Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Revealing The Biradicaloid Nature Inherited In Derivatives Of Thieno[3,4 -c][1,2,5]thiadiazole: A Computational Study

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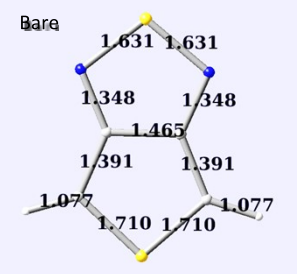
Electronic supplementary information: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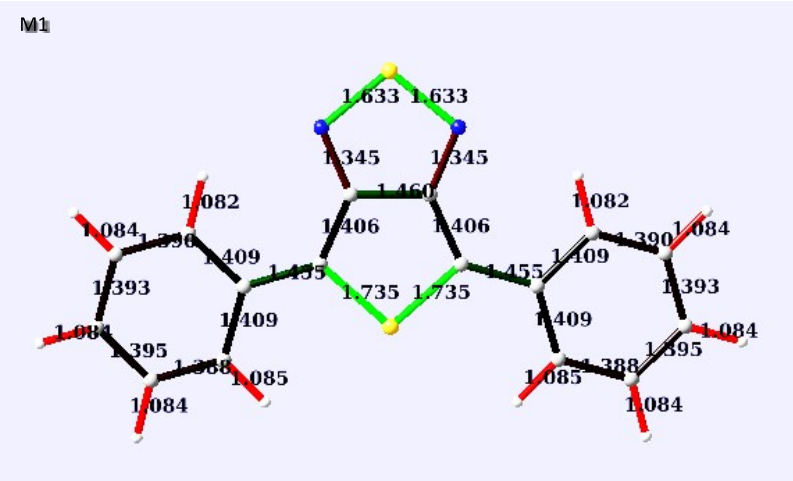
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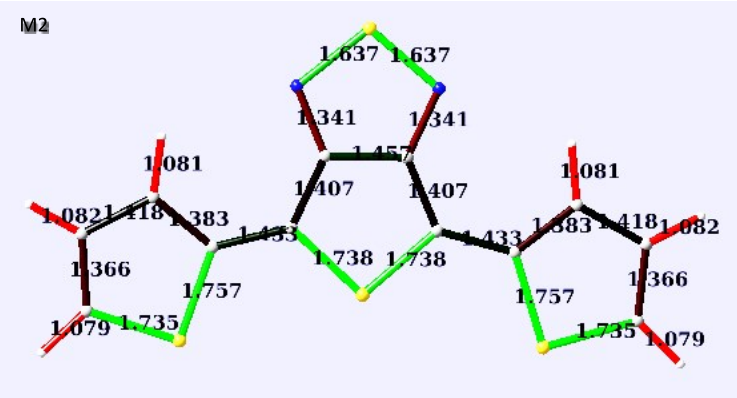
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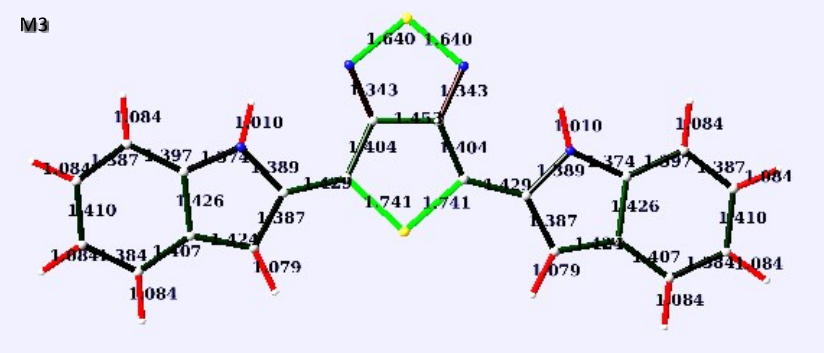
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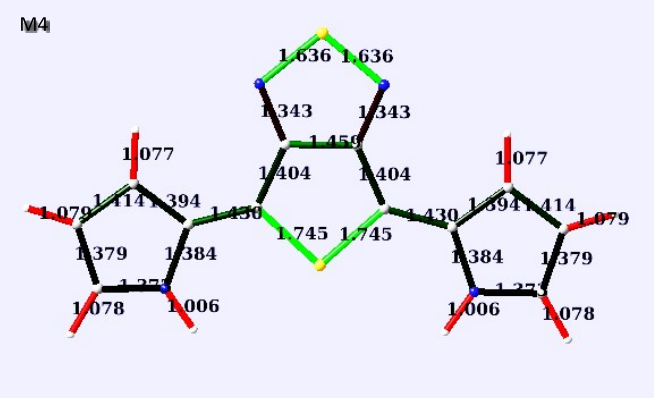
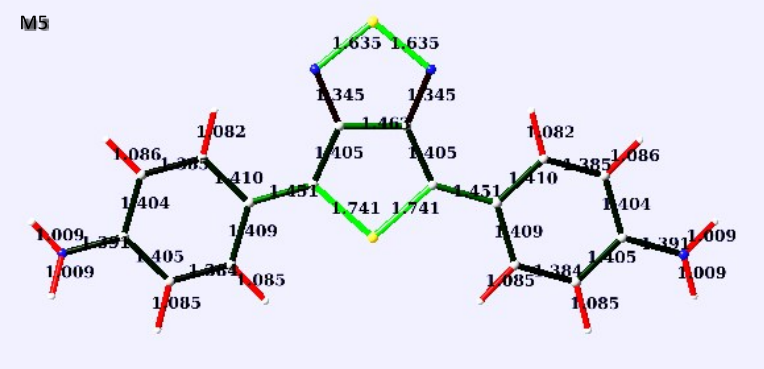
1.084





