviations are listed in Table I.

Discussion

A perspective view of the $[Rh(TFBA)(P(OPh)_3)_2]$ molecule as well as the numbering system of the atoms is shown in Fig. 1. Bond distances and bond

TABLE I. Fractional Atomic Coordinates and Thermal Parameters ($\times 10^3$) with Standard Deviations.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.34461(3)	0.08075(6)	0.40000	33.4(4)	36.3(4)	45.8(4)	0.6(7)	−6.5(5)	−0.01(5)
O_1	0.2672(3)	0.1790(6)	0.3606(4)	39(4)	40(4)	61(4)	3(3)	−6(3)	−3(4)
O_2	0.2921(3)	−0.0803(6)	0.3852(4)	45(3)	35(3)	72(6)	−7(3)	−15(4)	7(4)
P_1	0.4264(1)	−0.0251(2)	0.4367(1)	36(1)	40(1)	47(1)	2(1)	−7(1)	3(1)
P_2	0.3928(1)	0.2550(2)	0.4155(1)	39(1)	37(1)	43(2)	1(1)	−2(1)	−4(1)
O_{22}	0.4280(4)	0.3181(7)	0.3492(4)	71(5)	49(5)	58(5)	−18(4)	13(4)	−10(4)
O_{23}	0.4455(3)	0.2674(6)	0.4764(4)	51(4)	37(4)	60(5)	−2(3)	−13(4)	−8(4)
O_{21}	0.3480(3)	0.3741(6)	0.4299(4)	47(4)	40(4)	58(4)	6(3)	2(3)	−1(3)
O_{11}	0.4957(3)	0.0302(6)	0.4210(3)	32(3)	49(4)	51(5)	6(3)	−9(3)	−2(3)
O_{12}	0.4300(3)	−0.1671(5)	0.4075(5)	51(3)	42(3)	64(4)	7(3)	−7(5)	−5(4)
O_{13}	0.4350(3)	−0.0553(6)	0.5185(4)	39(4)	57(4)	54(4)	−8(3)	−11(3)	1(4)
C_1	0.2116(5)	−0.2144(9)	0.3491(7)	34(6)	39(6)	103(9)	2(5)	−6(6)	2(6)
C_2	0.2367(5)	−0.0833(9)	0.3551(6)	41(6)	35(6)	63(7)	−1(5)	−6(5)	−6(6)
C_3	0.2002(5)	0.0116(10)	0.3277(6)	49(6)	42(6)	63(7)	0(5)	−7(5)	1(6)
C_4	0.2161(4)	0.1381(9)	0.3323(5)	30(5)	51(6)	50(6)	−3(4)	−8(4)	−2(5)
C_5	0.1731(5)	0.2343(10)	0.3027(6)	42(6)	48(6)	59(7)	3(5)	−16(5)	−2(5)
C_{52}	0.1135(6)	0.2075(12)	0.2737(8)	52(7)	81(9)	99(10)	−8(7)	−13(7)	22(8)

