AN MNDO AND CNDO/S(S + DES CI) STUDY ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF A MODEL SQUARAINE DYE AND RELATED CYANINE

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The ground- and excited-state electronic structure of the highly polar squaraine dye bis(4-dimethylaminophenyl)squaraine, or 2,4-bis(4-dimethylaminophenyl)cyclobutadienediylium-1,3-diolate, is addressed using the MNDO and CNDO/S(S+DES CI) semi-empirical molecular orbital approximations. MNDO geometry optimizations indicate a distinct polyene-like single-double bondlength alternation. Such "quinoid" character is significantly enhanced when explicit solvent/solute interactions (complexation) were considered. The "quinoid" model yields $S_n \leftarrow S_0$ energy and transition intensity profiles in essential accord with the detailed UV/VIS solution-phase absorption spectrum above 2500 Å. Properties of the model squaraine are compared and contrasted to those of the underlying or "parent" straight-chain polymethine cyanine (CH₃)₂NCH(CH)₁₀N(CH₃)¹/₂. The intense long-wavelength transition of the squaraine is considerably less sensitive to correlation or configuration mixing than the corresponding cyanine transition. S₁ \leftarrow S₀ intramolecular charge-transfer character is discussed and referenced to solvent sensitive absorption properties of the model D⁺-A⁻ molecule *p*-nitroaniline (PNA).

1. Introduction

Certain dyes formed by 1,3-disubstitution of squaric acid have recently been found to fulfill materials requirements for a variety of device applications having commercial importance [1-5]. In accord with the nomenclature suggested by Schmidt [6], such dyes are named squaraines for the purposes of this work to emphasize the squaric acid parentage and proposed charge-separation characteristics.

Recent studies have concentrated on various properties of typical squaraines in the solid state where strong intermolecular interactions are indicated [7–10]. Although solid state interactions ultimately relate to the nature of the molecular

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electronic structure, many characteristics of the isolated or solution-phase species remain to be addressed. For example, bis(4-dimethylaminophenyl)squaraine (I) contains a highly polar and electron withdrawing central squaraine (C_4O_2) moiety disubstituted with strong electron donating dialkylaminophenyl groups. Such a symmetric " $D^+ \rightarrow A^- \leftarrow D^+$ "-like configuration is expected to lead to considerable intramolecular chargetransfer character in both the ground and excited states, in addition to supporting strong and complex solvation forces in solution. Experiment has recently shown, however, that I and closely related systems exhibit an extremely intense long-wavelength transition in solution ($\epsilon_{\text{max}} \approx 3.5 \times 10^5 \ell$ M^{-1} cm⁻¹ [5,7,9] whose position is relatively insensitive to variations in solvent polarity [9]. These observations suggest an excitation delocalized over the span of the molecule.

This paper discusses the results of semi-empirical molecular orbital calculations on the ground and excited states of I and related systems. Ground-state geometry optimizations were performed within the MNDO approximation, whereas excited states were calculated using the CNDO/ S(CI) approach. Emphasis is given to a description of ground-state conformational and solution-phase



Fig. 1. The UV/VIS absorption spectra of bis(4-dimethylaminophenyl)squaraine (I) (top panel) and bis(dimethylamino)undecamethine (II) perchlorate (bottom panel). The spectra of I were recorded on a Cary model 17D spectrometer using methylene chloride as solvent. A 25 cm path length cell was used due to low solubility, and balanced against solvent. The arrow at ≈ 5750 Å indicates a distinct low-intensity shoulder. The arrows above the dashed expanded higher-energy spectrum denote the five λ_{max} values in (chloroform) reported by Sprenger and Ziegenbein [14]. The single arrow under the dashed spectrum notes an additional distinct feature. The spectra of II (methylene dichloride) were constructed from the log(extinction coefficient) versus wavelength values given by Malhotra and Whiting [13]. The arrow at ≈ 6700 Å emphasizes a distinct low-intensity shoulder. The fwhm $(\Delta \tilde{\nu}_{1/2})$ of the long-wavelength transitions are given for comparison. The experimental oscillator strengths (f_E) were estimated in accord with the approximation of Suzuki [15] using the experimental $\Delta \tilde{\nu}_{1/2}$ values and ϵ_{max} of $3.5 \times 10^5 \ell M^{-1} cm^{-1}$ and $3.981 \times 10^5 \ell$ M⁻¹ cm⁻¹ for I and II, respectively.

spectroscopic properties. In accord with the composite molecule approach suggested by Fabian and co-workers [11,12], the electronic structure of I is addressed in terms of perturbations to the underlying symmetric polymethine cyanine framework. Indeed, important similarities in the spectroscopic properties of I and the "parent" bis(dimethylamino)undecamethine (II) closed-shell cation have been observed. The long-wavelength transition of the "parent" polymethine cyanine is comparably intense ($\epsilon_{\lambda=7330 \text{ \AA}} = 3.981 \times 10^5 \ell$ M^{-1} cm⁻¹) and appears in solution moderately red-shifted relative to that of I – $\Delta E \approx 0.282$ eV $(\lambda_{max} = 7330 \text{ versus } 6280 \text{ Å})$ [13] – see fig. 1. Also, the long-wavelength excitation of typical symmetric polymethine cyanines is likewise relatively insensitive to solvent polarity [12,16], although strong solvent coupling is unquestionably present in such formally charged systems.

