

**THE CRYSTAL AND MOLECULAR STRUCTURE OF
(-)₄₃₆-(η^5 -C₅H₅)Fe(CO)(CH₃CO)[Ph₂PNHCH(Me)(Ph)]**

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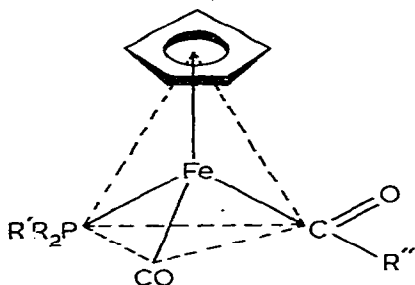
Summary

The X-ray crystal structure and absolute configuration of (-)₄₃₆-(η^5 -C₅H₅)-Fe(CO)(CH₃CO)[Ph₂PNHCH(Me)(Ph)] have been determined from single crystal diffraction data. The compound crystallizes in the monoclinic space group *P2*₁ with two molecules in a unit cell of dimensions *a* = 10.676(4), *b* = 8.913(7), *c* = 13.275(9) Å, and β = 91.36°. The structure was solved by the Patterson method and refined to a final *R* value of 4.7% using 2299 independent data. The iron atom has distorted octahedral coordination, and the configuration at the iron is found to be (*S*) for the (-)₄₃₆ diastereoisomer. The Fe–Cp distances average 2.131 Å, with an Fe–(ring centroid) distance of 1.76 Å. The Fe–acetyl distance is virtually identical to that found in another iron/acetyl complex, but shows substantial variation from other compounds where the nature of the C(=O)R group is changed. Comparison to the Mo-alkyl/Mo-acetyl series is made, and the argument for back-donation in transition metal acyls is strengthened.

The orientation of the acetyl group is determined by a strong NH \cdots O intramolecular hydrogen bond having an N \cdots O separation of only 2.86 Å. The phosphine ligand has a very short Fe–P bond which could be in part caused by the role of the adjacent nitrogen in hydrogen bonding. The remaining ligand geometry is the same as that found in a recently reported ruthenium structure, although the absolute configurations at the chiral carbons are reversed, with the current compound being designated (*S*) at this site.

Introduction

As part of our study of the fundamental stereochemical and chiroptical properties of organometallics having metals as chiral centers, we have characterized the behaviour of iron compounds of the basic type [1]:



(Ia, $R = R' = \text{Ph}$, $R'' = \text{OC}_{10}\text{H}_{19}$,

Ib, $R = \text{Ph}$, $R' = \text{NHCH}(\text{Me})(\text{Ph})$, $R'' = \text{CH}_3$)

Later, Brunner and Vogt studied the mechanism of epimerization of these substances by a variety of methods, including phosphine exchange [2]. Since the results are very peculiar in that they do not fall into the classical patterns expected either from concerted addition-elimination nor dissociation of the bound phosphine followed by competition between it and the other phosphine, we decided to make a detailed study of the conformation and absolute configurations of a number of the substances associated with the solution equilibrium studies [3]. Most specifically, given the stereochemical behavior of the Fe compound already published [1], it occurred to us that the acyl ($-\text{C}(\text{O})\text{R}$) group may play a role in the equilibration of the diastereoisomers and in the ligand displacement reactions mentioned above, since there may be a close contact between the acetyl oxygen and the H of the amino group on the aminophosphine used in the present case. For that purpose we carried out this detailed study of compound Ib.

Experimental

The synthesis and resolution of $(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{Ac})[\text{Ph}_2\text{PNHCH}(\text{CH}_3)(\text{Ph})]$ will be published elsewhere [4]. The crystal used for all X-ray measurements was an irregular amber fragment of approximate dimensions $0.65 \times 0.50 \times 0.35$ mm. An Enraf-Nonius CAD-4 automatic diffractometer was used with $\text{Mo-K}\alpha$ radiation monochromatized by a dense graphite crystal, assumed for all purposes to be ideally imperfect. Final cell constants, as well as other information concerning data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown to be either $P2_1$ or $P2_1/m$. Intensities were measured using the $\theta-2\theta$ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability, and they never showed any significant deviations from the initial measurements. In reducing the data, Lorentz and polarization factors were applied, but no absorption correction was made.