C_{53}	0.0736(6)	0.3053(14)	0.2476(9)	51(8)	89(10)	132(13)	2(8)	−27(8)	21(10)
C_{54}	0.0938(7)	0.4248(14)	0.2506(9)	102(11)	77(10)	112(12)	29(9)	−38(10)	19(10)
C_{55}	0.1557(9)	0.4564(12)	0.2762(9)	159(15)	50(8)	128(14)	28(9)	−90(13)	−10(8)
C_{56}	0.1960(7)	0.3572(11)	0.3018(8)	93(10)	57(7)	97(11)	18(7)	−52(9)	−8(7)
C_{211}	0.3040(4)	0.3848(9)	0.4851(6)	42(6)	40(6)	65(7)	3(5)	−10(5)	−21(6)
C_{212}	0.2161(8)	0.5040(16)	0.5336(10)	102(12)	94(11)	127(14)	13(10)	40(11)	−28(11)
C_{213}	0.2592(8)	0.3315(14)	0.5972(8)	88(10)	89(10)	90(10)	−8(9)	18(9)	−17(9)
C_{214}	0.2161(7)	0.4291(15)	0.5917(10)	80(10)	82(11)	127(14)	−5(9)	40(10)	−41(11)
C_{215}	0.3050(6)	0.3067(11)	0.5432(7)	84(9)	64(8)	65(8)	−4(7)	16(7)	9(7)
C_{216}	0.2607(6)	0.4825(11)	0.4774(7)	65(8)	63(8)	96(10)	15(7)	−9(8)	−22(8)
C_{111}	0.5538(4)	−0.0023(10)	0.4536(5)	33(5)	55(6)	46(6)	−3(5)	3(5)	−7(5)
C_{112}	0.5848(5)	0.0919(12)	0.4892(7)	49(6)	74(8)	88(9)	1(6)	0(7)	−9(8)
C_{113}	0.6468(5)	0.0638(13)	0.5196(7)	48(7)	85(9)	72(8)	−4(6)	−9(6)	3(7)
C_{114}	0.6731(6)	−0.0501(12)	0.5145(7)	57(8)	79(9)	61(8)	4(7)	9(6)	12(7)
C_{115}	0.6394(5)	−0.1454(11)	0.4799(7)	37(6)	76(8)	73(8)	5(6)	11(6)	21(7)
C_{116}	0.5785(5)	−0.1210(10)	0.4483(6)	37(6)	52(6)	72(8)	7(5)	6(6)	8(6)
C_{121}	0.4185(4)	−0.2048(10)	0.3402(6)	29(5)	54(6)	67(7)	6(5)	−8(5)	−5(6)
C_{122}	0.4064(6)	−0.3346(10)	0.3349(8)	53(7)	42(6)	112(11)	−2(5)	−8(7)	−20(7)
C_{123}	0.3956(6)	−0.3827(12)	0.2692(8)	71(8)	60(8)	112(11)	0(7)	−20(8)	−37(8)
C_{124}	0.3954(7)	−0.3079(15)	0.2092(8)	75(9)	100(11)	91(11)	10(9)	−21(8)	−25(10)
C_{125}	0.4070(7)	−0.1790(14)	0.2170(7)	79(10)	82(10)	67(9)	16(8)	−11(7)	−14(8)
C_{126}	0.4192(6)	−0.1296(11)	0.2821(6)	79(8)	53(7)	48(7)	5(6)	−5(6)	−5(6)
C_{131}	0.3840(6)	−0.0965(14)	0.5590(6)	52(7)	108(11)	44(7)	−7(8)	−17(6)	5(7)
C_{132}	0.3680(11)	−0.2170(20)	0.5570(9)	180(20)	160(19)	71(10)	−114(17)	−8(12)	23(12)
C_{133}	0.3131(20)	−0.2558(40)	0.6042(15)	318(50)	340(52)	103(22)	−267(45)	−103(27)	56(26)
C_{134}	0.2878(15)	−0.1587(48)	0.6402(19)	88(15)	399(80)	89(22)	−65(31)	−33(15)	−2(32)
C_{135}	0.3040(13)	−0.0427(40)	0.6486(13)	138(24)	412(59)	53(12)	154(31)	−1(15)	33(25)
C_{136}	0.3546(8)	−0.0097(21)	0.6006(7)	117(13)	221(21)	58(9)	101(15)	−6(9)	40(12)
C_{221}	0.4397(5)	0.2544(9)	0.2872(5)	55(6)	39(6)	33(5)	−4(5)	4(5)	2(5)
C_{222}	0.5021(6)	0.2195(12)	0.2735(7)	57(7)	84(9)	63(8)	5(7)	17(6)	16(7)
C_{223}	0.5144(8)	0.1621(15)	0.2090(8)	106(12)	100(12)	81(11)	15(10)	31(10)	−10(10)
C_{224}	0.4630(9)	0.1366(14)	0.1607(7)	146(14)	75(10)	49(8)	−3(10)	21(10)	−2(7)
C_{225}	0.4003(8)	0.1717(13)	0.1784(7)	106(11)	83(10)	50(8)	13(9)	−7(8)	−6(7)
C_{226}	0.3886(5)	0.2340(11)	0.2422(6)	61(7)	63(7)	42(6)	−8(6)	1(6)	5(6)
C_{231}	0.4770(5)	0.3774(9)	0.4944(6)	61(7)	38(6)	63(7)	1(5)	−14(7)	−8(5)
C_{232}	0.4644(7)	0.4236(14)	0.5601(7)	98(10)	74(9)	71(8)	−35(8)	2(8)	−14(8)
C_{233}	0.4976(9)	0.5324(15)	0.5819(8)	118(12)	106(14)	87(11)	−54(11)	22(10)	−33(10)
C_{234}	0.5403(7)	0.5867(14)	0.5386(9)	96(11)	79(10)	93(11)	−21(9)	−12(9)	−18(9)
C_{235}	0.5543(7)	0.5391(14)	0.4737(9)	92(11)	88(11)	112(11)	−26(9)	−10(10)	−38(10)
C_{236}	0.5226(6)	0.4289(12)	0.4498(8)	63(8)	78(9)	108(11)	−32(7)	10(7)	−21(9)
F_1	0.2505(4)	−0.2838(6)	0.3140(5)	78(5)	70(4)	174(9)	−6(4)	18(5)	−61(5)
F_2	0.2063(4)	−0.2649(6)	0.4117(6)	151(7)	58(4)	140(7)	−22(5)	7(8)	15(6)
F_3	0.1552(3)	−0.2223(7)	0.3190(6)	57(4)	69(5)	245(11)	−17(4)	−65(6)	−3(6)

