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Comparison between experimental studies and DFT computed structural and spectral parameters of some dipyrromethanes

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ABSTRACT

The structural and spectral properties of the previously synthesized and structurally characterized compounds: 5methyl-5-(4-methylphenyl)dipyrromethane (1), 5-methyl-5-(4-methoxyphenyl)dipyrromethane (2) and 5-methyl-5-(4chlorophenyl)dipyrromethane (3) are here theoretically examined by density functional theory (DFT) at B3LYP level. The geometries of isolated molecules were optimized using 6-31G + (d, p) basis set to calculate structural and spectral parameters (IR, ¹H NMR, ¹³C NMR) of the listed compounds (1) - (3). The calculated parameters are in good agreement with experimental data. The energies of frontier orbitals (HOMO-LUMO) have also been calculated. The nature of substituents at meso- position alters the energy gaps of frontier orbitals.

Key words: DFT study, crystal structures, dipyrromethanes, vibrational spectra, HOMO-LUMO, NMR.

INTRODUCTION

Dipyrromethanes are important building blocks for polypyrrolic compounds [1-7] of wide interest in several areas [8-12]. Dipyrromethanes and its charge transfer complexes have been used as sensors [13-18]. Metal complexes of dipyrromethanes are also known to catalyze many reactions [19-20]. Dipyrromethanes have been generally synthesized by condensation of carbonyl compounds with an excess of pyrrole in the presence of acids [21-26]. Theoretical studies of anion complexes of DPM have predicted 2:1 and 1:1 stoichiometry in compliance with experimental observation [16, 18]. Till date crystal structures of few *meso*- dialkyl/alkylaryldipyrromethanes have been reported [16, 25]. Recently crystal structures of three substituted *meso*-alkyl-*meso*-aryldipyrromethanes have been reported by us [27]. The DFT /B3LYP model exhibits good performance in predicting vibrational frequencies and geometry of organic compounds. The present work involves the optimization of structure and vibrational parameters of compounds (1) – (3) and their comparison with already reported experimental parameters [27] to establish the performance of B3LYP hybrid density functional theory (DFT) method together with the 6-31G + (d, p) basis set to study dipyrromethanes. The energies of frontier orbitals *i.e.* HOMO-LUMO have also been computed.

MATERIALS AND METHODS

The input coordinates were obtained from already reported crystal structure data [27]. The quantum chemical calculations (DFT calculations) giving molecular geometries of minimum energies, vibrational spectra, ¹H NMR, ¹³C NMR assignments and energies of frontier molecular orbitals (HOMO-LUMO) of the title compounds were performed using the Gaussian 03 package [28]. Molecular orbitals are visualized using "Gauss view". The method used was Becke's three-parameter hybrid-exchange functional, the nonlocal correlation provided by the Lee, Yang and Parr expression, and the Vosko, Wilk, and Nuair 1980 local correlation functional (III) (B3LYP) [29]. DFT calculations were performed in the gas phase using 6-31G + (d, p) basis set. The geometry of tetramethylsilane (TMS) was also fully optimized. ¹H and ¹³C NMR chemical shifts were calculated with gauge including atomic

orbital (GIAO) approach applying the same method and the basis sets as used for geometry optimization [30]. The predicted ¹H and ¹³C NMR chemical shifts were derived from the equation $\delta = \Sigma_0 - \Sigma$, where δ is the chemical shift, Σ is the absolute shielding and Σ_0 is the absolute shielding of the standard (TMS), whose values are 31.64 ppm and 192.65 ppm for