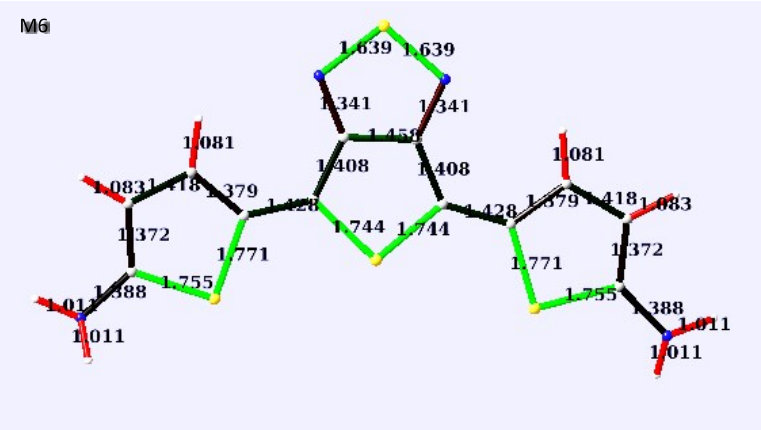
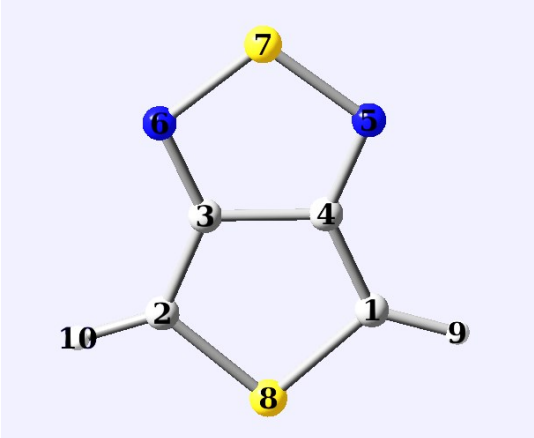


Fig. S1. Ground state singlet bond lengths obtained using RB3LYP/6-311G(d,p)

Table S1. Natural Atomic Charge and Natural Population Analysis of Bare Molecule.