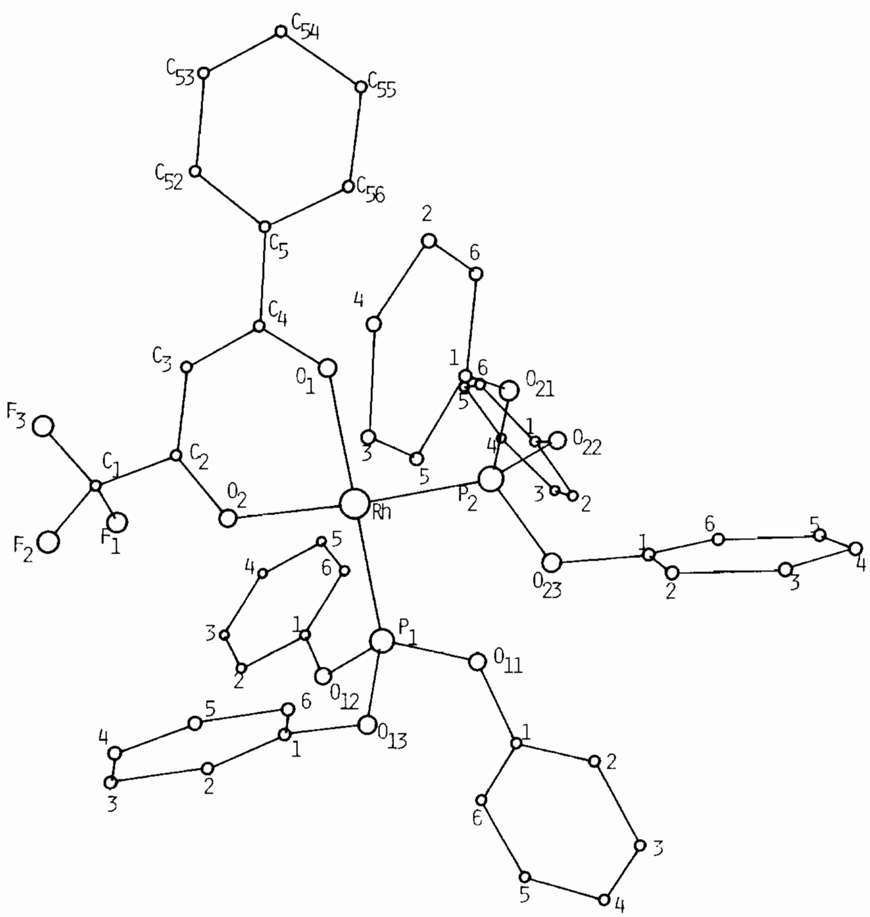

Fig. 1. Perspective view of the [Rh(TFBA)(P(OPh)$_3$)$_2$] molecule. The numbering system of the atoms of the phenyl rings of the phosphite groups is as follows (see Table I): the first digit refers to the phosphorous atom, the second digit refers to the oxygen atoms bonded to the phosphorous atom and the third digit refers to the carbon atoms of the phenyl ring bonded to the oxygen atom.

TABLE II. Interatomic Distances (Å) with Estimated Standard Deviations in Parentheses.

Rh–O_1	2.067(6)	C_2–O_2	1.286(11)
Rh–O_2	2.070(6)	C_4–O_1	1.269(11)
Rh–P_1	2.161(2)	C_1–F_1	1.288(14)
Rh–P_2	2.150(2)	C_1–F_2	1.315(16)
P_1–O_{11}	1.587(6)	C_1–F_3	1.307(13)
P_1–O_{12}	1.632(7)	C_2–C_3	1.376(14)
P_1–O_{13}	1.600(8)	C_1–C_2	1.512(14)
P_2–O_{21}	1.611(7)	C_3–C_4	1.407(14)
P_2–O_{22}	1.608(8)	C_4–C_5	1.481(14)
P_2–O_{23}	1.599(8)	C_5–C_{52}	1.409(16)
O_{11}–C_{111}	1.400(11)	C_{52}–C_{53}	1.437(20)
O_{12}–C_{121}	1.365(14)	C_{53}–C_{54}	1.357(22)
O_{13}–C_{131}	1.384(14)	C_{54}–C_{55}	1.454(24)
O_{21}–C_{211}	1.397(12)	C_{55}–C_{56}	1.419(20)
O_{22}–C_{221}	1.387(12)	C_5–C_{52}	1.378(16)
O_{23}–C_{231}	1.399(12)		

angles are given in Tables II and III respectively. The structure consists of well separated discrete molecular units.