In line with these similarities the present study reflects certain parallels between the electronic structures of the polymethine cyanine subchain and I. However, in contrast to the polymethines which have a tendency toward bondlength equalization along the chain, the squaraine model is found to have a distinctly "polyene"-like or single-double bondlength alternation scheme. Several solvation models are considered and shown to promote such a squaraine "quinoid" structure. Also, the intense long-wavelength $S_1 \leftarrow S_0$ transition of I is found to be significantly less sensitive to correlation or configuration mixing contributions than that of the parent polymethine cyanine.

2. Computational

The closed-shell spin-restricted MNDO procedure [17,18] was used as contained in the MOPAC series of programs [19] $\stackrel{*}{}$ to perform geometry optimizations. SCF convergence and energy minimization criterion were limited to the program default values assuming a single-determinant ground state. Solvation effects were directly included in the optimization cycle as set forth in MOPAC by placing + and - charge centers

^{*} This program was successfully run as received on a VAX 11/780.

("sparkles") at appropriate places opposite the molecule of interest.

Computations on relevant ground and excited states were also carried out within the CNDO/S molecular orbital approximation developed by Jaffé and co-workers [20,21] using the Nishimoto-Mataga two-center integral approximation [22]. Correlation contributions are examined by comparing results obtained by a configuration interaction between energy-selected singly excited (SECI) configurations [20,21] and singly + doubly excited terms (S + DECI) [23,24].

3. Ground-state properties

The MNDO optimized geometry for the bis(4dimethylaminophenyl)squaraine (I) free molecule is given in the upper panel of fig. 2. In addition to the imposed symmetry relationships noted in the caption to fig. 2, the dimethylaminophenyl groups were held as rigidly planar π -electron frameworks. Rotation about the squaraine-phenyl bonds was allowed. Optimization of all dihedral angles within the squaraine moiety was carried out with the requirement that variations from planarity be



BIS (4-DIMETHYLAMINOPHENYL) SQUARAINE

Fig. 2. The MNDO optimized geometry for the bis(4-dimethylaminophenyl)squaraine (I) free molecule (upper panel). The resulting π and $\sigma + \pi$ ground-state atomic charge densities are given in the lower panel. Bondlengths and bond angles in parentheses indicate values imposed by program option symmetry constraints. Additional symmetry restrictions and considerations of planarity are discussed in the text. An idealized planar "aromatic" π -electron framework was used as an input geometry. Initial bondlengths were: squaraine C-C = 1.40 Å; C-O = 1.26 Å; squaraine-phenyl, N-CH₃ and phenyl-N linkages = 1.45 Å; phenyl C-C = 1.40 Å; and C-H = 1.09 Å.



BIS (4-AMINOPHENYL) SQUARAINE

Fig. 3. The MNDO optimized geometry, and π and $\sigma + \pi$ ground-state atomic charge densities for the bis(4-aminophenyl)squaraine (III) free molecule – see caption to fig. 2.

symmetric about the long and short in-plane molecular axes. The final dihedral angles deviated from the initial planar values by $\leq 0.1^{\circ}$.

The planar final geometry reflects the crystal structures of methyl, hydroxyl and methoxy substituted aminophenyl- and phenyl-squaraines [5,8, 9,25] $\stackrel{*}{\sim}$. A "relaxation" from the ideal aromatic input structure to a geometry with distinct "quinoid" or alternating bondlength characteristics is indicated. The MNDO squaraine C–O and C–C bondlengths of 1.223 and 1.485 Å, respectively, are in reasonably good agreement with experiment [25], and MINDO/3 and QCFF computations [26] on related systems (see below). Charge density variations are as anticipated: namely, the oxygen atoms attract a large excess electron density, and the four-membered carbon moiety is largely electron deficient. Slightly more than 1/4of the excess π -electron density on the oxygens is derived from the electron donating dimethylaminophenyl groups.

The influence on the computational results due to replacing the methyl groups with hydrogens is

^{*} Ref. [25] contains a redetermination of the structure of bis(methoxyphenyl)squaraine - C₁₈H₁₄O₄. After this work was accepted for publication we became aware of an earlier structure determination of bis(methoxyphenyl)squaraine by Farnum et al. [47]. The authors stressed the "quinoid" nature of the compound.



Fig. 4. Isopotential energy plots in the space surrounding bis(aminophenyl)squaraine (III) for the indicated planes. Atomic charge densities were used in accord with approximation II of Giessner-Prettre and Pullman [31] to construct the maps.

shown in fig. 3. The dominant structural change is a shortening of the nitrogen-phenyl bondlength from 1.404 to 1.377 Å. The relevant charge densities are relatively unperturbed by methyl \rightarrow hydrogen replacement. Bis(aminophenyl)squaraine (III) can thus be used as a useful model compound

to address more complex properties of the dimethylamino analog.

The (aminophenyl)squaraines of figs. 2 and 3 are already largely bipolarized in the free molecule due to charge transfer between spatially distant fragments. In terms of simple electrostatics it is expected that areas or centers of the molecule which are negatively charged will attract positive regions of the solvent, whereas negative solvent fragments will approach the positive solute centers [27,28]. Such a macroscopic reaction-field approach to solvent interactions has been widely successful in the interpretation of spectroscopic properties of bipolar molecules. Solvation shifts as a function of solvent polarity have been used to establish intramolecular charge-transfer character in the ground and excited states of such systems [27-30]. Isopotential energy diagrams in the space surrounding bis(aminophenyl)squaraine are given in fig. 4. These plots reveal that around the center of the molecule the large net charge on the oxygen atoms completely overshadows the positive contributions from the squaraine fragment carbon centers. Fig. 4 thus suggests the formation of a "positively charged" solvent cage encapsulating the squaraine fragment. The cumulative positive terms arising from the aminophenyl groups likewise overshadow the relatively large negative contributions from the nitrogens. The donor groups are encapsulated by negatively charged solvent