Natural Population

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	-0.49184	1.99903	4.47671	0.01611	6.49184
C	2	-0.49145	1.99903	4.47632	0.01611	6.49145
C	3	0.07722	1.99897	3.90036	0.02345	5.92278
C	4	0.07737	1.99897	3.90020	0.02347	5.92263
N	5	-0.64156	1.99946	5.61409	0.02801	7.64156
N	6	-0.64161	1.99946	5.61414	0.02801	7.64161
S	7	0.96999	9.99918	4.96055	0.07028	15.03001
S	8	0.59061	9.99898	5.36398	0.04643	15.40939
H	9	0.27567	0.00000	0.72300	0.00133	0.72433
H	10	0.27560	0.00000	0.72306	0.00133	0.72440

	Energy (in au)	

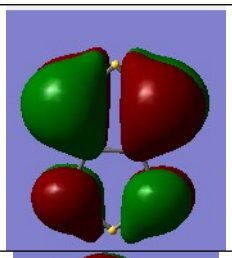
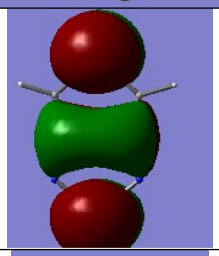
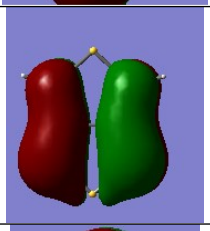
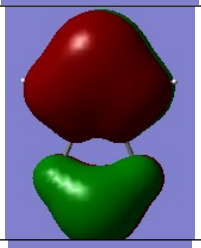
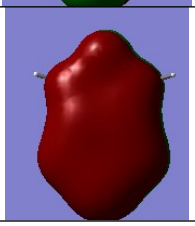
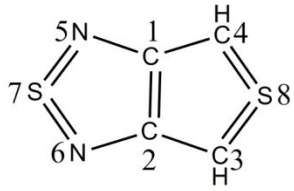
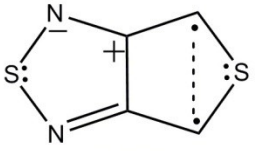
HOMO	-0.22032	
HOMO-1	-0.27180	
(π)HOMO-2	-0.33007	
(π)HOMO-3	-0.37632	
(π)HOMO-4	-0.45506	

Fig. S2. π- MOs of Bare Molecule



Other Important Structures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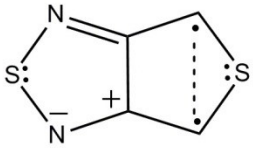
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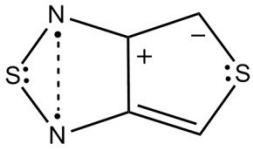
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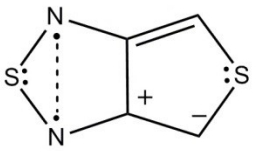
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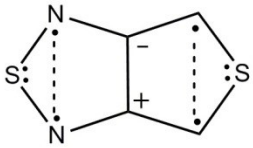
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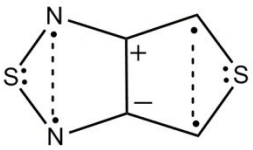
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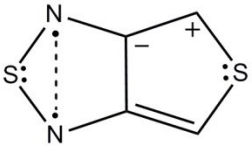
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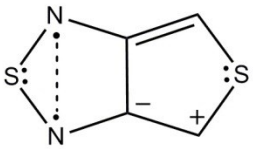
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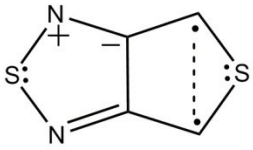
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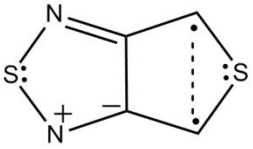
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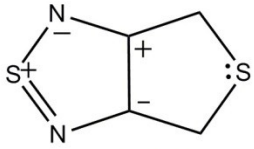
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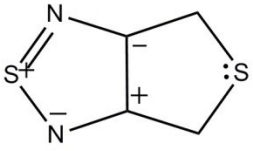

