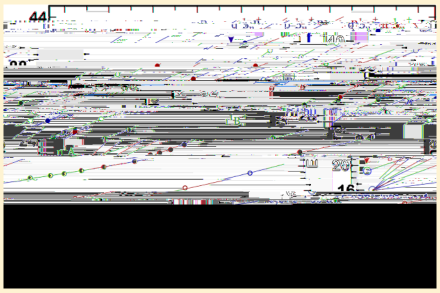
Energetics and Dynamics of the Low-Lying Electronic States of Constrained Polyenes: Implications for Infinite Polyenes

L. C ,*[†] M M E ,[‡,#] L. ,[§,#] A . - ,[†] C ,[||] ,[||] ,[⊥] H A. F ,*[‡] B *[‡,§]

[†]D C , B C , B , 04011,
[‡]D C , C , , C 06269-3060,
[§]D & C B , C , , C 06269-3125,
[||]D C , T , C , 02139,
[⊥] B , , B , Č B , C

Supporting Information

A A : - 5–23 , ( ). T fl $^1B^+$ $^1A^-$. T $^1B^+$ fi 15 900 ± 100 $^{-1}$. T $^1A^-$, , (~9000 $^{-1}$)



, . $\sim$1400 $^{-1}$

$1^1A^- \rightarrow 1^1B^+$ N = 7–11 (2). T

, fi

,$^{12-14}$

1^1A^- 2^1A^-

1^1A^- ,[25]

fi

-, $1^1B^+ \rightarrow n^1A^-$. A,

(~840 N = 7; ~1400 N = 19). T

1^1B^+ (90–180) AD

(T 1). T $1^1A^- \rightarrow 1^1B^+$ (0–0)

$1^1B^+ \rightarrow n^1A^-$

n^1A^-.

T

,,

- (2).

T

(~100×)

.[26]

. , 2^1A^- → 1^1B^+ [27,57,71]. T (7000–11 000 $^{-1}$) fi 2^1A^- → 1^1B^+ ((0–0)). 7. 77 fl N =

7 2^1A^- → 1^1B^+ 7. C 2^1A^- → 1^1B^+ (0–2) 1^1A^- → 1^1B^+ (0–2) N = 7 2^1A^- - 18 800 ± 90 $^{-1}$ (532). 6 (0–0) 77 $_1$ → $_0$ fl (19 900 $^{-1}$, 503). T 1000 $^{-1}$ 77 5 6 ( ). T N = 7 fl $_1$ → $_0$ (0–0), 77 2^1A^- → 1^1B^+ 7.

N = 7 fl , ~8500 $^{-1}$ N = 7–19 (0–2) 2^1A^- → 1^1B^+. C (0–2) 2^1A^- → 1^1B^+ 1^1A^- → 1^1B^+ 2^1A^- T 2. A 7, 1^1B^+ – 2^1A^- (5900 ± 200 $^{-1}$) N = 7–19 (5800 ± 300 $^{-1}$) N = 5, ( ). 1^1B^+–2^1A^- , , . ., ~4500 $^{-1}$

8,

,[93]

fi

N = 19 β- = 27809981.0951 39(924234439(21T /)-6116457006.7-1

. 2^1A^-
$2^1A^- \rightarrow 1^1B^+$
$2^1A^- \rightarrow n^1B^+$
2^1A^-
.

12 fi
- (N = 9–13) (N = 7–19). **T** fi 2^1A^-
(~2000 $^{-1}$) N. **T**
,
2^1A^-
-
, . $^{-1}$ = 4.5 $^{-1}$ =
6.1 N = 11 . C
(13)

N. -
, 2^1A^- .
T , β-
(N = 9–19). (**T** 4,
) 2^1A^- N = 15

(95) [illegible], [illegible].; C[illegible], [illegible].; [illegible], [illegible].; B[illegible], [illegible]. [illegible].; [illegible], B. [illegible].; [illegible], [illegible].; [illegible], [illegible]. A. J. Phys. Chem. A [illegible], 101, 2023−2032.

(96) [illegible], [illegible].; [illegible], [illegible].; [illegible], A.; [illegible], T.; [illegible], [illegible].; T[illegible], [illegible]. Chem. Phys. [illegible], 232, 161−174.

(97) A[illegible], [illegible]. [illegible].; [illegible], [illegible].; [illegible], D.; C[illegible], [illegible]. [illegible].; [illegible], [illegible]. [illegible].; [illegible], [illegible].; C[illegible], [illegible]. Chem. Phys. [illegible], 373, 115−121.

(98) B[illegible], [illegible]. [illegible].; [illegible], [illegible]. [illegible].; [illegible]-A[illegible], [illegible].; [illegible], [illegible].; [illegible], C. [illegible].; [illegible], [illegible]. Biochemistry [illegible], 41, 4127−4136.

(99) [illegible], [illegible]. [illegible].; [illegible], D. [illegible].; B[illegible], [illegible]. [illegible].; [illegible], [illegible]. D. J. Chem. Phys. [illegible], 91, 6691−6697.