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Synthesis and spectra of tris(4-dimethylaminophenyl)divinylenes

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Abstract

Condensation of 1,1-bis(4-dimethylaminophenyl)ethylene with substituted ketones in acetic anhydride in the pr sence of perchloric acid yielded NIR polymethine dyes. The VIS-NIR spectra of the dyes were measured and inte preted by the semiempirical AM1 method. The influence of molecular structure variations as well as of the electr density distribution, on the position of the peaks at longest wavelength has been studied. The results indicate that t additional (dimethylamino)phenyl bonded to C_5 atom might lead to λ_{max} increase. On the other hand, the use of su stituents with higher electron donor or acceptor character should not significantly affect the position of λ_{max}. © 19 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During recent years, a number of polymethine dyes absorbing in the NIR region have been synthesised [1]. Among them, di- and tri- aryl methanes and related compounds containing electron-donating substituents such as the amino group in the ortho or para position are of especial interest [2–4].

The VIS-NIR electron spectra characteristics of tris(4-dimethylaminophenyl)divinylenes are determined by the π-electron structure of the chromophores (divinylene chains, benzene rings), their mutual interactions, as well as by external influences. The changes in the geometry and electr structure of the dye molecule are related to bo the changes in spectral lines positions and the intensities. A quantum-chemical interpretation these spectra might be helpful in elucidation of t most important factors affecting the position intense NIR peaks.

The geometry of a molecule may be describ by interatomic distances, bond angles and dihedr angles. The electron structure of a molecule usually explained in terms of atomic charges a bond indices [5]. For large molecules, howeve such a description is too complicated and uncle Consequently, some collective characteristics mu be introduced. Statistical characteristics, such arithmetic mean values ($\bar{\chi}$) and root mean squa deviations (σ) [see Eq. (1)] are usually applied bond distances, atomic charges and bond indic

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over the carbon skeleton of individual chromophores [6,7].

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(\chi_i - \bar{\chi})^2}{n}} \qquad (1)$$

In addition, deviations from planarity are important for the chromophore structure (perturbations of planar π-bond framework).

In this paper, a series of simple 1,1,5-tris(4-dimethylaminophenyl)-divinylenes has been synthesised. Their VIS-NIR electron spectra have been measured and interpreted on the basis of mutual chromophores interaction and its relationship to the geometry and electron structure (its variations being modelled by various total charges of the molecule). For comparison, simpler compounds like (dimethylamino)benzene and 1,5-bis(4-dimethylaminophenyl) divinylene carbenium were also studied in the same way.

2. Results and discussion

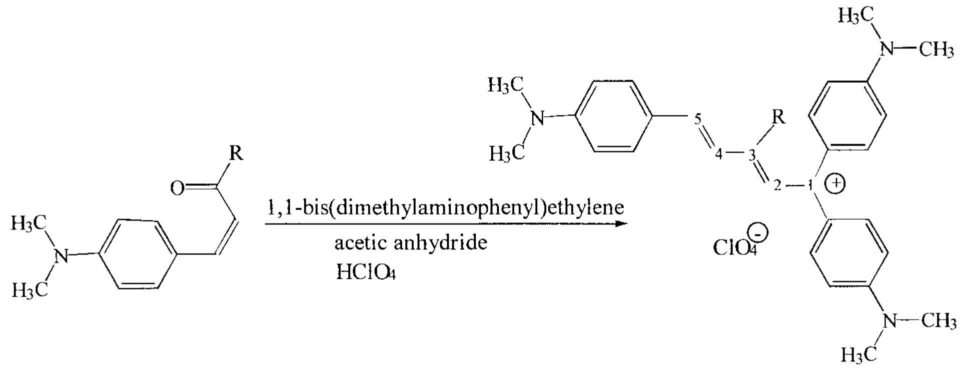
The synthesis of triaryl polymethine dyes by condensing 1,1-bis(4-dimethylaminophenyl)ethylene with substituted ketones in acetic anhydride in the presence of perchloric acid is shown in Scheme 1.