Table 1	Experimental and	optimized	geometric	parameters	(selected	bond distances	(Å),	, bond	l angles	(°) of	f compound	s (1)) - (.	3)
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Bond distances (Å)	Exp. ^a	The.	Dev.	Bond angles (°)	Exp. ^a	The.	Dev.
Comp.(1)							
C5-C4	1.344	1.379	0.035	C16-C1-C2	109.18	110.51	1.33
C2-C3	1.363	1.387	0.023	C6-C1-C2	109.55	108.08	1.48
N2-C5	1.359	1.377	0.018	C6-C1-C10	111.54	111.85	0.31
C2-N2	1.368	1.380	0.012	C10-C1-C2	109.71	109.85	0.14
C12-C13	1.378	1.404	0.026	C16-C1-C10	111.54	107.83	3.72
C17-C13	1.506	1.511	0.005	C16-C1-C6	108.67	108.74	0.07
C1-C6	1.508	1.524	0.016	C1-C10-C11	120.12	120.07	0.05
C1-C2	1.510	1.525	0.015	C1-C2-N2	120.74	121.16	0.42
C1-C10	1.533	1.548	0.015	C1-C6-C7	131.69	132.17	0.48
C1-C16	1.543	1.555	0.012	N2-C2-C3	106.82	106.62	0.20
C10-C11	1.387	1.406	0.019	C17-C13-C14	121.66	121.65	0.01
C4-C3	1.415	1.428	0.013	C17-C13-C12	121.07	120.89	0.18
C11-C12	1.38	1.393	0.013	C7-C8-C9	107.76	107.24	0.52
C15-C10	1.383	1.398	0.015	C10-C11-C12	121.36	121.25	0.11
Comp. (2)					_		
C8-C9	1.349	1.380	0.031	C6-C1-C2	108.27	108.00	0.27
C9-N1	1.365	1.375	0.010	C6-C1-C10	111.46	111.76	0.30
C7-C6	1.371	1.386	0.015	C2-C1-C10	108.13	109.96	1.82
C6-N1	1.364	1.379	0.140	C6-C1-C16	109.30	108.72	0.58
C1-C2	1.516	1.525	0.009	C2-C1-C16	110.79	110.45	0.34
C17-O1	1.419	1.422	0.003	C10-C1-C16	109.32	107.95	1.37
C10-C15	1.380	1.396	0.016	N2-C2-C3	106.99	106.63	0.37
C14-C13	1.379	1.397	0.018	N2-C2-C1	121.56	121.15	0.41
C12-C11	1.373	1.389	0.016	N1-C6-C1	120.96	120.96	0.00
C1-C6	1.515	1.524	0.009	N1-C6-C7	106.55	106.80	0.25
C8-C7	1.414	1.427	0.013	C15-C10-C11	117.28	117.37	0.09
C13-01	1.375	1.369	0.006	C11-C10-C1	123.16	120.17	2.99
Comp. (3)							
C15-C14	1.399	1.399	0.000	C6-C1-C10	111.16	111.80	0.64
C12-C11	1.383	1.395	0.012	C6-C1-C16	111.16	108.77	2.39
C2-C3	1.368	1.387	0.019	C16-C1-C2	111.16	110.61	0.55
	1./51	1.761	0.010	C10-C1-C2	108.72	109.74	1.02
C6-C1	1.524	1.523	0.001	C16-C1-C2	108.75	108.23	0.52
C1-C2	1.52	1.525	0.005		108.80	107.69	1.11
	1.545	1.548	0.003		125.10	122.09	1.01
C10 C15	1.549	1.333	0.000		121.22	119.99	0.13
C10-C15	1.384	1.400	0.010	C1-C2-C3	131.22	101.85	0.03
C11 C10	1.419	1.428	0.009	C1-C2-N2	122.20	121.21	1.05
C5 N2	1.39/	1.405	0.008	C1-C6-C/	132.30	132.10	0.40
C2 N2	1.373	1.3/0	0.001	N2 C2 C2	121.80	121.01	0.79
C12 C12	1.370	1.360	0.004	1N2-U2-U3	100.90	117.07	0.20
C13-C12 C14 C12	1.370	1.390	0.020		108.20	107.86	0.17
C4 C5	1.373	1.392	0.019	$C_{14} C_{12} C_{11}$	110.30	1107.00	0.44
C4-C3	1.349	1.379	0.030	C14-C13-C11	119.73	119.74	0.01
				C12-C13-C11	119.00	119.34	0.06

^a data from ref [27]

B3LYP/6-31G + (d, p). Structural parameters obtained from the latter were compared with those of optimized geometries.

RESULTS AND DISCUSSION

The comparison of experimental, theoretical structural and spectral parameters of the title compounds is given in Tables 1–4. The optimized geometric structure of the title compounds with their previously reported crystal structures [27] are shown in Fig. 1-3. As shown in Table 1 most of the calculated bond lengths and bond angles are consistent with the experimental crystal structure data.