BIS (4-AMINOPHENYL) SQUARAINE

Fig. 5. The MNDO optimized geometry, and π and $\sigma + \pi$ ground-state atomic charge densities for the bis(4-aminophenyl)squaraine (III) + "sparkles" supermolecule – see the caption to fig. 2 and discussion in the text.

cages. Such interactions are expected to induce an even greater $D^+ - A^- - D^+$ ground-state character in order to arrive at the strongest solvent/solute bonding condition. Dahne, for example, has emphasized the characteristically high π -electron polarizability of polymethine chains [16]. Attempts have been made to put the nature of solvent interactions on a qualitative level by including terms directly in the quantum-mechanical hamiltonian to reflect appropriate electronic structure perturbations. The MOPAC series of programs allow simulation of solvent interactions through the incorporation of "sparkles" directly in the geometry optimization procedure. "Sparkles" are essentially unpolarizable ions whose bondlengths and bond angles, relative to a reference "solute" center, can be optimized in response to structural and/or electronic changes induced in the "solute". Fig. 5 shows the results of a geometry optimization on III with (+) "sparkles" (+1.0)e) placed opposite the oxygen atoms and (-)"sparkles" $(-1.0 \ e)$ placed opposite the amino groups. "Sparkles" yield an enhanced "quinoid"

structure for III which is 4.627 eV more stable than the III free molecule. No attempt was made to optimize geometries using multiply charged "sparkles".

The MNDO phenyl and squaraine fragment bondlengths optimized with the "sparkles" are in relatively good agreement with the crystal structure values found for corresponding bonds in bis(methoxyphenyl)squaraine [25]: C-O = 1.240 Å versus 1.232 Å observed; C-C (squaraine) = 1.478 Å, versus 1.464 Å observed; C-C (squarainephenyl linkage) = 1.410 Å, versus 1.407 Å observed; $C_{\alpha}-C_{\beta}$ (phenyl) = 1.444 Å, versus 1.407 Å observed; and, $C_{\beta}-C_{\gamma}$ (phenyl) = 1.380 Å, versus 1.372 Å observed. With the exception of the $C_{\alpha}-C_{\beta}$ (phenyl) bonds, the "sparkles" induce bond shortening or lengthening, relative to the "free molecule" (fig. 3), which promotes the "experimental" or "quinoid"-like structure. Methoxy substitution may selectively reduce the C_{α} - C_{β} (phenyl) bondlength. The crystal structure of a hydroxyl analog of I and II reveals an intermolecular packing consistent with the placement of the (+) and



BIS (DIMETHYLAMINO) UNDECAMETHINE

Fig. 6. The MNDO optimized geometry, and π and $\sigma + \pi$ ground-state atomic charge densities for the bis(dimethylamino)undecamethine (II) closed-shell cation (free molecule). MOPAC program input constraints were applied to yield a rigidly planar π -electron framework, and bond angle and bondlength symmetrization about the center of the molecule.

(-) "sparkles" in the geometry optimization procedure [9].

Experimentally bis(amino)squaraines do not exhibit the strong and distinct IR absorptions characteristic of conjugated C-C bonding interactions [32]. This has been tentatively attributed to intramolecular bond delocalization involving the four-membered ring [6]. These observations are consistent with both calculated C-C bond distances (1.478 Å) within the ring, and the highly positive carbon π -charge densities. Although the calculated C-O separation of 1.240 Å parallels the bondlength of an idealized carbon-oxygen double bond of ≈ 1.22 Å, absorptions expected of the carbonyl group are likewise absent in the IR spectrum [32]. An orthogonalized CNDO Cohen bond order analysis [33,34] on the "quinoid" form of III (see fig. 5) without "sparkles" gave a C-O bond order of 1.884. This is significantly less than the idealized double bond value of 2.0, and the comparison computational results of 2.220 and 2.073 for the C-O bond in formaldehyde and coumarine, respectively [34]. A C-C bond order for the fourmembered ring of 1.372 was obtained, compared to 1.812 for aromatic benzene [34]. It is probable that the polar environment ("sparkles") skews the C-O charge densities such that the bonding contributions are further reduced. Intramolecular electrostatic attractions, therefore, appear to considerably influence the final C-O separation.

In addition to enhancement of bondlength alternation, "sparkles" significantly increase the $D^+-A^--D^+$ ground-state charge separation (fig. 5, lower panel). Although the CNDO/S approximation to the total energy is well known to often yield unreliable energy minima as a function of bond rotation, the technique has been found useful when considering variations in bondlengths of a planar structure [35]. In accord with the MNDO results, the CNDO/S method indicates the "quinoid" structure to be considerably more stable than the model "aromatic" system used as input for geometry optimization.

The result of a MNDO geometry optimization on the bis(dimethylamino)undecamethine closedshell radical cation (II), performed without "sparkles", is given in fig. 6. Although the calculated values are not in exact agreement with comparion experimental results, MNDO does correctly reflect the tendency toward C-C bondlength equalization [14]. In contrast to the slight C-C bondlength alternation suggested in fig. 6, the MINDO/3 approximation yielded 1.40 Å for all C-C bondlengths in bis(amino)heptamethine [36]. Fabian and Mehlhorn [36] noted that the experimentally asymmetric bondlengths and bond angles found in straight-chain cyanines are likely due to a non-symmetric cation/counterion arrangement. Squaraines I and III have large ground-state charge density differences along the chain charateristic of II, although O and C-O substitution to form the squaraine disrupts charge density alternation at the center of the carbon chain.