The ketones, i.e. 4-(dimethylamino)benzalacetone, 4-(dimethylamino)chalcone, 1-(4-dimethylaminophenyl)-1-penten-3-one and 4,4′-bis(dimethyl amino) benzalacetone, were prepared by condensation of 4-(dimethylamino) benzaldehyde with ketones (acetone, ethylmethylketone and acetophenone) in aqueous ethanol solution in the presence of NaOH. 1,1-Bis(4-dimethylaminophenyl)ethylene used was obtained from Michler's ketone by Grignard reaction with methylmagnesium iodide in diethylether. The dyes C–F were prepared by the reaction of ketones with 1,1-bis(4-dimethylaminophenyl)ethylene. Selected experimental characteristics of the dyes under study are presented in Table 1 (for atom numbering see Scheme 1).

The most intense wavelengths values (λ_{max})
well as the maximal calculated wavelengths valu
(λ_m) of the systems under study are presented
Table 2. The geometry of the B1a (B1b) system
obtained from the B1 system by setting sing
(both) benzene ring(s) perpendicular to the a
phatic chain plane (see Table 3). Similarly, t
C1a, C1b and C1c systems correspond to C1 ge
metry with single, two and three benzene rin
being perpendicular to the aliphatic chain pla
(see Table 3). The B1i, B1j and B1k systems mim
the interaction of C1 with solvent molecules. Th
structures are practically identical with that of C
and these are not, therefore, presented in t
tables. The C1h system originates in the C1 syste
with a single proton H^+ bonded to the mo
negative C_2 atom. Analogously, C1m and C
systems originate in the C1 system with 3 H^+ an
1 H^+ bonded to N atoms. In Tables 3, 4 and 6, t
rings bonded to C_1 are presented before the
bonded one in every table cell. In the Tables 6 an
7, the data presented in parentheses correspond
extended divinylene chains, including addition
chain-to-(dimethylamino)phenyl bonds.

The calculated (λ_{max}) values (B1, C1, D1,
and F1 systems) exhibit a systematic shift towar
lower wavelengths in comparison with the expe
mental data (Tables 1 and 2). This may
explained by neglecting all external interactions
isolated model systems. Higher wavelength valu
may be obtained by the dye molecule (ion) char
variation, but the intensity of the maximal wav
length (λ_m) decreases significantly in such syste
(Table 2). Our results indicate that the bo
lengths increase with the positive charge of the d
for all chromophores, but this may not hold f
their standard deviations and for inter-chrom
phore bonds (Tables 4–7). The reverse trend hol
for bond order values. Mean atomic charges da
indicate a relatively uniform distribution of t
additional charges among individual chrom
phores.

Our results indicate the key role of chrom
phore planarity in the dyes (Table 3). The (dim
thylamino)phenyl rings bonded to the same
atom cannot be co-planar with the pentamethi
chain (their deviations depend on the molecu
charge) and this leads to the (λ_{max}) increa



Scheme 1.

Table 1
Selected experimental characteristics of the dyes under study

Dye	Compd	M.W.	Yield (%)	λ_{max} (nm)
B	1,5-Bis(4-dimethylaminophenyl) divinylene carbenium perchlorate			783
	1,1,5-Tris(4-dimethylaminophenyl)-3-R-divinylene carbenium perchlorates			
C	R = –CH_3	552.111	40	627, 690, 8
D	R = –CH_2CH_3	566.138	45	578, 615, 8
E	R = –phenyl	614.182	60	639, 692, 8
F	R = –CH = CH–Ph(CH_3)$_2$	683.288	53	629, 690, 8

However, their perpendicularity causes the decrease of (λ_{max}) (compare C1, C1b and C1c systems). On the other hand, the perpendicularity of the single (dimethylamino)phenyl ring bonded to C_5 atom (B1a and C1a systems) increases (λ_{max}). All these deformations cause significant changes in the electronic structure of individual chromophores (Tables 4–7). From this point of view the additional (dimethylamino)phenyl bonded to C_5 might be promising for (λ_{max}) increase.