XXXIV

Fig. S3. Initially studied VB structures

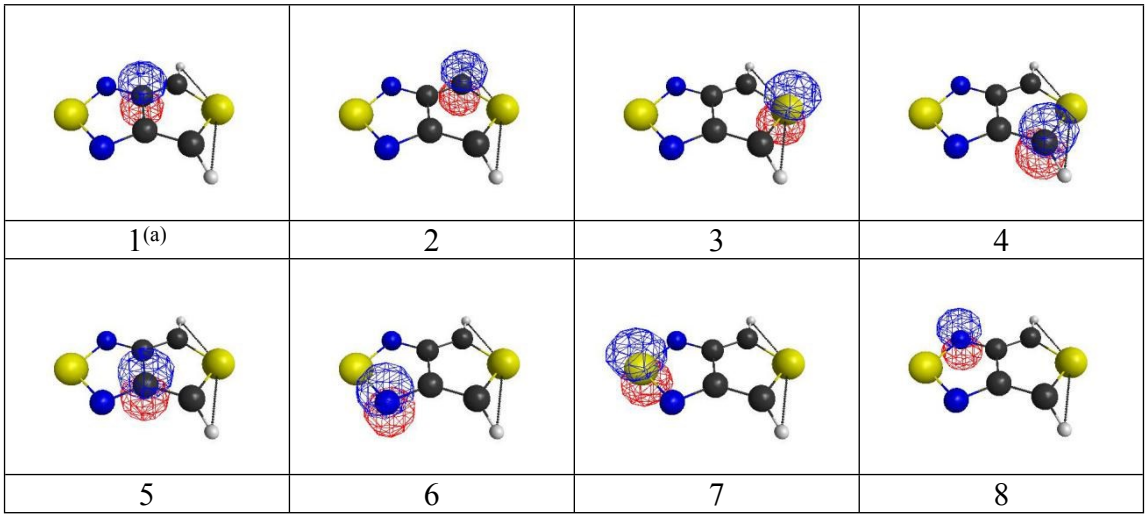
Bare-Π dye VBSCF Calculation Report I

The Bare-Π dye is a planar compound. Its geometry is described in Table S2.

Table S2 Bare-Πdye geometry

Label	Atom	x/(Armstrong)	y/(Armstrong)	z/(Armstrong)
1	C	0.05444900	0.73281600	-0.00009300
2	C	0.05436700	-0.73239300	0.00019700
3	C	-1.22875000	-1.27000200	0.00008400
4	C	-1.22832800	1.27084800	0.00005700
5	N	1.29145800	1.26858000	-0.00001200
6	N	1.29113900	-1.26862700	-0.00002300
7	S	2.31659100	-0.00022600	-0.00025100
8	S	-2.37331400	-0.00026500	0.00016500
9	H	-1.54037300	-2.30076500	0.00005800
10	H	-1.54066700	2.30134500	0.00009200

Selecting 10 active electrons and 8 active orbitals, we do the VBSCF calculation using XMVB 3.0 with basis 6-31G(d,p), and the active orbitals are shown in Fig.S4.