4. Excited-state properties

A geometry for I suitable for the calculation of excited-state properties, assuming an enhanced "quinoid"-like character arising from the probable solvent interactions ("sparkles") discussed above, was constructed from the optimized fragment structures given in figs. 2, 3 and 5. Coordinates for the bis(diphenyl)squaraine fragment were taken from fig. 5. The $(CH_3)_2N-C(phenyl)$ bondlengths were taken from fig. 2 and reduced by the difference in $H_2N-C(phenyl)$ bondlengths given in figs. 3 and 5. Fig. 7 compares the calculated $S_n \leftarrow S_0$ spectrum with experiment and the results of a comparison CNDO/S(CI) computation on an "aromatic" model reflecting polymethine bondlength equalization.

Although the "aromatic"-model long-wavelength excitation ($S_2 \leftarrow S_0$) is considerably higher in energy than experiment (> 0.50 eV), the calculated oscillator strength (f_T) is already less than experiment (prior to adjustment for probable reduction by higher-lying configuration interaction – see below). The "aromatic" model also fails to place any excitations between 3300 and 4500 Å where at least three peak maxima are observed. Excited-state computations on the MNDO model yield: (1) an intense long-wavelength transition in good agreement with experiment ($\Delta E = 0.067$ eV and $f_T = 1.2640$ versus $f_E \approx 1.234$); (2) transition energies and relative intensities between 3300 and



Fig. 7. Comparison of the CNDO/S(CI) UV/VIS excitation profiles of I (MNDO optimized geometry (center panel) and the model "aromatic" structure (bottom panel)) with the detailed experimental spectrum. The CI selections are noted in the diagram. The calculated transition energies have been *uniformly* red-shifted relative to the multiconfigurational CI ground state to account for additional correlation due to quadruple excitations as suggested by Schulten et al. [37] – see discussion in text. These shifts are 0.3016 eV for the MNDO structure and 0.1398 eV for the "aromatic" model. The energy and number of "negligibly" weak transitions are indicated below the respective base lines. The percentages of doubly excited character of selected excited states are noted in the center panel. As in fig. 1 the experimental absorption features

4500 Å which correlate with experimental features b, c and d; (3) three moderately intense transitions at ≈ 2500 Å with $f_T \ge 0.060$ which collectively reflect feature f, and; (4) a transition at ≈ 2900 Å with $f_T \approx 0.05$ which tentatively correlates with absorption e. The experimental half-width of feature f is $\approx 4.32 \times 10^3$ cm⁻¹, or about five times broader than the long-wavelength transition. Approximate curve resolution yields an optical density ratio of ≈ 0.132 between absorptions f and a. This translates to $\epsilon(f) \approx 4.63 \times 10^4 \ell$ M cm⁻¹ and $f_E(f) \approx 0.864$ – see caption to fig. 1. The oscillator strength of the three transitions calculated between 2400 and 2875 Å sum to $f_T = 0.6558$.

Calculated properties of the excited states contributing to the spectral assignments are given in table 1. The wavefunction character is reflected in terms of the molecular orbitals given in fig. 8. The two transitions with $f_{\rm T} \ge 0.200$ at ≈ 2500 Å (the $3^{1}B_{2}(\pi \rightarrow \pi^{*})$ and $3^{1}B_{1}(\pi \rightarrow \pi^{*})$ transitions of table 1), and which correlate with absorption f in fig. 7, are relatively independent of variations in geometry and the amount of CI (single or single + double excitations). Table 1 and fig. 8 indicate that these transitions are 80-90% singly excited and involve orbitals which have distinct squaraine character. The assignment of these transitions to absorption f is further suggested by the observation that the "parent" cyanine (II) has no experimental absorption of comparable relative intensity at ≈ 2500 Å – see fig. 1.

Comparison CNDO/S(CI) computations were performed on the "parent" cyanine subchain, $(CH_3)_2N-(CH)_{11}-N(CH_3)_2^{\oplus}$, to establish a basis for rationalization of "cyanine character" in the excited states of I. Fig. 9 shows that a "limited" 200×200 CI expansion is clearly insufficient to yield a theoretical agreement with experiment comparable to that obtained for I. S₁ is significantly above the experimental energy, and the

a-f are those reported by Sprenger and Ziegenbein [14] as distinct maxima. The shaded area emphasizes the range of \approx 3200-4500 Å for ease of comparison of experimental and calculated features. The arrows in the lower panels note the wavelengths of the one-electron highest-occupied (HOMO) to lowest unoccupied (LUMO) promotion (1E), and the calculated intensely absorbing final-state referenced to the S+DES CI correlated ground state.

Table 1

Upper part: The CNDO/S (CI) singlet state properties of interest for l obtained from the constructed MNDO geometry optimized fragments as noted in the text. Appropriate experimental values are given for comparison. Experimental oscillator strengths (f_E) were approximated as described in the caption to fig. 1 and in the text. The calculated $S_n \leftarrow S_0$ energies have been uniformly red-shifted 0.3016 eV relative to the energy of the multiconfigurational CI ground state to account for additional selective correlation due to quadruple excitations as outlined by Schulten and co-workers [37]. Lower part: Tabulation of the leading elements of the wavefunctions for the states of the upper part of the table. The wavefunctions are given in terms of spin-adapted Slater determinants involving single (0, j | | k, 0), or double (i, j | | k, l) orbital replacements relative to the SCF ground state (0, 0 | | 0, 0). The percent doubly excited character (% DES) and the percent of the total wavefunction contained in the terms tabulated are indicated