The highest (λ_{max}) values are obtained for the highest similarity of all statistical parameters of the benzene rings with the aliphatic divinylene chains and extended divinylene chains including additional chain-to-phenyl bonds (Tables 2–7). This also explains the increase of (λ_{max}) values for perpendicular benzene rings in comparison with B1 and C1 systems. This similarity condition seems to be more important than the maximal planarity condition.

The symmetrical influence of solvent molecules causes little increase of (λ_{max}) due to interactions of the van der Waals type, independent of the s vent molecule (Table 2). The decrease of (λ_{m} values with protonation of the dye molecule is agreement with experimental condition of apro solvents for all the above mentioned NIR dy (Tables 2,6 and 7).

The small changes of (λ_{max}) with different substituents (Tables 1,2,6 and 7) may be explain by the small changes in the electronic structure the (dimethylamino)phenyl chromophores (despi significant changes of the divinylene chain system From this point of view, the use of substituen with higher electron donor or acceptor charact might not lead to (λ_{max}) increase.

Finally, it must be mentioned that our calcul tions are related to isolated systems, and are n capable to account for (λ_{max}) values shift due interactions with real solvents. These might deduced by analogy with the similar chang caused by ionisation and/or deformation of t dye molecule. As the real B and C systems a paramagnetic, a positive charge of +1 may

Table 2
The most intense wavelengths λ_{max} and maximal λ_m values in VIS-NIR spectra of the systems under study (oscillator strength valu are in parentheses)

Compd	System	Charge	λ_{max} (nm)	λ_m (nm
(Dimethylamino)benzene	A0	0	326 (0.1)	335 (0.0
	A1	1	432 (0.1), 389 (0.3)	832 (0.0
1,5-Bis(4-dimethylaminophenyl) divinylene carbenium	B0	0	504 (0.1), 395 (0.2)	1027 (0.0
	B1	1	659 (1.9), 368 (0.2)	659 (1.9
	B2	2	1068 (0.1), 588 (0.4)	1068 (0.1
	B3	3	630 (2.4), 325 (0.2)	630 (2.4
	B1a	1	900 (1.1), 432 (0.4) 382 (0.1), 317 (0.1)	900 (1.1
	B1b	1	791 (1.0), 372 (0.1) 337 (0.4), 320 (0.1)	791 (1.0
B1 + NH_3 (0.48 nm from N)	B1i	1	653 (1.8), 366 (0.2)	653 (1.8
B1 + 2 NH_3 (0.48 nm from N)	B1j	1	655 (1.9), 367 (0.2)	655 (1.9
B1 + 2 CH_3OH (0.44 nm from N)	B1k	1	655 (1.9), 367 (0.2)	655 (1.9
1,1,5-tris(4-dimethylaminophenyl)-3-R- divinylene carbenium R = –CH_3	C0	0	432 (0.6), 414 (0.8) 323 (0.2)	668 (0.0
	C1	1	604 (1.3), 500 (0.8)	604 (1.3
	C2	2	537 (0.2), 508 (1.0) 426 (1.2), 329 (0.1)	738 (0.6
	C3	3	692 (1.6), 545 (1.1)	1450 (0.2
	C1a	1	744 (0.8), 489 (0.8) 415 (0.2), 316 (0.1)	744 (0.8
	C1b	1	540 (1.4), 342 (0.4)	664 (0.0
	C1c	1	741 (0.3), 734 (0.5) 343 (0.5), 310 (0.1)	741 (0.3
C1 + H^+ (bonded to C_2 atom)	C1h	2	545 (1.2), 429 (1.7)	545 (1.2
C1 + 3H^+ (bonded to N atoms)	C1m	4	475 (1.4), 314 (0.1)	475 (1.4
C1 + H^+ (bonded to N atom)	C1n	2	535 (1.1), 404 (1.0) 319 (0.2)	535 (1.1
R = –CH_2CH_3	D1	1	595 (1.2), 501 (0.8) 360 (0.2), 333 (0.1)	595 (1.2
	D2	2	696 (0.2), 531 (0.1) 498 (0.2), 492 (0.8)	902 (0.0
R = –phenyl	E1	1	573 (1.2), 475 (0.8) 381 (0.3), 320 (0.1)	573 (1.2
	E2	2	539 (0.1), 507 (1.0) 407 (1.7), 334 (0.1)	717 (0.0
R = –CH = CH–Ph	F1	1	584 (1.4), 498 (0.1) 453 (0.7)	584 (1.4
	F2	2	543 (0.2), 485 (0.8) 458 (0.6), 446 (0.9)	742 (0.0