(a) The number represent active orbitals' order

Fig. S4. Active Orbitals (Ten π electrons in eight orbitals (10e/8o) that are localized on each single atom in the bicyclic ring are included in the active space)

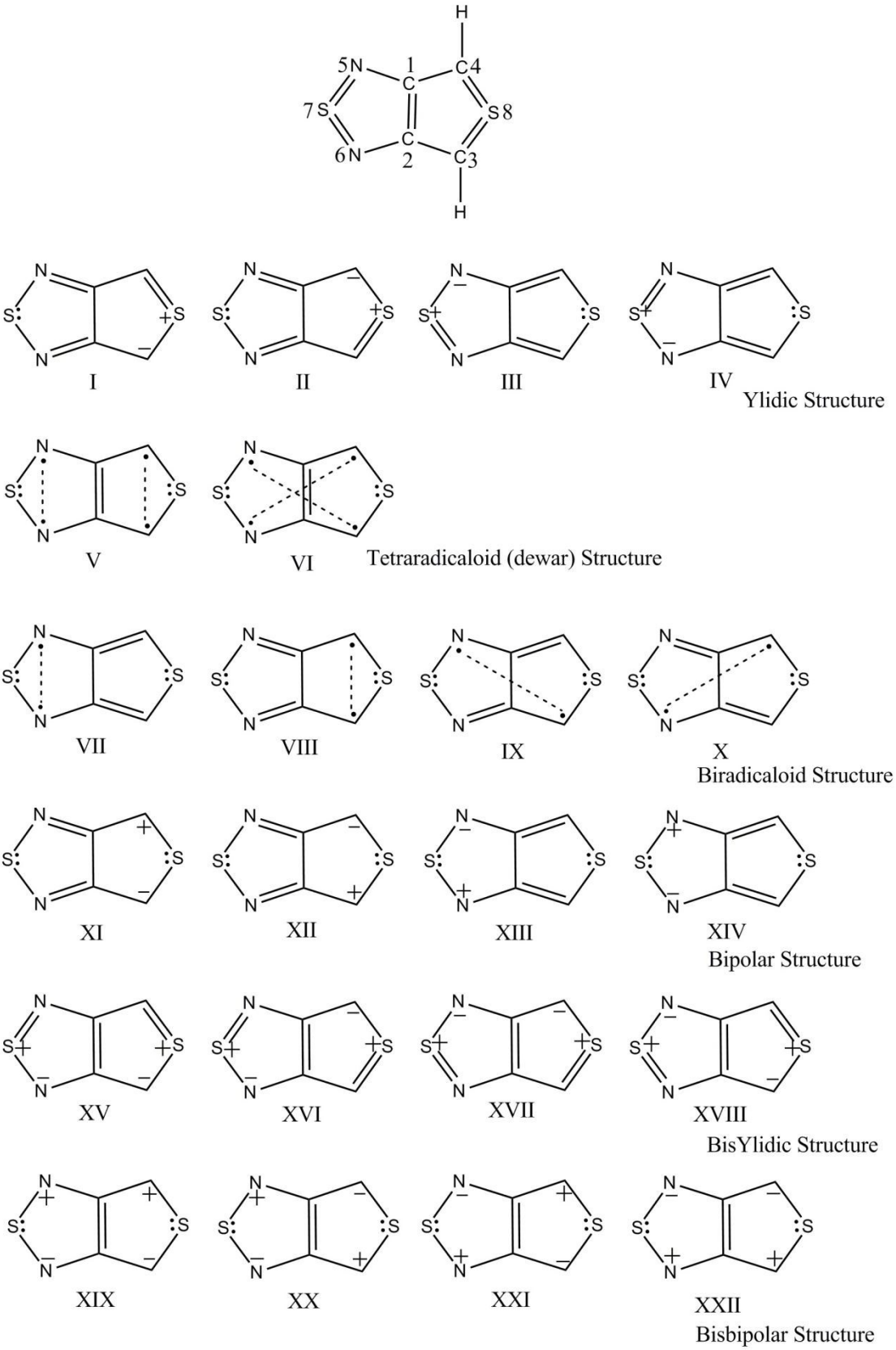


Fig. S5. 22 structures selected in the present investigation

However, the 6th structure in Tetraradicaloid structure class is linear dependent according to Rumer's rule. So we delete the 6th structure in our further VBSCF calculation.