Since there were only two molecules per unit cell, with no possible molecular symmetry beyond identity (1), the non-centrosymmetric space group $P2_1$ was chosen. The structure was solved by interpretation of the Patterson map, which gave the position of the iron atom. The remaining non-hydrogen atoms,

TABLE 1

SUMMARY OF DATA COLLECTION AND PROCESSING PARAMETERS

Space group	<i>P</i> 2 ₁ , monoclinic
Cell constants	<i>a</i> = 10.676(4) Å <i>b</i> = 8.913(7) Å <i>c</i> = 13.275(9) Å β = 91.36° <i>V</i> = 1262.7 Å ³
Molecular formula	FePO ₂ NC ₂₈ H ₂₈
Molecular weight	497.36
Molecules per cell	2
Density	ρ = 1.31 g cm ⁻³
Absorption coefficient	μ = 5.7 cm ⁻¹
Radiation (Mo- <i>K</i> _α)	λ = 0.71073 Å
Collection range	4° ≤ 2 θ ≤ 64°
Scan width	$\Delta\theta$ = (0.95 + 0.35 tan θ)°
Maximum scan time	180 sec
Scan speed range	0.5 to 6.7° min ⁻¹
Total data collected	3954
Independent data with <i>I</i> > 3 σ (<i>I</i>)	2299
Total variables	139 (Cp and O as rigid groups)
$R \sum F_o - F_c / \sum F_o $	0.047
$R [\sum_w (F_o - F_c)^2 / \sum_w F_o^2]^{1/2}$	0.039
Weights	$w = \sigma(F)^{-2}$
Goodness-of-fit	2.0

as well as H(N) and H(21), were found in subsequent difference Fourier syntheses. Since there was no reason to expect any abnormal distortions of the phenyl rings and the cyclopentadiene ring, they were refined as rigid bodies with idealized hydrogens. The acetyl methyl was also treated in this manner. The remaining atoms were refined anisotropically, except for hydrogens. After all shift/e.s.d. ratios were less than 0.2, the refinement converged to the agreement factors listed in Table 1. The only unusually high correlations occurred

(Continued on p. 360)

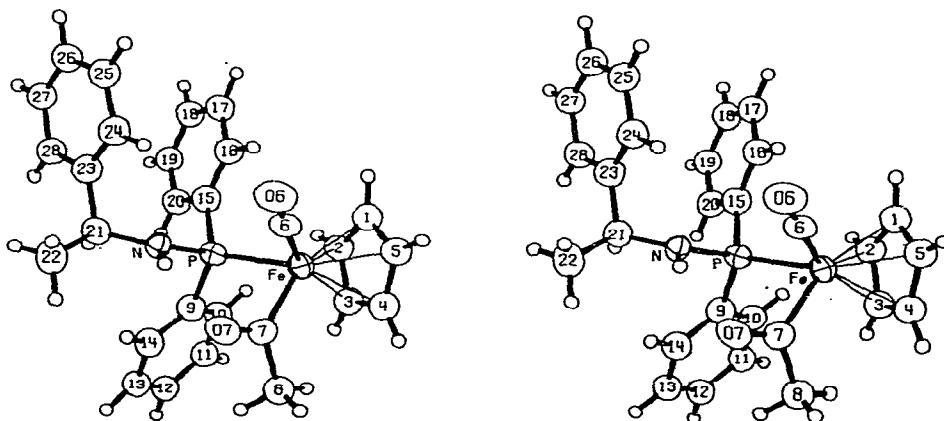


Fig. 1. Stereoscopic view of the molecule showing the atom labeling scheme. The non-hydrogens are shown as 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter. Note the (*S*) configuration of C(21), and (*S*) at iron.