assumed for their cations in solution. Consequently, (λ_{max}) should be shifted towards higher values (see B1j and B1k systems in Table 2). This is analogous to positive charge transfer to the benzene rings (caused by the solvent permittivity) and/or their torsion (caused by steric effects of the solvent).

3. Experimental

3.1. General

VIS-NIR spectra were recorded using a dio array fibre optic spectrometer (Ocean Optics S100

Table 3
Deviations from planarity in the systems under study

System	(C–C–C)$_{\text{phen}}$–N	(C–C)$_{\text{phen}}$–N–C$_{\text{met}}$	(C–C–C)$_{\text{phen}}$–C$_{\text{chain}}$	(C–C)$_{\text{phen}}$–(C–C)$_{\text{chain}}$	(C–C–C–C)$_{\text{chain}}$
A0	4	20	–	–	–
A1	0	1	–	–	–
B0	4, 4	19, 19	0, 0	1, 3	0
B1	0, 0	0, 0	0, 0	0, 0	0
B2	0, 0	0, 0	0, 0	0, 0	0
B3	0, 0	0, 0	0, 0	0, 0	0
B1a	see B1	see B1	see B1	90, 0	see B1
B1b	see B1	see B1	see B1	90, 90	see B1
C0	4, 4, 4	20, 23, 20	4, 6, 0	39, 66, 1	23
C1	0, 0, 0	0, 0, 0	28, 31, 0	28, 32, 1	6
C2	1, 1, 0	2, 2, 1	79, 82, 0	25, 20, 0	0
C3	3, 2, 0	1, 1, 1	25, 28, 0	28, 33, 1	9
C1a	see C1	see C1	see C1	28, 32, 90	see C1
C1b	see C1	see C1	see C1	90, 90, 1	see C1
C1c	see C1	see C1	see C1	90, 90, 90	see C1
C1h	2, 1, 1	1, 0, 0	63, 66, 0	31, 21, 3	31
C1m	1, 1, 0	63, 62, 62	5, 6, 0	44, 78, 2	16
C1n	2, 1, 0	1, 1, 62	59, 62, 6	24, 57, 6	0
D1	1, 0, 1	1, 0, 1	36, 39, 0	28, 30, 1	7
D2	1, 0, 0	1, 0, 1	3, 2, 1	27, 86, 0	0
E1	1, 0, 1	2, 1, 1	32, 36, 0	30, 28, 4	8
E2	1, 1, 0	2, 1, 1	79, 83, 0	25, 22, 0	0
F1	0, 1, 0	1, 1, 0	27, 31, 0	26, 38, 1	5
F2	2, 0, 0	4, 2, 3	45, 49, 0	24, 26, 7	3

Ethyl orthoformate, ethylmethylketone, acetophenone, 4-(*N*,*N*-dimethylamino) benzaldehyde and Michler's ketone were supplied by Aldrich. All chemicals were of reagent grade and used without further purification unless otherwise specified.