Using the rest structures, we calculate the VBSCF energy and the results are listed in Table S3.

Table S3 VBSCF Energy

	Energy/(Hatree)
Full Structures(1176 structures)	-1056.49531

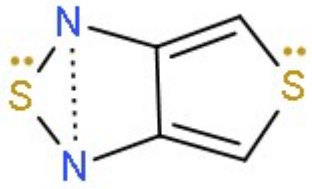
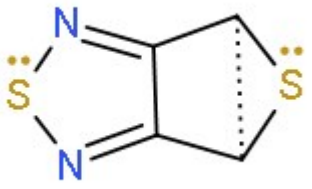
The number of full structures can be calculated by Weyl's formula:

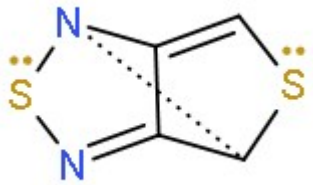
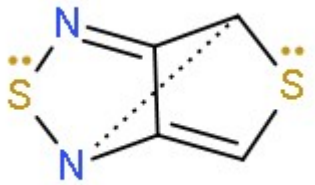
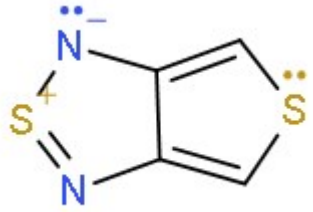
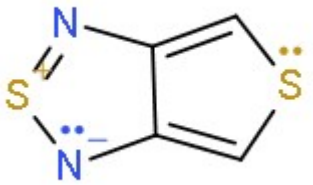
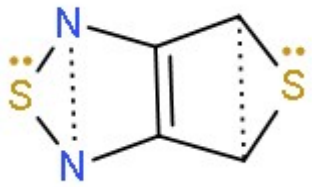
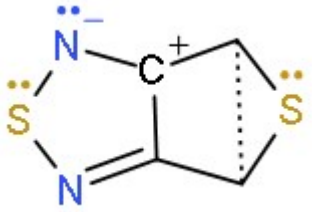
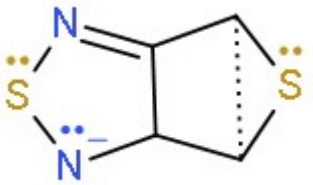
$$g_S^{N,m} = \frac{2S+1}{m+1}\binom{m+1}{\frac{N}{2}+S+1}\binom{m+1}{\frac{N}{2}-S} = \frac{2\times 0+1}{8+1}\binom{8+1}{\frac{10}{2}+0+1}\binom{8+1}{\frac{10}{2}-0} = 1176$$

where N, m, 2S+1 represent active orbitals' number, active electron's number and spin multiplicity of the system, respectively.

Here we also have the weights of different structures when all 1176 structures are involved.

Table S4. Full Structures' Weight

	Structure	Weight
1		0.09517 (VII)
2		0.091 (VIII)

3		0.03056 (IX)
4		0.03048 (X)
5		0.02939 (III)
6		0.02936 (IV)
7		0.0256 (V)
8		0.02074 XXIII
9		0.02072 XXIV

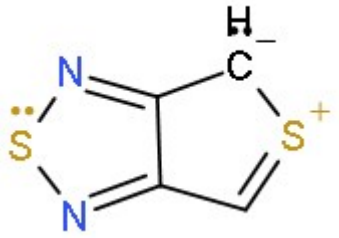
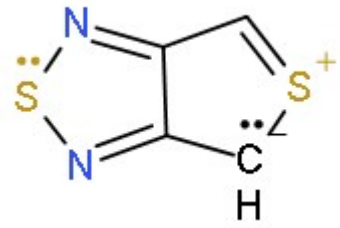
10		0.02021 (II)
11		0.02016 (I)
...	...	...
89	(XVI)	0.00221
90	(XVIII)	0.00221
...	...	...
107	(XII)	0.00178
...	...	...
110	(XI)	0.00176
...	...	...
115	(XVII)	0.00168
116	(XV)	0.00168
...	...	...
156	(XIII)	0.00098
157	(XIV)	0.00097
...	...	...
342	(XX)	0.00015
343	(XXI)	0.00015
...	...	...
602	(XXII)	0.00001
604	(XIX)	0.00001
...	...	...