3.1 Geometrical structures

DFT calculations have been performed to calculate the structural parameters (bond distances and angles), spectral parameters (IR, ¹H NMR, ¹³C NMR) and electronic properties of the compounds (1) - (3). Only selected experimental and calculated structural parameters have been listed due to space limitations. The optimized structures

have revealed that steric crowding due to presence of bulky aryl group at *meso*- carbon leads to deviation in tetrahedral geometry for compounds (1) - (3) (Fig 1-3). The calculated structures obtained in this study have similar conformations and structural features as the reported by X - ray crystal structures [27] (Fig. 1-3, Table 1).

Overall, the calculated bond lengths are in good agreement with experimental results (Table 1) with maximum deviations of bond lengths 0.035 Å, 0.031 Å and 0.02 Å for compounds (1), (2) and (3) respectively. Similarly maximum deviations in calculated and experimental bond angles are 3.72° , 2.99 ° and 2.39 ° for compounds (1) - (3) respectively (Table 1). The



Fig. 1. 5-methyl-5-(4-methylphenyl)dipyrromethane (1): (a) Optimized geometric structure (b) ORTEP diagram [27]



Fig. 2. 5-methyl-5-(4-methoxyphenyl)dipyrromethane (2): (a) Optimized geometric structure (b) ORTEP diagram [27] torsion angles provided by strain energy minimized structures reproduced the observed crystal structures to a maximum tolerance of 8.374°, 7.02 and 8.183° for compounds (1), (2) and (3) respectively

3.2 Spectral Studies

The theoretical vibrational frequencies, ¹H NMR and ¹³C NMR chemical shifts of compounds (1) - (3) have been computed by Gaussian 03 using DFT/ B3LYP method with 6-31 G + (d,p) and compared with the experimental data which are in compliance with experimental results. Experimental and calculated vibrational frequencies, ¹H NMR and ¹³C NMR chemical shifts along with corresponding assignments are given in Table 2, 3 and 4 respectively.

3.2.1 Infrared spectra

Vibrational spectroscopy has been widely used as a standard tool for structural characterization of molecular systems by DFT calculations [31-33]. In the IR spectra of compounds (1) - (3) the strong band at 3422.5 cm⁻¹,

 3410.4 cm^{-1} and 3430.9 cm^{-1} is assigned to the N—H stretching mode of pyrrole ring while the DFT computations gave the wavenumber of these bands at 3643.0 cm^{-1} 3640.9 cm^{-1} and 3639.8 cm^{-1} .



Fig. 3. 5-methyl-5-(4-chlorophenyl)dipyrromethane (3) (a) Optimized geometric structure (b) ORTEP diagram [27] These discrepancies in bond lengths and bond angles are very small and are attributable to packing interactions within lattice which are not modelled during computational study

Table 2 The experimental IR and the calculated vibrational frequencies (cm^{-1}) for compounds (1) - (3)

Compou	nd (1)	Compo	und (2)	Compo	und (3)	Assignment			
Exp. ^a (cm ⁻¹) The.		Exp. ^a (cm ⁻¹)	The. (cm^{-1})	Exp. ^a (cm ⁻¹)	The. (cm^{-1})	Assignment			
3422.5	3643.0	3410.4	3640.9	3430.9	3639.8	ν (NH)			
3123.3	3248.5	3051.7	3221.9	3099.8	3249.6	v (=CH)			
2986.9	3118.1	2981.0	3119.0	2980.0	3139.2	$\mathbf{u} \in \mathbf{U} (\mathbf{C} \mathbf{U}) (\mathbf{a} \mathbf{u} \mathbf{m} \mathbf{m})$			
2916.3	3086.6	2905.6	3078.1	2917.9	3121.9	$V C - \Pi (CH_3)$ (asymmin)			
2870.3	3013.1	2835.4	3015.6	2849.2	3051.4	v С-п (Сп ₃) (Symm.)			
1666.3-1414.2	1616.1-1413.7	1602.9-1457.7	1620.8-1455.0	1553.3-1485.6	1525.5-1496.8	v (C=C)			
		1025.1	1045.5	718.6	718.3	v (C-R1)			
^a Data from rof [27]									

^a Data from ref [27]