The ketones, i.e. 4-(dimethylamino)benzalacetone, 4-(dimethylamino)chalcone, 1-(4-dimethylaminophenyl)-1-penten-3-one and 4,4′-bis(dimethyl amino) benzalacetone, were synthesised by established methods [8]. 1,5-bis(4-dimethylaminophenyl) divinylene carbenium perchlorate was prepared by reduction of 4,4′-bis(4-dimethylamino) benzalacetone [9].

3.2. Preparation of 1,1-bis(4-dimethylaminophenyl)ethylene [10]

A suspension of methylmagnesium iodide (prepared from 7.29 g of Mg and 18.58 ml CH_3I) in 75 ml of diethyl ether under argon was treated with 19.2 g of Michler's ketone, dissolved 225 ml of hot benzene. After heating under reflu for 6 hr., the mixture was chilled and treated wi saturated ammonium chloride solution. The cru product was fractionally crystallised from ethan to give 7.5 g (60%) of 1,1-bis(4-dimethylamin phenyl)ethylene, m.p. = 122–124°C. The materi balance indicates that a by-product is al obtained, i.e. 2,2-bis-(4-dimethylaminophenyl)-pr pane, m.p. = 60–75°C.

3.3. Preparation of 1,1,5-tris-(4-dimethylamino-phenyl)-3-R-divinylene carbenium perchlorates

A mixture of 1.0 g (3.75 mmol) of 1,1-bis(dimethylaminophenyl)ethylene, 3.75 mmol of t appropriate ketone and 10 ml of acetic anhydri was treated with a solution of 0.26 g (1.9 mmol) 71% perchloric acid in 10 ml of acetic anhydric The blue mixture was heated on a steam bath f 70 min with occasional swirling. After coolin

Table 4
Statistical characteristics of benzene rings in (dimethylamino)benzene and 1,5-bis(4-dimethylaminophenyl) divinylene carbeni cations

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
A0	1.4000	0.0117	−0.1112	0.0915	1.3938	0.0386
A1	1.4112	0.0246	−0.062	0.0715	1.3170	0.1488
B0	1.4027	0.0113	−0.0905	0.0892	1.3678	0.0688
	1.4028	0.0113	−0.0908	0.0894	1.3678	0.0686
B1	1.4088	0.0254	−0.0802	0.1551	1.3352	0.1581
	1.4088	0.0254	−0.0802	0.1551	1.3353	0.1580
B2	1.4202	0.0458	−0.0560	0.1440	1.2995	0.2981
	1.4133	0.0330	−0.0510	0.0948	1.3183	0.2109
B3	1.4255	0.0542	−0.0272	0.1056	1.2933	0.3513
	1.4245	0.0563	−0.0273	0.1053	1.2933	0.3513
B1a	see B1	see B1	−0.0807	0.1385	1.3437	0.1301
			−0.0785	0.1539	1.3312	0.1683
B1b	see B1	see B1	−0.0742	0.1485	1.3312	0.1698
			−0.0982	0.1423	1.3628	0.0909

Table 5
Statistical characteristics of the aliphatic chains in 1,5-bis(4-dimethylamino-phenyl) divinylene carbenium cations (values parentheses correspond to extended chains including chain-to-phenyl bonds)

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
B0	1.3855	0.0225	−0.1268	0.0089	1.4240	0.1310
	(1.4053)	(0.0335)			(1.1342)	(0.5310)
B1	1.3898	0.0073	−0.0582	0.1803	1.3900	0.0510
	(1.3972)	(0.0120)			(1.3372)	(0.0855)
B2	1.3998	0.0304	−0.0644	0.0536	1.3815	0.2688
	(1.3997)	(0.0445)			(1.3822)	(0.2495)
B3	1.4070	0.0150	−0.0528	0.1401	1.3060	0.1010
	(1.3997)	(0.0205)			(1.3927)	(0.1477)
B1a	see B1	see B1	−0.0509	0.1482	1.3782	0.0483
					(1.3185)	(0.0993)
B1b	see B1	see B1	−0.0464	0.1682	1.4070	0.1616
					(1.3189)	(0.1972)

ether was added, the product collected, washed with acetic acid followed by ether, and dried under vacuum.