TABLE 2
 ATOMIC COORDINATES AND THERMAL PARAMETERS ($\times 10^3$, Fe and P $\times 10^4$)

Atom	X/A	Y/B	Z/C	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Fe	0.65931(7)	0.67169(0)	0.84857(6)	335(4)	369(5)	412(4)	12(5)	3(8)	20(6)
P	0.7131(1)	0.7391(2)	0.7581(1)	379(8)	322(9)	374(9)	-1(8)	-14(7)	4(8)
O(6)	0.5617(4)	0.3649(5)	0.7818(3)	73(3)	37(3)	76(3)	-6(3)	-10(3)	-17(3)
O(7)	0.75663(4)	0.5199(5)	0.9470(3)	53(3)	50(3)	51(3)	9(2)	-13(2)	3(2)
N	0.8127(4)	0.5990(6)	0.7435(3)	36(3)	42(3)	40(3)	5(2)	5(2)	-2(2)
C(6)	0.5595(6)	0.4855(8)	0.8073(4)	44(4)	51(4)	37(3)	-4(3)	-7(3)	-5(3)
C(7)	0.6826(6)	0.6223(7)	0.9527(4)	45(3)	50(5)	37(3)	-10(3)	5(3)	4(3)
C(21)	0.9223(5)	0.5976(8)	0.6783(5)	39(4)	39(4)	52(4)	-2(3)	1(3)	-4(3)
C(22)	1.0213(8)	0.5009(14)	0.7274(7)	57(4)	113(9)	61(5)	23(6)	3(4)	-5(6)
C(1)	0.3738(4)	0.7257(5)	0.7838(3)	60(1)					
C(2)	0.4456(4)	0.8588(5)	0.7964(3)	60(1)					
C(3)	0.4753(4)	0.8754(5)	0.9006(3)	60(1)					
C(4)	0.4218(4)	0.7526(5)	0.9525(3)	60(1)					
C(5)	0.3691(4)	0.6601(5)	0.8803(3)	60(1)					
C(8)	0.6970(6)	0.7273(80)	1.0448(5)	62(2)					
C(9)	0.8030(4)	0.8980(5)	0.8111(3)	57(1)					
C(10)	0.7535(4)	1.0428(5)	0.8123(3)	57(1)					
C(11)	0.8194(4)	1.1580(5)	0.8610(3)	57(1)					
C(12)	0.9348(4)	1.1285(5)	0.9084(3)	57(1)					
C(13)	0.9842(4)	0.9839(5)	0.9071(3)	57(1)					
C(14)	0.9183(4)	0.8684(5)	0.8585(3)	57(1)					
C(15)	0.6768(4)	0.7988(5)	0.6282(2)	59(1)					
C(16)	0.5904(4)	0.7130(5)	0.5727(2)	59(1)					
C(17)	0.5678(4)	0.7442(5)	0.4709(2)	59(1)					
C(18)	0.6314(4)	0.8613(5)	0.4246(2)	59(1)					
C(19)	0.7178(4)	0.9470(5)	0.4802(2)	59(1)					
C(20)	0.7405(4)	0.9158(5)	0.5820(2)	59(1)					
C(23)	0.8902(4)	0.5466(5)	0.5707(2)	59(1)					
C(24)	0.8033(4)	0.4323(5)	0.5525(2)	59(1)					

C(25)	0.7764(4)	0.3859(5)	0.4540(2)	59(1)
C(26)	0.8365(4)	0.4537(5)	0.3737(2)	59(1)
C(27)	0.9284(4)	0.5680(5)	0.3919(2)	59(1)
C(28)	0.9502(4)	0.6144(5)	0.4904(2)	59(1)
H(N)	0.8167(40)	0.3174(55)	0.7999(38)	32(15)
H(1)	0.3396(4)	0.8853(5)	0.7185(3)	80(0)
H(2)	0.4708(4)	0.9285(5)	0.7415(3)	80(0)
H(3)	0.5251(4)	0.9590(5)	0.9320(3)	80(0)
H(4)	0.4274(4)	0.7345(5)	1.0268(3)	80(0)
H(5)	0.3128(4)	0.5653(4)	0.8949(3)	80(0)
H(6A)	0.6411(6)	0.8282(8)	1.0416(5)	90(0)
H(6B)	0.7940(6)	0.7564(8)	1.0591(5)	90(0)
H(6C)	0.6648(6)	0.6560(8)	1.1047(5)	90(0)
H(10)	0.6708(4)	1.0640(5)	0.7783(3)	80(0)
H(11)	0.7839(4)	1.2619(5)	0.8619(3)	80(0)
H(12)	0.9820(4)	1.2111(5)	0.9433(3)	80(0)
H(13)	1.0669(4)	0.9624(5)	0.9411(3)	80(0)
H(14)	0.9538(4)	0.7646(5)	0.8675(3)	80(0)
H(16)	0.5448(4)	0.8291(5)	0.6058(2)	80(0)
H(17)	0.5059(4)	0.8827(5)	0.4311(2)	80(0)
H(18)	0.6151(4)	0.8836(5)	0.3617(2)	80(0)
H(19)	0.7634(4)	1.0309(5)	0.4471(2)	80(0)
H(20)	0.8024(4)	0.9773(5)	0.6218(2)	80(0)
H(21)	0.9592(46)	0.7060(73)	0.6744(40)	50(19)
H(22A)	1.0848(42)	0.4963(57)	0.6869(34)	26(15)
H(22B)	1.0032(59)	0.3851(99)	0.7270(57)	122(37)
H(22C)	1.0463(58)	0.5200(84)	0.7976(48)	90(0)
H(24)	0.7602(4)	0.3837(5)	0.6101(2)	80(0)
H(25)	0.7141(4)	0.3040(5)	0.4409(2)	80(0)
H(26)	0.8172(4)	0.4204(5)	0.3030(2)	80(0)
H(27)	0.9664(4)	0.6166(5)	0.3343(2)	80(0)
H(28)	1.0126(4)	0.6963(5)	0.5034(2)	80(0)