The corresponding peaks were observed in the range of 3369 cm^{-1} to 3409 cm^{-1} for dipyrromethanes (Sobral et al. 2003). The two asymmetric and symmetric stretching vibrations of CH₃ group are observed at 2986.9 cm⁻¹, 2916.3 cm⁻¹, 2870.3 cm⁻¹ and 2981.0 cm⁻¹, 2905.6 cm⁻¹ and 2835.4 cm⁻¹ in the experimental IR spectra while corresponding theoretically predicted IR bands are at 3118.1 cm⁻¹, 3086.6 cm⁻¹, 3013.1 cm⁻¹ and 3119.0 cm⁻¹, 3078.1 cm⁻¹, 3015.6 cm⁻¹ for compounds (1) and (2) respectively. In aromatic rings, C-H stretching vibrations appeared above 3000 cm⁻¹ and are typically exhibited as weak to moderate bands. The theoretically computed vibrations at 3248.5 cm⁻¹ and 3051.7 cm⁻¹ in compounds (1) and (2) respectively. The aromatic C-C stretching appeared at 1666.3-1414.2 cm⁻¹ and 1602.9-1457.7 cm⁻¹ in experimental IR spectra while computationally calculated at 1616.1-1413.7 cm⁻¹ and 1620.8-1455.0 cm⁻¹ for compounds (1) and (2) respectively. Similar peaks have been observed for compound (3) in the same region (Table 2). The peak at 1025.1 cm⁻¹ and 718.6 cm⁻¹ in IR spectra of (2) and (3) are assigned to C—O stretching frequency and C—Cl streching frequency respectively while corresponding vibrations computed at 1045.5 cm⁻¹ and 718.3 cm⁻¹ knows good correlation with experimental data.

3.2.2 ¹H-NMR spectra

The characterization of the compound was further enhanced by the use of ¹H and ¹³C NMR spectroscopy which is the most powerful and widely used spectroscopic method for the determination of molecular structures. The NMR was calculated using the B3LYP/GIAO with 6-31G + (d, p) calculations and compared with experimental ¹H and ¹³C chemical shift values. The simulated NMR spectra provide the discrete signal for each proton. For clarity, the simulated NMR signals have been reported in the present work as the average chemical shift for magnetically equivalent protons. The calculated chemical shift values are in good agreement with experimental data. The signal belonging to NH protons appeared at 7.6 ppm, 7.7 ppm and 7.8 ppm in experimental ¹H NMR spectra for compounds (1) - (3) respectively, while the same was observed at 7.4 ppm, 7.6 ppm and 7.5 ppm, in the simulated ¹H NMR spectra in agreement with already reported data of dipyrromethanes and calix [4]pyrrole (Sobral *et al.* 2003). There are three kinds of pyrrolic CH protons: α (H9 and H5), β - (H3 and H7)) and β '-pyrrolic protons (H4 and H8) (Table 3). The downfield chemical shifts are observed for α pyrrolic CH protons (H9 and H5) relative to other pyrrolic CH hydrogens as the former are adjacent to electronegative nitrogen atom in the title compounds. Experimental and simulated ¹H NMR spectra displayed the signals corresponding to these magnetically

Co	mpound (1)		Compound (2)			Co	Assignment			
Exp. ^a (ppm).	The.(ppm)	Average	Exp. ^a (ppm)	The.(ppm)	Average	Exp. ^a (ppm)	The (ppm)	Average	Assignment	
7.6	7.2 7.5	7.4	7.7	7.7 7.4	7.6	7.8	7.3 7.7	7.5	H1a H2b	
5.8	5.9 6.4	6.2	5.9	6.3 5.9	6.1	5.9	6.3 6.4	6.4	H3 H7	
6.0	6.5 6.3	6.4	6.1	6.3 6.4	6.3	6.2	6.5 6.3	6.4	H4 H8	
6.5	6.7 6.9	6.8	6.6	6.8 6.7	6.8	6.7	6.7 6.9	6.8	H5 H9	
6.8-6.9	7.7 6.4	7.0	6.7-6.8	6.6 7.7	7.1	6.9-7.1	7.6 6.4	7.0	H11 H15	
7.0-7.2	7.4 7.0	7.2	6.9-7.0	6.4 7.1	6.8	7.2-7.3	7.4 7.2	7.3	H12 H14	
1.9	1.9 1.8 1.7	1.8	2.0	1.9 1.7 1.9	1.8	2.00	1.9 1.9 1.7	1.8	H16a H16b H16c	
2.2	2.5 1.9 2.6	2.3	3.7	4.1 3.6 3.6	3.8	-	-	-	H17a H17b H17c	