4. Quantum-chemical calculations

The standard semiempirical AM1 method of quantum chemistry (AMPAC program package) [11,12] has been used in order to find the optimal geometries of (dimethylamino)benzene, 1,5-bis(4-dimethylaminophenyl)divinylene carbenium a 1,1,5-tris(4-dimethylaminophenyl)-3-R-divinylen carbenium cations with various charges (s Table 1). All calculations were performed higher precision (keyword PRECISE) using t Davidon–Fletcher–Powell optimization procedu [13,14]. The electronic structure characteristics a evaluated in terms of charges of individual ato and bond indices of individual bonds [5,15]. T electron spectra lines of the systems under stu were calculated using the single excited confi

Table 6
Statistical characteristics of (dimethylamino)benzene rings in 1,1,5-tris(4-dimethylaminophenyl)-3-R-divinylene carbenium cations

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
C0	1.4022	0.0111	−0.0915	0.0887	1.3765	0.0532
	1.4025	0.0107	−0.0922	0.0889	1.3817	0.0445
	1.4025	0.0109	0.0913	0.0871	1.3702	0.0647
C1	1.4077	0.0228	−0.0940	0.1431	1.3417	0.1406
	1.4070	0.0218	−0.0895	0.1538	1.3453	0.1294
	1.4053	0.0186	−0.0868	0.1402	1.3555	0.1051
C2	1.4117	0.0307	−0.0783	0.1622	1.3233	0.2007
	1.4108	0.0297	−0.0795	0.1614	1.3255	0.1936
	1.4140	0.0336	−0.0503	0.0990	1.3202	0.2105
C3	1.4155	0.0384	−0.0318	0.1041	1.3088	0.2466
	1.4140	0.0356	−0.0258	0.1044	1.3188	0.2314
	1.4245	0.0533	−0.0702	0.1049	1.2973	0.3258
C1a	see C1	see C1	−0.0847	0.1576	1.3397	0.1466
			−0.0898	0.1549	1.3428	0.1367
			−0.0898	0.1244	1.3633	0.0839
C1b	see C1	see C1	−0.0970	0.1427	1.3633	0.0888
			−0.0988	0.1404	1.3633	0.0858
			−0.0828	0.1503	1.346	0.1299
C1c	see C1	see C1	−0.0973	0.1447	1.3622	0.0908
			−0.0993	0.1428	1.3620	0.0879
			−0.0862	0.1359	1.3542	0.1069
C1h	1.4117	0.0313	−0.0802	0.1615	1.3228	0.2029
	1.4110	0.0299	−0.0827	0.1617	1.3258	0.1919
	1.4178	0.0425	−0.0632	0.1583	1.3037	0.2831
C1m	1.4013	0.0058	−0.0802	0.0120	1.3925	0.0286
	1.4012	0.0050	−0.0903	0.0044	1.3972	0.0219
	1.4037	0.0082	−0.0722	0.0447	1.3782	0.0514
C1n	1.4110	0.0299	−0.0795	0.1644	1.3253	0.1926
	1.4102	0.0279	−0.0822	0.1618	1.3297	0.1786
	1.3842	0.0356	−0.0868	0.0464	1.3885	0.0406
D1	1.4080	0.0237	−0.0850	0.1593	1.3400	0.1456
	1.4073	0.0220	−0.0885	0.1551	1.3437	0.1333
	1.4050	0.0184	−0.0877	0.1383	1.3573	0.1004
D2	1.4118	0.0311	−0.0680	0.1049	1.3313	0.1733
	1.4060	0.0178	−0.0813	0.1077	1.3533	0.1109
	1.4180	0.0415	−0.0628	0.1568	1.3053	0.2738
E1	1.4073	0.0227	−0.0868	0.1559	1.3420	0.1390
	1.4073	0.0223	−0.0845	0.1549	1.3425	0.1361
	1.4052	0.0184	−0.0878	0.1388	1.3575	0.0996
E2	1.4117	0.0302	−0.0778	0.1623	1.3240	0.1988
	1.4108	0.0290	−0.0815	0.1584	1.3302	0.1763
	1.4150	0.0348	−0.0535	0.1044	1.3188	0.2169
F1	1.4072	0.0219	−0.0860	0.1564	1.3445	0.1330
	1.4060	0.0197	−0.0895	0.1488	1.3513	0.1128
	1.4057	0.0191	−0.0867	0.1429	1.3545	0.1070
F2	1.4122	0.0313	−0.0778	0.1623	1.3240	0.1988
	1.4107	0.0275	−0.0815	0.1584	1.3302	0.1763
	1.4165	0.0383	−0.0535	0.1044	1.3188	0.2169