State		Energy (eV)	λ (Å)		f _T	f _E
			theor.	exp.		
$(1)^{1}A_{1}(g)$	s)	0.0	_	_	-	
$(2) 1^{1} \mathbf{B}_{2}($	(π*←π)	2.033	6072	6280(a)	1.2640	1.2340
$(4) 1^{1}A_{1}($	[π* ← σ]	2.875	4294	4150(b)	0.0018	0.0005
$(5) 2^{1}B_{2}($	(π*←π)	2.985	4136	3920(c)	0.0345	0.0310
$(7) 1^{1} B_{1}$	π*←π)	3.443	3586	3700(d)	0.0367	0.0520
$(9) 2^{1}B_{1}($	(π* ← π)	4.265	2894	3050(e)	0.0533	0.0460
$(11) 3^{1}B_{2}($	(π*←π)	4.295	2874)		0.2594)	
(13) 3 ¹ B ₁	[*] π*←π)	4.784	2580	2630(f)	0.3318	0.8640
$(16) 4^{1}B_{2}$	(π* ← π)	5.027	2456)		0.0646)	
state	wavefunc	tion			Ψ_{T}	DES
					(%)	(%)
(1)	$-0.9512(0, 0 0, 0) + 0.2232(61, 61 62, 62) + \dots$				95.50	9.01
(2)	- 0.9536($0, 61 \ 62, 0) + 0.1565$	(61, 61 62, 63) + 0.1	1014(61, 61 62, 70) +	94.40	7.71
(4)	0.9547(0, 57 62, 0) + 0.1966	$(0, 57 \parallel 66, 0) - 0.111$	35(57, 61 62, 63) +	96.30	4.20
(5)	- 0.5020($0, 59 \parallel 62, 0) + 0.5217$	$(0, 61 \ 66, 0) + 0.453$	51(61, 61 62, 63) +	73.10	46.17
(7)	0.7682($0, 61 \ 64, 0 + 0.3632 \ $	(0, 56 62, 0) + 0.379	93(61, 61 62, 65) +	86.60	23.81
(9)	0.3225($0, 61 \parallel 64, 0) - 0.7805$	(0, 56 62, 0) + 0.24)	13(61, 61 62, 65) +	77.10	23.98
(11)	0.7177(0, 59 62, 0) + 0.4900	$(0, 61 \ 66, 0) + 0.26$	17(61, 61 62, 63) +	82.40	19.99
(13)	0.1166(0, 56 62, 0) - 0.9292	(0, 61 67, 0) - 0.248	7(61, 61 63, 67) +	93.90	10.67
(16)	-0.6059	(0, 61 69, 0) - 0.3131)	(0, 54 62, 0) + 0.23	57(61, 61 62, 68) +	52.10	47.72

energies and intensities of the higher-lying excitations do not unambiguously correlate with the weak absorptions below 5000 Å. No attempt was made to achieve size consistency with I in the CI expansion. However, the smaller size of II and the absence of low-lying oxygen σ orbitals gives a CI expansion encompassing a comparable number and energetic spread of pure π -electron configurations. Such configurations are most certainly the origin of most of the correlation corrections of interest. The CNDO/S(CI) work of Schulten and co-workers [37] implies that a moderate increase in the CI space for **II** is unlikely to significantly enhance agreement with experiment. Although Schulten et al. [37] obtained excellent computational agreement with experimental $S_1 \leftarrow S_0$ transitions of shorter-chain cyanines, large CI expansions were involved. For example, computations were restricted to singly and doubly excited π electron configurations where a CI matrix of dimension 703 was reached for $H_2N-(CH)_9-NH_2^{\oplus}$. One important point of agreement between the conclusions of Schulten and co-workers [37] and the present results on II is the position (≈ 1.0 eV above S₁), relative intensity $(f(S_2)/f(S_1) \approx 0.01)$, and largely doubly excited character of S_2 . This excited state appears to account for the first absorption maximum above the intense transition. A state having comparable properties does, in fact, appear in the spectrum of \mathbf{I} – see fig. 7. Replacing the cyanine methyls with hydrogens as done by Schulten et al. [37] shifted $S_1 \leftarrow S_0$ only 0.053 eV to higher energy. This is in accord with the similar nitrogen localization in the HOMO and LUMO



Fig. 8. The CNDO/S ordering ($C_{2\nu}$ symmetry) and energies of selected levels of I for the MNDO constructed geometry. Contour plots of the π orbitals are included to resolve the wavefunctions given in table 1. The molecular orbitals were constructed using the CNDO/S coefficients and a modification of the program of Lichtenberger and Fenske [38]. The orbital plane lies 0.5 Å above the molecular plane. Zero value contours which mask the bondlength projections have been eliminated.

levels; a condition also calculated for I – see fig. 8. In comparison, Schulten and co-workers [37] report an ≈ 0.28 eV CNDO/S(CI) depression in $S_1 \leftarrow S_0$ on going from the hydrogen to methyl substituted cyanines. The present CNDO/S parameterization yields HOMO and LUMO destabilizations of 0.288 and 0.246 eV, respectively, due to methyl substitution. Even at the level of estimation given in fig. 9, correlation contributions for II are already *much* larger than indicated for I. The top panel in fig. 10 shows that, in accord with the arguments of Fabian and co-workers [11,12], O and CO substitution of II to yield I does not "severely" perturb the HOMO-LUMO energy difference. The net positive charge on II is neutralized on going to I and



Fig. 9. Comparison of the CNDO/S(CI) UV/VIS excitation profiles of II (equal C-C bondlength (1.40 Å) model (center panel) and the MNDO optimized model exhibiting a slight tendency toward bondlength alternation (bottom panel)) with the detailed experimental spectrum of Malhotra and Whiting [13]. See the caption to fig. 7 for details.