Table 3 Experimental and calculated ¹H NMR chemical shifts (ppm) of compounds (1) - (3)

^a Data from ref [27]

equivalent α -pyrrolic protons at 6.5 ppm and 6.8 ppm for compound **1**, 6.6 ppm and 6.8 ppm for compound **2** and 6.7 ppm and 6.8 ppm for compound **3**,. The experimental signal for β pyrrolic protons (H3 and H7) appeared at 5.8 ppm, 5.9 ppm, 5.9 ppm for (**1**), (**2**) and (**3**) while calculated spectrum exhibited the corresponding signal at 6.2 ppm, 6.1 ppm and 6.4 ppm for (**1**), (**2**) and (**3**) respectively. While in compound (**1**) – (**3**) β '-pyrrolic protons (H4 and H8) appeared at 6.0 ppm, 6.1 ppm, and 6.2 ppm and computationally calculated at 6.4 ppm, 6.3 ppm and 6.4 ppm respectively.

Two multiplets at 6.9-7.1 ppm (H11, H15) and 7.2-7.3 ppm (H12, H14) are assigned to aromatic protons of phenyl ring in (3) which are computed at 7.0 ppm, 7.3 ppm by DFT. The downfield shift of latter protons is due to the presence of the electron withdrawing chloro group at adjacent carbon atom. two multiplets at 6.8-6.9 ppm (H11, H15), 7.0-7.2 (H12, H14) and 6.7-6.8 ppm, 6.9-7.0 ppm are assigned to aromatic protons of phenyl ring which are computed at 7.0 ppm, 7.2 ppm and 7.1 ppm, 6.8 ppm by DFT in compounds (1) and (2) respectively. Methyl protons appeared at 1.9 ppm, 2.0 ppm and 2.0 ppm for (1), (2) and (3) in experimental spectra, although computers they are calculated at 1.8 p.m. for all three compounds. OCH₃ protons appeared at 3.70 ppm in (2) which is computed at 3.76 ppm by DFT.

3.2.3 ¹³C-NMR spectra

The studies of 13 C-NMR spectra of substituted methylphenyldipyrromethanes (1) – (3) revealed downfield shifts of phenyl carbon atoms, the most downfield shifts exhibited by ipso carbon atoms (C13) of (2) than (1) and (3) in the decreasing order i.e. 158.2 ppm, 136.3 ppm and 132.5 ppm respectively owing to the presence of oxygen atom of the methoxy group adjacent to it and computationally calculated at 155.9 ppm, 134.7 ppm and 140.1 ppm respectively. The *meso*- carbon of (1) - (3) appeared nearly at 44.4 ppm, 44.1 ppm, 44.4 ppm and computationally calculated at 49.9 ppm, 49.6 ppm and 49.8 ppm respectively. The peaks corresponding to the pyrrole carbon atoms of all the synthesized compounds also appeared downfield but the most downfield effect was seen at α position where *meso*-carbon was attached with pyrrole (C2, C6) as observed experimentally at 137.7 ppm, 137.8 ppm and 136.9 ppm and computationally at 134.3 ppm, 134.7 ppm, 133.4 ppm for compounds (1) - (3). It seemed that α pyrrole carbon atoms of (1)-(3) were having different electron densities but β and β ' carbon of each compound were having the same electron densities as was apparent from the shifts (Table 4). In the pyrrole ring β (C3, C7) and β ' (C8, C4) carbon signals were observed at 106.1, 108.2 for (1) , 108.2, 106.2 for (2) and 108.3, 106.3 for (3) that have been calculated