The Rh atom has approximately a square planar coordination as proved by calculation of the best plane through the atoms Rh, O_1, O_2, P_1 and P_2 of the coordination polyhedron. The chelate ring Rh, O_1, O_2, C_2, C_3 and C_4 is also planar and makes an angle of 4.4° with the coordination polyhedron.

According to the polarization theory and the σ-*trans* effect [12, 13] the *trans* influence of the oxygen atom nearest to the phenyl group O(1), in the chelate ring, should have a larger *trans* influence than the oxygen atom O(2) nearest to the more electronegative CF_3 group. The Rh–P(1) bond distance (2.161(2) Å) *trans* with respect to O(1) is in fact longer than the Rh–P(2) bond distance (2.150(2) Å). However, before this small but significant difference in bond distances can be attributed solely to a

TABLE III. Selected Bond Angles (Degrees) with Estimated Standard Deviations in Parentheses.

O_1–Rh–O_2	88.4(2)	Rh–P_2–O_{21}	116.9(3)
O_1–Rh–P_2	87.9(2)	Rh–P_2–O_{22}	118.3(3)
O_2–Rh–P_1	90.8(2)	Rh–P_2–O_{23}	119.4(3)
P_1–Rh–P_2	93.0(1)	C_{211}–O_{21}–P_2	124.9(6)
Rh–O_1–C_4	128.8(6)	C_{221}–O_{22}–P_2	122.5(6)
Rh–O_2–C_2	123.6(6)	C_{231}–O_{23}–P_2	124.7(7)
O_2–C_2–C_3	130.0(9)	C_{111}–O_{11}–P_1	127.1(6)
C_2–C_3–C_4	124.7(9)	C_{121}–O_{12}–P_1	126.3(7)
O_1–C_4–C_3	124.0(9)	C_{131}–O_{13}–P_1	121.4(7)
Rh–P_1–O_{11}	116.9(3)	C_2–C_1–F_1	111.5(9)
Rh–P_1–O_{12}	115.0(3)	C_2–C_1–F_2	110.4(10)
Rh–P_1–O_{13}	120.7(3)	C_2–C_1–F_3	113.8(9)

thermodynamic *trans* influence, the study is at present extended with Rh phosphite complexes containing several different substituents on the β-diketone chelate ring.

The mentioned Rh–P bond distances in the present structure are significantly shorter than Rh–P bond distances in the similar Rh phosphine complexes. The Rh–P bond distances in [Rh(acac)(CO)(PPh$_3$)] [1], [Rh(TTA)(CO)(PPh$_3$)] [2] and [Rh(TFDMAA)(CO)(PPh$_3$)] [14] are 2.244(2), 2.245(4) and 2.239(2) Å respectively. The smaller Rh–P bond distances in the case of the phosphite complex are probably the result of the strong π-electron acceptor properties of the phosphite ligand [6] resulting in a relatively stronger Rh–P bond.

There is no significant difference between the Rh–O bond distances in the present structure (2.067(6) and 2.070(6) Å) and Rh–O distances (oxygen atom *trans* to the phosphine group) in the complexes [Rh(acac)(CO)(PPh$_3$)] [1] and [Rh(TTA)(CO)(PPh$_3$)] [2] which are 2.087(4) and 2.085(7) Å respectively.

The P_1–Rh–P_2 bond angle of 93.0° (1) in the present structure is significantly larger than the P–Rh–C bond angles of 87.8° (2) and 87.1° (4) in the Rh–phosphine complexes [Rh(acac)(CO)(PPh$_3$)] [1] and [Rh(TTA)(CO)(PPh$_3$)] [2] respectively. This difference in bond angles may be explained by the fact that the two P(OPh)$_3$ groups with a cone angle of 128°, *cis* to one another, will experience a larger steric hindrance than a PPh$_3$-group and a CO-group *cis* to each other.

Each of the two P atoms are tetrahedrally surrounded by the Rh atom and three oxygen atoms (see Table III). The average P–O bond distance of 1.606 Å compare well with the average 1.59 Å found in [RhBr$_2$(NO)(P(OPh)$_3$)$_2$] [15]. The average C–O bond lengths in the P(OPh)$_3$-groups of 1.389 Å is also in good agreement with the value of 1.40 Å found in [Rh(Br$_2$)(NO)(P(OPh)$_3$)$_2$] [15].

The seven phenyl rings are planar within experimental error and the average C–C bond distances and bond angles in the phenyl rings are within experimental error identical to the accepted values of 1.399 Å and 120° for phenyl rings [16].

The average C–F bond lengths of 1.303 Å agrees well with previously published values [2, 8].

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