the HOMO and LUMO levels are thus destabilized by nearly the same amount ($\Delta \epsilon_{avg} = 2.422$ eV) [39]. Such approximately off-setting "substituent" contributions also correlate with the observed similarities in optical properties of less extensively substituted squaraines [40] and the correspondingly shorter-chain cyanines [12]. The moderately enhanced destabilization of the HOMO level relative to LUMO indicates that at the Hartree–Fock level I absorbs at lower energy than II. This incorrect ordering is carried over even when one-electron (1E) exchange ($K_{ii'}$) and



Fig. 10. The CNDO/S HOMO and LUMO energies (eV) for I and II (top panel). Correlation terms leading to the S_1 final-state energy are compared in the bottom panel. $Q\langle PROJ \rangle$ notes the S_1 energy after projecting the S + DES CI results to account for quadruply excited configurations as described in the text.

Coulomb $(J_{ij'})$ interactions are considered for HOMO \rightarrow LUMO excitation: $E_{ij'}(1E) = \epsilon_{j'} - \epsilon_i - J_{ij'} + 2K_{ij'}$ (fig. 10 bottom panel). As indicated, the S₁ \leftarrow S₀ energy gap of I is relatively insensitive to S + DES CI, whereas the corresponding transition in II undergoes a rather large depression. As shown in the bottom panel of fig. 10, this serves to reverse the energetic ordering of the S₁ state in I and II to reflect the experimental positions. Table 1 shows that most of the correlation contributions to S₁(I) are doubly excited in nature: 90.9% singly excited HOMO \rightarrow LUMO, 7.71% DES and 1.39% higher-lying SES. S₁(II) has a similar nature: 88.6% singly excited HOMO \rightarrow LUMO, 8.98% DES and

2.42% higher-lying SES. Since the calculated energies indicated in fig. 10 are referenced to the S + DES CI-correlated ground states, the large difference in S_1 depression between I and II arises as the sum of two terms. $S_1(I)$ is stabilized by S + DES CI 0.553 eV relative to the uncorrelated Hartree-Fock ground state, but when referenced to the final ground state at -0.4899 eV yields the indicated net stabilization of only 0.063 eV. A similar final-state S_1-S_0 energy difference was obtained by reducing the CI matrix to a dimension of 200, i.e. the correlation contributions to S_1 and S_0 remain approximately equal. $S_1(II)$, however, is stabilized by 0.876 eV relative to the Hartree-Fock ground state. Referencing to the correlated S_0 level at -0.2940 eV yields a net $S_1 - S_0$ depression of 0.582 eV. Dinur and co-workers [41] have emphasized the strong depression of S_1 in cyanines due to doubly excited configurations, and contrasted such behavior with the much reduced shifts characteristic of the alternating bondlength polyenes.

Schulten and co-workers [37] further established a connection between the final correlation contributions expected from a complete singly (S), doubly (D), triply (T) and quadruply (Q) excited CI expansion, and the energy depression of the ground (S₀) and excited (S_n) states reflected in the limited S + DES basis set. By referencing $E(S_n)_{S+D}$ and $E(S_0)_{S+D}$ separately to the SCF Hartree-Fock ground state, it was shown that

$$\Delta E(\mathbf{S}_n \leftarrow \mathbf{S}_0) = E(\mathbf{S}_n)_{\mathbf{S}+\mathbf{D}} - (5/N)E(\mathbf{S}_0)_{\mathbf{S}+\mathbf{D}} \quad (1)$$

produced an excellent correlation with experimental energies for the chain systems of interest. N is the number of π -conjugated centers in the chain, and as such reflects the length of the system. Therefore, N = 13 was used to obtain the Q projected final-state energies for both I and II. Increasing N in the analysis of I does not significantly shift the spectrum. Inherent to eq. (1) is that T + Q excited configurations selectively stabilize excited states, and that such stabilization is uniform.

The large $S_1 \leftarrow S_0$ oscillator strength of I is a direct consequence of HOMO-LUMO orbital *de*-*localization* over a spatially extended framework, and in this regard does reflect the underlying cyanine structure. The oscillator strength is calcu-

lated according to [15]

$$f_{\rm T}({\rm S}_1 \leftarrow {\rm S}_0) = 1.085 \times 10^{-5} \tilde{\nu} |M(r_i)|^2,$$
 (2)

where $\tilde{\nu}$ is the calculated excitation frequency (cm^{-1}) and $M(r_i)$ is the $S_1 \leftarrow S_0$ transition moment,

$$M(\mathbf{r}_i) = \langle {}^{1}\Psi(\mathbf{S}_1) | \mathbf{r}_i | {}^{1}\Psi(\mathbf{S}_0) \rangle.$$
(3)

Only the Δx components contribute to the $S_1 \leftarrow S_0$ transition moments of I and II. Expanding (3) in terms of the spin-adapted CI functions given in table 1 (reflecting $\approx 95\%$ of ${}^{1}\Psi(S_1)$ and ${}^{1}\Psi(S_0)$) and performing the appropriate integration yields

$$M(\Delta x) = 2^{1/2} (0.907 \langle 61 | \Delta x | 62 \rangle -0.149 \langle 61 | \Delta x | 62 \rangle +0.035 \langle 62 | \Delta x | 63 \rangle +0.023 \langle 62 | \Delta x | 70 \rangle).$$
(4)