TABLE 3
INTRAMOLECULAR BOND DISTANCES (Å)

Fe—C(1)	2.142(4)	N—H(N)	1.04(5)
Fe—C(2)	2.136(5)	C(6)—O(6)	1.128(7)
Fe—C(3)	2.123(5)	C(7)—O(7)	1.208(6)
Fe—C(4)	2.122(4)	C(7)—C(8)	1.544(7)
Fe—C(5)	2.134(4)	C(21)—C(22)	1.500(10)
Fe—P	2.188(2)	C(21)—C(23)	1.530(7)
Fe—C(6)	1.749(7)	C(21)—H(21)	1.05(6)
Fe—C(7)	1.976(6)	Fe—Cent ^a	1.756(4)
P—N	1.655(5)		
P—C(9)	1.841(3)	cp (ideal)	1.420
P—C(15)	1.837(3)	phen (ideal)	1.395
N—C(21)	1.472(7)	C—H (ideal)	1.00

^a Cent = the geometric center of the Cp ring.

between parameters within some of the rigid groups, and these were all less than 80%. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions [5]; for hydrogen those of Stewart, Davidson, and Simpson were used [6]. The anomalous dispersion coefficients of Cromer and Liberman [7] were used for iron and phosphorous. Bond lengths, angles, least squares planes, and torsion angles are presented in Tables 3–6, based on the final positional parameters of Table 2. The *Y* coordinate of iron had to be fixed in order to define the origin, and it, along with the fixed hydrogen temperature factors, shows an e.s.d. of zero. The atomic labeling scheme is shown in Fig. 1.

Discussion

Based on the analysis of 10 Bijvoet pairs of reflections [8], the correct absolute configuration of the molecule was determined to be that shown in Fig. 1. Applying the extension of the *R*, *S* system [9] for polyhapto ligands in organometallic compounds [10], the configuration at the iron atom is designated (*S*),

TABLE 4
INTRAMOLECULAR BOND ANGLES (°)

P—Fe—C(6)	93.2(2)	P—N—C(21)	126.7(4)
P—Fe—C(7)	84.8(2)	P—N—H(N)	117(3)
C(6)—Fe—C(7)	88.8(3)	C(21)—N—H(N)	113(3)
N—P—Fe	111.5(2)	N—C(21)—C(22)	108.1(6)
C(9)—P—Fe	114.0(2)	N—C(21)—C(23)	112.8(4)
C(15)—P—Fe	116.5(2)	N—C(21)—H(21)	109(3)
N—P—C(9)	107.1(2)	C(22)—C(21)—C(23)	112.0(6)
N—P—C(15)	103.3(2)	C(22)—C(21)—H(21)	107(3)
C(9)—P—C(15)	103.4(2)	C(23)—C(21)—H(21)	108(3)
Fe—C(6)—O(6)	178.9(6)		
Fe—C(7)—O(7)	124.5(5)	P—Fe—Cent ^a	125.7(2)
Fe—C(7)—C(8)	118.3(4)	C(6)—Fe—Cent	124.3(2)
O(7)—C(7)—C(8)	117.0(5)	C(7)—Fe—Cent	128.0(2)

^a Cent = the center of the Cp ring.