Table 7
Statistical characteristics of the aliphatic chains in 1,1,5-tris(4-dimethylaminophenyl)-3-R-divinylene carbenium cations (values parentheses correspond to extended chains including chain-to-phenyl bonds)

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
C0	1.3908	0.0294	−0.0924	0.0394	1.4162	0.1648
	(1.4201)	(0.0408)			(1.2570)	(0.2238)
C1	1.3980	0.0305	−0.1286	0.1821	1.3895	0.2104
	(1.4133)	(0.0291)			(1.2841)	(0.2010)
C2	1.4085	0.0557	−0.0278	0.1226	1.3698	0.3406
	(1.4124)	(0.0428)			(1.3197)	(0.2662)
C3	1.4147	0.0143	−0.1002	0.0436	1.3038	0.0895
	(1.4100)	(0.0205)			(1.3147)	(0.1247)
C1a	see C1	see C1	−0.0314	0.1963	1.3810	0.2272
					(1.2746)	(0.2147)
C1b	see C1	see C1	0.0126	0.2611	1.3998	0.1227
					(1.2519)	(0.1999)
C1c	see C1	see C1	0.0090	0.2482	1.3910	0.1253
					(1.2374)	(0.2030)
C1h	1.4450	0.0570	−0.0182	0.1568	1.2060	0.3074
	(1.4253)	(0.0503)			(1.2817)	(0.2618)
C1m	1.3978	0.0269	0.0150	0.2296	1.4130	0.1944
	(1.4250)	(0.0390)			(1.2526)	(0.2397)
C1n	1.4047	0.0563	−0.0390	0.1492	1.4158	0.3885
	(1.4144)	(0.0456)			(1.3207)	(0.3215)
D1	1.3988	0.0338	−0.1326	0.1794	1.3918	0.2343
	(1.4134)	(0.0307)			(1.2876)	(0.2154)
D2	1.4023	0.0390	−0.0264	0.1185	1.3845	0.2537
	(1.4147)	(0.0423)			(1.3044)	(0.2613)
E1	1.3993	0.0331	−0.0182	0.1568	1.3880	0.2282
	(1.4137)	(0.0301)			(1.2846)	(0.2108)
E2	1.4093	0.0559	−0.0102	0.1304	1.3578	0.2957
	(1.4129)	(0.0428)			(1.3100)	(0.2315)
F1	1.3978	0.0258	−0.0330	0.2371	1.3038	0.0895
	(1.4140)	(0.0272)			(1.2300)	(0.1098)
F2	1.4115	0.0501	−0.0102	0.1304	1.3578	0.2957
	(1.4131)	(0.0380)			(1.3100)	(0.2315)

uration interaction method with 163 (singlet states) or 162 configurations (doublet states) [16].

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