Expansion of the molecular orbitals in terms of LCAO coefficients gives $\langle 61 | \Delta x | 62 \rangle = +2.082$, $\langle 62 | \Delta x | 63 \rangle = +2.228, \quad \langle 62 | \Delta x | 70 \rangle = +0.149,$ and $M(\Delta x) = 2.346$. The first term in eq. (4) arises from the singly excited HOMO \rightarrow LUMO excitation and as expected is the largest contributor. The second term arises from LUMO contributions to the correlated ground state and reduces $M(\Delta x)$. The destructive interference of the first two terms is general for the types of systems considered here since S_0 acquires HOMO \rightarrow LUMO character. The remaining elements describing only excited orbitals come from cross terms involving two doubly excited configurations. These positively contribute to the final-state transition moment. Since $f_{\rm T}$ varies as $|M(\Delta x)|^2$, the $\approx 10\%$ deviation in S₁ and S₀ from single component character serves to reduce $f_{\rm T}$ by \approx 40%. Therefore, adequate modelling of I and II must reference a structure which yields $f_{\rm T}({\rm HOMO} \rightarrow {\rm LUMO}) \gg f_{\rm E}$. As noted above this restriction is not satisfied by the "aromatic" squaraine construction. The CO coefficients which establish squaraine character do not contribute to the HOMO \rightarrow LUMO transition moment summation since the LUMO level contains a node along the short in-plane axis. When the sign of Δx is considered all $M(\Delta x)$ contributions are in-phase

for HOMO \rightarrow LUMO excitation. When the magnitude of Δx is considered, $M(\Delta x)$ becomes large (2.346) simply due to the size of the molecule.

Ohmine and co-workers [42] have shown for linear polyenes that the T + Q configurations, which account for the significant $S + DES \rightarrow$ $Q\langle PROJ \rangle$ correlation energy shifts discussed above, do not seriously perturb transition moment values obtained from a limited S + DES CI expansion. The favorable comparison of $f_{\rm T}({\bf I}) = 1.2640$ versus $f_{\rm F}(\mathbf{I}) = 1.234$ is therefore considered a sensitive indication of the quality of the analysis. The fact that $f_{T}(\mathbf{II}) > f_{E}(\mathbf{II})$ in the S + DES CI calculation is simply taken to imply that II has an enhanced sensitivity to the dimension of the CI expansion relative to I. This assumption is further reflected in the values of the one-electron HOMO \rightarrow LUMO oscillator strengths: $f_{\rm T}(\mathbf{I})_{1\rm E} = 1.817$ and $f_{\rm T}({\rm II})_{1{\rm E}} = 2.441$. Correlations of essentially one-electron CNDO/S oscillator strengths with experimental values for a series of pyryliums indicated $f_{\rm T} \approx 1.5 f_{\rm E}$ [43]. Such deviation is commonly assumed a consequence of neglect of correlation (mainly doubly excited). Reducing the one-electron oscillator strengths by a factor of 1.5 yields: $f_{\rm T}({\rm I} {\rm adj.})_{1{\rm E}} = 1.211$ versus $f_{\rm E}({\rm I}) = 1.234$; and $f_{\rm T}({\rm II} {\rm I} {\rm I})$ $adj.)_{1E} = 1.627$ versus $f_{E}(II) = 1.599!$

At the one-electron level HOMO \rightarrow LUMO excitation of I yields only a net electron transfer of $0.074 \ e$ to the squaraine moiety. Intramolecular charge transfer is inhibited because the oxygen atoms, which characterize the squaraine moiety as electron accepting in the ground state, serve as excited-state electron donors. The largest chargetransfer term occurs from the carbonyl groups $[C(\Delta q = +0.026 \ e); \ O(\Delta q = +0.094 \ e)]$ to the squaraine carbons lying on the long molecular axis $(\Delta q = -0.157 e)$, i.e. a charge transfer essentially confined within the squaraine part. The nitrogen atoms each lose only 0.019 e. S + DES CI essentially doubles the net charge gained by the squaraine fragment (0.128 e). S + DES CI removes carbonyl character from the ground state (the (61,61 | |62,62) component) while adding some to S_1 (the (61,61) | 62,63) component). This reduces the difference in carbonyl contributions allowing the acceptor properties of the long-axis squaraine carbons to become more dominant:

 $CO(\Delta q = +0.011 \ e)$; $C(\Delta q = -0.075 \ e)$. Again, the nitrogens each lose only 0.022 e.

It is instructive to compare donor/acceptor properties calculated for I with those of the model $D^+ \rightarrow A^-$ molecule *p*-nitroaniline (PNA). The PNA HOMO orbital is largely localized on the amino nitrogen, whereas the LUMO level has considerable nitro group character [27]. The PNA transition with the dominant HOMO \rightarrow LUMO configuration experimentally exhibits an ≈ 1.0 eV red-shift on going from the vapor phase to the most polar condensed media [27,29,44]. CNDO/S(S + DES CI) computations on the PNA free molecule indicate electronic displacements of $\Delta q(NH_2) = +0.130 \ e \ and \ \Delta q(NO_2) = -0.626 \ e$ accompanying the transition compared to $\Delta q(NH_2) = +0.183 \ e \ and \ \Delta q(NO_2) = -0.611 \ e$ for pure HOMO \rightarrow LUMO excitation. In terms of ground-state charge densities I can be viewed as two PNA molecules coupled end-to-end: $D^+ \rightarrow$ $A^-: A^- \leftarrow D^+$. The orbitals best approximating the PNA CT transition, however, are both doubly occupied in I (second HOMO and HOMO). Although such a transition is impossible in the neutral molecule, it is expected to be strongly allowed in the radical cation ($\langle 60 | \Delta x | 61 \rangle = -2.544$) where the HOMO level is singly occupied [45,46]. Orbital coefficients suggest charge density changes of Δq (squaraine) = -0.318 e and $\Delta q(N) =$ +0.106 e relative to the neutral molecule ground state for second HOMO \rightarrow HOMO excitation.