TABLE 5

LEAST SQUARES PLANES, OUT-OF-PLANE DISTANCES (Å) AND DIHEDRAL ANGLES (°)

<i>A. C(1)–C(5)</i>			
$0.843x - 0.525y - 0.117z + 1.457 = 0$			
Fe	1.756	C(6)	2.753
P	3.037	C(7)	2.956
<i>B. O(7), C(7), C(8)</i>			
$0.628x + 0.585y - 0.512z - 1.159 = 0$			
Fe	0.123	C(6)	-0.522
P	2.176	C(1)	-0.350
<i>C. P, C(6), C(7)</i>			
$0.782x - 0.610y - 0.129z - 0.454 = 0$			
Fe	-1.139	C(3)	-3.005
C(1)	-2.810	C(4)	-2.885
C(2)	-2.959	C(5)	-2.756
<i>D. C(9)–C(14)</i>			
$0.485x + 0.209y - 0.849z + 3.437 = 0$			
<i>E. C(15)–C(20)</i>			
$0.735x - 0.633y - 0.245z + 1.384 = 0$			
<i>F. C(23)–C(28)</i>			
$-0.731x + 0.679y - 0.072z + 4.053 = 0$			
<i>Interplanar angles</i>			
A, B	73.6	C, D	68.9
A, C	6.0	C, E	7.3
A, D	66.6	C, F	167.5
A, E	11.4	D, E	64.5
B, C	78.4	E, F	161.6
B, D	30.4		

using the ranking order $C_p > P > C(CO) > COCH_3$. The coordination about the iron is that of a distorted octahedron, with three facial points occupied by the cyclopentadiene ring. The average of the three angles defined by Fe, P, C(6), and C(7) is 88.9° , essentially the expected value of 90° . Such coordination is quite common in iron complexes containing π -bonded arenes [1,11–14]. The Fe–C(Cp) distances average 2.131 Å, with an Fe–(ring centroid) distance of 1.76 Å. These values are in excellent agreement with previous reports [1,12–16], although longer than noted in ferrocene derivatives [17–19]. As pointed out earlier, this difference is due to the varying ability of the ligands to

TABLE 6

TORSION ANGLES (°)

O(7)–C(7)–Fe–C(6)	24.1
O(7)–C(7)–Fe–P	-69.3
C(6)–Fe–P–N	-30.6
Fe–P–N–C(21)	172.6
Fe–P–C(15)–C(16)	-43.5
Fe–P–C(9)–C(10)	-70.2
P–N–C(21)–C(22)	147.8
P–N–C(21)–C(23)	-87.8
N–C(21)–C(23)–C(24)	-37.9

compete for the Fe electrons [1]. Since our Fe—Cp values agree so well with the results for similar complexes, it can be safely assumed that no information was lost by treating the cyclopentadiene ring as a rigid body during the refinement. One advantage of this procedure, which we have recently employed more often, is that it allows rapid discovery of any disorder of the arene ring [20]. In the present case no such static disorder was noted, quite possibly since the position adopted by the Cp ring staggers the acetyl methyl group and is thus the lowest energy configuration. As pointed out by Albright et al., in the absence of such a bulky interfering ligand the barrier to rotation of the Cp ring is exceedingly small in ML_3 cases [21].

The carbonyl parameters are within the range reported for similar compounds [1,12–16,22–24]. Only one other Fe-acetyl structure has been reported [25], and our distances and angles compare remarkably well, including the widely disparate Fe—C(7)—O(7) and Fe—C(7)—C(8) angles (124.5 and 118.3° vs. 124.3 and 119.0°). Several iron complexes with C(O)R are known [1,26–29], but the geometry of the substituted acetyl group shows substantial variation with the nature of the R group. The Fe—C(7) distance of 1.976 Å is virtually identical to those found in the other reported iron-acetyl compound (1.968 Å) [25] and an iron-benzoyl (1.97 Å) [30], but is significantly shorter than the 2.11 Å reported for the alkyl C_3H_5 derivative [31]. A similar pattern is seen in the Mo-alkyl [32] Mo-acetyl [33] series, with the shorter values being attributed to d_π — p_π back-donation [33]. The observed variations in both cases are certainly more than just the 0.03 Å difference in covalent radii between sp^2 - and sp^3 -hybridized carbon atoms, and thus our results must serve to enhance the argument for back-donation in transition metal acyls.