Co	ompound (1)		Compound (2)				Compound (Assignment			
Exp. ^a (ppm)	The. (ppm)	Average	Exp. ^a (ppm)	The. (ppm)	Average	Exp. ^a	The. (ppm)	Average	Assignment		
28.9	29.9		29.0	31.0		28.8	30.2		C16		
44.4	49.9		44.1	49.6		44.4	49.8		C1		
1377	135.2	134.3	137.8	135.3	134.7	136.9	132.1	133.4	C2 C6		
137.7	133.3	154.5	157.0	134.1			134.6		02,00		
116.8	111.6	1123	113.4	113.1	112.2	117.2	113.2	112.6	C5 C9		
110.8	112.9	112.5	113.4	111.2		117.2	112.1	112.0	0,09		
106.1	103.1	104.7	104.7	108.2	102.7	104.0	108.3	103.4	104.9	C3C7	
100.1	106.3	104.7	108.2	105.3	104.0	100.5	106.4	104.9	03,07		
108.2	105.3	105.2	105.2	106.2	105.7	106.1	106.3	105.3	105.3	C8 C4	
100.2	105.1		100.2	106.6	100.1	100.5	105.6	105.5	0,04		
144.3	144.1		139.5	138.2		146.0	145.2		C10		
136.3	134.7		158.2	155.9		132.5	140.1		C13		
127.4	124.0	122.0	129.5	125.6	126.2	126.2	126.2	100.0	125.1	124.5	Db 11 C14 12
127.2	124.0	125.9	128.5	126.8		128.2	123.9	124.3	Рп-п С14,12		
128.9	125.5	125.0	116.0	104.0	100.0	120.8	125.3	125.2	Dh U C6 11		
128.8	126.2	123.9	110.9	114.1	109.0	129.0	127.1	123.2	FII- H C0,11		
20.9	22.6		55.3	53.5		-	-		R1		

 Table 4 Experimental and calculated ¹³C NMR chemical shifts (ppm) of compounds (1) – (3)

^a Data from ref [27] at 104.7 ppm, 105.2 ppm for compound (1), 104.0 ppm, 106.1 ppm for (2), 104.9, 105.3 for compound (3).

3.3. HOMO - LUMO analysis

Frontier molecular orbital energies have been calculated with B3LYP/6-31G + (d, p) level (Fig. 4). The HOMO and LUMO energy characterize the ability of electron giving and electron accepting. The gap between HOMO and LUMO characterizes the molecular chemical stability [34]. The energy gaps are largely responsible for the chemical and spectroscopic properties of molecules. It has been found that LUMO is mainly distributed over the phenyl ring in compounds (1) –(3). The HOMO is mainly distributed over the pyrrole rings in 5-methyl-5-(4-methylphenyl)dipyrromethane (1) while in 5-methyl-5-(4-methoxyphenyl)dipyrromethane (2) distributed over the entire molecule.

HOMO is mainly distributed over one pyrrole ring and phenyl ring in 5-methyl-5-(4-chlorophenyl)dipyrromethane (3). The energy gap between the highest occupied and the lowest unoccupied molecular orbitals, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The energy gap values for (1) - (3) are 3.862 eV, 3.835 eV and 3.699 eV respectively. Thus the nature of substituents influences the electronic properties of dipyrromethanes. It seems that substitution of chloro group at p-position of phenyl ring at *meso*- carbon leads to relatively smaller energy gaps between HOMO and LUMO as compared to methyl/methoxy substituted derivative.





HOMO = - 9.112 eV (3) Fig. 4. Frontier molecular orbitals (HOMO-LUMO) of the compounds (1) - (3) with energy gaps

CONCLUSION

A systematic investigation of the structural (bond lengths, bond angles and torsion angles) and spectroscopic properties (vibrational, ¹H NMR, ¹³C NMR and HOMO-LUMO) of dipyrromethanes (1) – (3) have been performed at the DFT level and compared with already reported experimental results. Optimised geometries of dipyrromethanes displayed distorted tetrahedral geometry with *anti*- conformation in agreement with crystal structures. The theoretical structural and spectral parameters (IR ¹H NMR and ¹³C NMR) of optimized structures are in excellent agreement with crystal data and spectroscopic data confirming suitability of DFT studies using B3LYP 6-31G +(d, p) level for reproducing the experimental results for these synthetically important heterocyclic derivatives. The small discrepancies in geometric and vibrational parameters are attributable to packing interactions within the lattice which are not modelled during computational study. Energy calculations of frontier orbitals (HOMO-LUMO) have revealed that nature of substituents at *meso*- position of dipyrromethanes lead to variable energy gaps of frontier orbitals, thus influencing their electronic properties.

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