Although the $S_1 \leftarrow S_0$ transition energy of I is relatively stable to variations in solvent polarity as noted in the introduction, a slight but distinct blue-shift is observed upon increasing the solvent dielectric constant [9]. This experimental result is not necessarily in contradiction with the MNDO work and arguments for a large net HOMO \rightarrow LUMO red-shift as a consequence of solvent-induced structural relaxation. It is likely that even a mildly polar environment, or specific solvent/solute complexation, leads to a rapid saturation of "quinoid"-character enhancement allowing interactions of a purely electrostatic nature to dominate at higher dielectric constants. In reference to such a static conformationally relaxed $D^+ - A^- - D^+$ ground state ($D^+ - A^-$ in the case of PNA), orbitals with dominant donor (D⁺) character will be destabilized, and levels with acceptor (A^-) character will be stabilized by increasing solvent polarity [27,39]. These guidelines rationalize the relative absorption properties of PNA and I, i.e. upon increasing solvent polarity the PNA HOMO and LUMO levels move closer together (red-shifted excitation energy), whereas the HOMO level of I is destabilized relative to the LUMO orbital due to its dominant acceptor character (blue-shifted excitation energy).

To verify such shifts computationally the diagonal CNDO/S Hartree-Fock matrix elements were modified to reflect a reaction field,

$$F_{\mu\mu}^{A} = -\frac{1}{2} (IP_{\mu} + EA_{\mu}) + \left[Q_{1} (P_{AA} - Z_{A}) - \frac{1}{2} (P_{\mu\mu} - 1) \right] \Gamma_{AA} + Q_{2} \sum_{A \neq B} (P_{BB} - Z_{B}) \Gamma_{AB},$$
(5)

where A denotes the atomic center and μ the particular orbital. $P_{AA} - Z_A = \Delta q_A$ and $P_{BB} - Z_B$ $= \Delta q_{\rm B}$. Rather than including new terms which are charged oppositely to the atomic centers, and scaled proportionately, simple factors (Q_1, Q_2) were used to scale down $\Delta q_{\rm A}$ and $\Delta q_{\rm B}$. Q_1 scales the atomic "self-interaction" and Q_2 modifies the interatomic component. $Q_1 = Q_2 = 1.0$ yields the unperturbed molecule. On going from $Q_1 = Q_2 =$ $1.0 \rightarrow 0.5$ the one-electron HOMO \rightarrow LUMO transition of PNA is red-shifted by 0.26 eV, whereas that of I ("aromatic" model) is blue-shifted by 0.33 eV. Although the direction of these "electrostatically" induced shifts parallels experiment, additional work is needed to sort out the details of the sensitive balance and interrelationship of such perturbations and those due to structural relaxation.

5. Summary and conclusions

The nature of selected ground- and excited-state properties of the highly polar squaraine dye bis(4dimethylaminophenyl)squaraine (I) and the related closed-shell cyanine cation bis(dimethylamino)undecamethine (II) have been compared. MNDO ground-state geometry optimization of I indicated a distinctive alternating single-double bondlength pattern. This was shown to be in marked contrast to II which gave nearly complete C-C chain bondlength equalization paralleling experimental results for shorter cyanine systems. Furthermore, the "quinoid"-like character of I was significantly enhanced when explicit solvent/ solute interactions were considered. Bondlengths and bond angles obtained by MNDO geometry optimization of a model "supermolecule" squaraine/solvent complex were in excellent agreement with crystal structure values reported for related systems.

CNDO/S(S + DES CI) computations were carried out for the low-lying singlet excited states of I and II. Calculations on I, using the MNDO optimized ground-state geometry, produced $S_n \leftarrow S_0$ excitation and transition intensity profiles in essential accord with the detailed solution-phase absorption spectrum above 2500 Å. Particularly, six of the eight suggested and/or clearly resolved absorptions between 2500 and 6500 Å (see fig. 7) were "firmly" assigned in accord with the CNDO/S(CI) results. Although not emphasized in the discussion, the two remaining features reflecting relatively weak absorption ($\lambda_{max} \approx 3400$ Å and $f_{\rm E} \approx 0.02$; $\lambda_{\rm max} \approx 4650$ Å with $f_{\rm E} \ll 0.01$) appear in near energetic coincidence with calculated weakly allowed transitions ($f_{\rm T} < 10^{-3}$). An "aromatic" or "cyanine"-like model was shown to be clearly insufficient to reflect squaraine excitedstate properties.

The nature and magnitude of singly + doubly excited correlation contributions were considered, and their consequences to final-state S_1-S_0 separation and the $S_1 \leftarrow S_0$ oscillator strength discussed in detail. The intense long-wavelength transition of II was shown to be considerably more sensitive to doubly excited CI than the corresponding excitation of I. The CNDO/S(CI) results correctly reflected the relative $S_1 \leftarrow S_0$ transition energies and oscillator strengths.

Finally, the effects of solvent/solute interaction (complexation) on the $S_1 \leftarrow S_0$ transition energy of I were rationalized in terms of a sensitive balance between induced structural relaxation and weaker selective "electrostatic" components which depend on relative HOMO-LUMO localization. The slight blue-shift experimentally observed in the long-wavelength transition as a function of increasing solvent polarity was shown to be consistent with the calculated intramolecular charge-transfer character (orbital localization). Solvent sensitive properties were contrasted with those of the model D^+-A^- molecule *p*-nitroaniline (PNA).

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