The orientation of the acetyl group can be seen qualitatively in Fig. 1 and quantitatively in Tables 5 and 6. The most obvious steric constraints are the Cp ring and the C(9)—C(14) phenyl ring, with an attractive force being the NH group available for hydrogen bonding. The H bond parameters are $N\cdots O(7) = 2.86$ Å, $H\cdots O(7) = 2.07$ Å, angle at H = 131° . According to a recent survey by Whuler et al. [34], this would be classified as a very strong N—H \cdots O type hydrogen bond. The angle at the hydrogen is quite small due to geometric constraints; however, such a low value has been seen before under similar circumstances [35]. This hydrogen bonding locks both the acetyl and phosphine ligands into place, and possibly accounts for the well-behaved thermal parameters during the refinement.

Fe—P distances have been shown to be a function of the phosphorous substituents [36], and our value is one of the shortest yet reported for unoxidized phosphines [1,23,24,36–39]. This could be a result of the altered electronic environment on the nitrogen caused by hydrogen bonding, as we have noted the same phenomenon in an unrelated ruthenium complex containing the same phosphine ligand hydrogen bonded to chlorine [20]. The Fe—P—C(N) angles average 114° , much larger than the ideal tetrahedral value: a consequence of Fe—P π bonding and quite common in transition metal phosphines [1,38–42]. The P—C distances average 1.839 Å, which is normal in complexes [1,38–42] and compares well with the value found in free $P(Ph_3)$ [43]. The P—N distance of 1.655 Å is the same as that found in the Ru structure [20] and only mar-

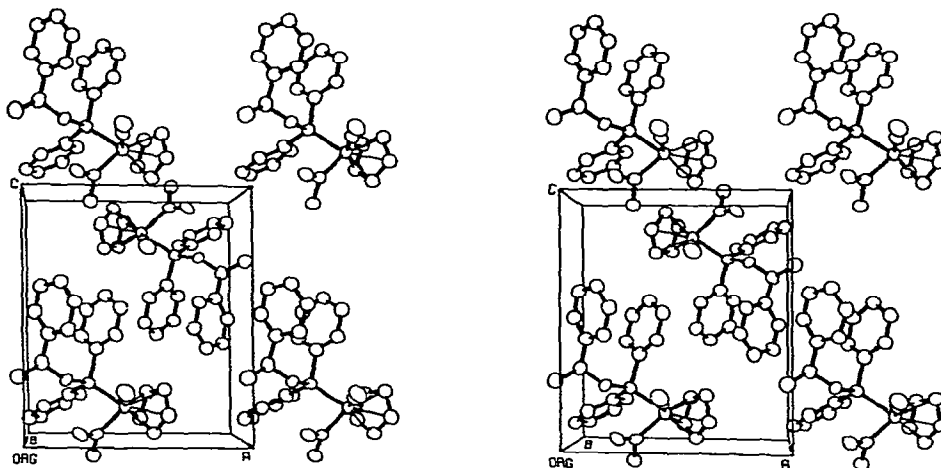


Fig. 2. Stereoscopic view of the molecular packing in the crystal lattice, with hydrogens omitted for clarity. The 2_1 screw axis along b is clearly shown.

ginally smaller than the value found in tetrametaphosphimic acid [44]. The N—C(21) distance is as expected for a pure single bond [45]. The phosphine ligand has a chiral center at C(21) which can be seen in the figures to be in the (*S*) configuration, the opposite of that reported for the Ru structure [20]. (Since the phosphine ligands used in the preparations in these two experiments were of opposite chirality, both reactions are found to proceed with retention of configuration at the optically active carbon). This necessarily causes a difference in packing when coupled with the constraints of an intramolecular hydrogen bond. Two of the phenyl planes are forced into parallel (planes E and F in Table 5), and this grouping can be seen to pack very efficiently in a herringbone arrangement in Figure 2.

Acknowledgments

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