Table S5. VBSCF Energy of Provided Structures

Structure Label	Energy[(a)]	Structure Label	Energy	Structure Label	Energy
I	-1056.10055	IX	-1056.21697	XVI	-1055.92018
II	-1056.10072	X	-1056.21692	XVII	-1055.86988
III	-1056.12407	XI	-1055.89363	XVIII	-1055.92006

IV	-1056.12399	XII	-1055.89405	XIX	-1055.27890
V	-1056.14364	XIII	-1055.80277	XX	-1055.48661
VII	-1056.22325	XIV	-1055.80259	XXI	-1055.42567
VIII	-1056.21683	XV	-1055.86968	XXII	-1055.27948
XXIII	-1055.9826	XXVII	-1055.86324	XXXI	-1055.85486
XXIV	-1055.98259	XXVIII	-1055.86314	XXXII	-1055.85489
XXV	-1055.93691	XXIX	-1055.98687	XXXIII	-1055.90004
XXVI	-1055.93679	XXX	-1055.98705	XXXIV	-1055.90007

(a) Energy/(Hatree)

Appendix A: Input File for Full Structure of XMVB 3.0

Bare-full

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nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

str=full

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end

Appendix B: Input File for Ylidic Structure of XMVB 3.0

Bare-Ylidic

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nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

nstr=4

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$str

4 4 7 7 1 8 2 3 5 6

2 2 7 7 1 8 3 4 5 6

3 3 8 8 1 2 4 5 6 7

3 3 6 6 1 2 4 5 7 8

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end

Appendix C: Input File for Tetraradicaloid Structure of XMVB 3.0

Bare-Tetra

$ctrl

iprint=3

nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

nstr=5

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$str

3 3 7 7 1 5 2 4 6 8

3 3 7 7 1 2 4 5 6 8

3 3 7 7 1 8 2 4 5 6

3 3 7 7 1 2 4 8 5 6

3 3 7 7 1 8 2 6 4 5

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end

Appendix D: Input File for Biradicaloid Structure of XMVB 3.0

Bare-Biradicaloid

$ctrl

iprint=3

nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

nstr=4

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$str

3 3 4 4 7 7 1 8 5 6

2 2 3 3 7 7 1 8 5 6

3 3 7 7 8 8 1 2 4 5

3 3 6 6 7 7 1 2 4 5

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end

Appendix E: Input File for Bipolar Structure of XMVB 3.0

Bare-Bipolar

$ctrl

iprint=3

nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

nstr=4

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$str

4 4 6 6 1 5 2 3 7 8

2 2 6 6 1 5 3 4 7 8

2 2 8 8 1 5 3 4 6 7

4 4 8 8 1 5 2 3 6 7

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end

Appendix F: Input File for BisYlidic Structure of XMVB 3.0

Bare-BisYlidic

$ctrl

iprint=3

nao=8 nae=10

itmax=20000

bprep

orbtyp=gen

guess=unit

nstr=4

iscf=5

sort

$end

$bfi

31 32

1-26 28 29 31 32 33

5 9 12 14

20 24 27 29

35 39 42 44

50 54 57 59

65 69 72 74

80 84 87 89

99 103 106 108

118 122 125 127

$end

$str

3 3 4 4 6 6 7 7 1 5

2 2 3 3 6 6 7 7 1 5

3 3 4 4 6 6 8 8 1 5

2 2 3 3 7 7 8 8 1 5

$end

$orb

*4*8*

1-4

13-16

29-32

9-12

5-8

21-24

25-28

17-20

$end