

THE ELECTRONIC SPECTRA  
OF 1,3-DIAZAADAMANTANOID DERIVATIVES.  
THE INTERACTION OF ISOLATED CHROMOPHORS

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The existence of complex chromophoric systems in 1,3-diazaadamantanoid derivatives *1a-c*, which manifests by absorption bands of the intensity  $\epsilon \approx 10^3 \text{ cm}^2 \text{ mol}^{-1}$ , was confirmed. This conclusion is based on confrontation of the electronic spectra of model compounds *2*, *3a-c*, *4a*, *4b*, *5a-c*, and of dihydrochlorides *6a-c* and on discussion of symmetry of interacting orbitals on the basis of extended Hückel theory. A new synthesis of 1,3-diazaadamantane (*3b*), using corresponding 6-ketone as a starting compound, is reported.

An interaction of various unconjugated groups in organic molecules "through bonds" or "through space" belongs to interesting problems of current theoretical chemistry<sup>1</sup>. While various long-range effects *via* delocalized  $\pi$ -bonds are well-known property of a variety of conjugated systems, analogous effects through more or less localized  $\sigma$ -bonds are rarer and also less studied. If interacting groups are chromophors, then convenient experimental method for studying their mutual influencing may be electronic absorption spectra<sup>2</sup>. The absorption of interacting chromophors\* differs in excitation energy and oscillator strength from the absorption of noninteracting chromophors.

The aim of this study was to investigate to a greater detail the interaction of three simple chromophors  $\text{>C=X}$  and  $\text{—}\bar{\text{N}}\text{—}$  in 1,3-diazaadamantanoid derivatives *1a-c*. Fixed arrangement of the bonds in these substances (Fig. 1) ensures that the lobes of nonbonding AO's on nitrogen atoms,  $\sigma$ -MO's of central C—C bonds and of  $\pi$ -MO's of  $\text{>C=X}$  groups are approximately parallel.

It has been shown<sup>3-8</sup> that in the spectra of various compounds containing this fragment there occurs additional red shift, and, particularly, the intensity of the absorption maximum of long-wavelength band is *increased*, compared to the compounds which are not able or are unlikely to attain the geometry A because of steric reasons. Cookson, Henstock, and Hudec<sup>6</sup> termed the interaction of this type "sigma coupling" and it has been recently considered<sup>8</sup> to be the consequence of the splitting of  $\pi$  and  $\pi^*$  levels of the chromophor  $\text{>C=X}$  by  $n$  levels on  $\text{—}\bar{\text{N}}\text{—}$ .

\* Strictly speaking, each two chromophors present in a given molecule are perturbed by the other bonds and atoms. The term "interaction" refers in this work to such an influencing which significantly affects the above mentioned spectral characteristics.

Hoffmann, Imamura and Hehre<sup>9</sup> predicted for simplified carbon model B (Fig. 1) on the basis of quantum chemical calculations considering all valence electrons the possibility of relatively strong interaction of the depicted nonbonding orbital lobes through central  $\sigma$ -bonds.

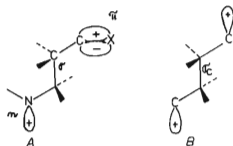


FIG. 1

Spatial Orientation of Bonds in System of Interacting Chromophors

Our findings concerning the electronic spectra of compounds *1b*, *c* were in part reported in short communications<sup>4,7</sup>. In the present work the study was extended to further model compounds and complemented by interpretation on the basis of EHT method.

## EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined with Boetius hot plate microscope, except for compounds *1c* and *2* which were measured in sealed capillary tubes.

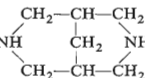
### Chemicals

The preparation and some physical properties of spectrograde compounds *1a*, *1b*, *4a*, *4b*, and *6a* were reported in a previous study<sup>10</sup>, characteristic data for compounds *5a* and *5b* have been determined only recently<sup>11</sup>. Diethyl ester *1c* (m.p. 117–118°C) and tetramethyl ester *2* (m.p. 283–284°C) were prepared by condensation reactions<sup>4,12</sup> and 1,3-diaza-6-hydroxyadamantane (*3c*) was obtained by the procedure<sup>13</sup> (colourless crystals, m.p. 295–299°C, mass spectrum;  $[M]^+$   $m/e$  154, relative intensity 100%; ref.<sup>13</sup> records m.p. 270°C/dec.). Dihydrochlorides *6b* and *6c* were prepared by mixing ethanolic solutions of appropriate bases *1b* and *1c* with an excess of ethanolic solution of hydrogen chloride and by evaporating the reaction mixture under vacuum. Substance *6b* had m.p. 184–186°C. An analogous constant for substance *6c* could not be determined due to extreme sensitivity of this compound to air moisture (in both cases colourless crystals). The urotropine used (*3a*) was commercial preparation of analytical purity grade.

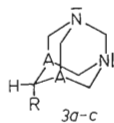
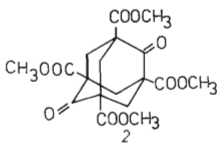
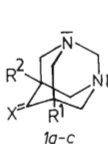
1,3-Diazaadamantane (*3b*) was prepared by Kizhner–Wolff reduction of 6-ketone *1b*. A mixture of 1.0 g of compound *1b*, 2.0 g of anhydrous sodium acetate, 13 ml of c. 90% hydrazine, and 46 ml of diethylene glycol was refluxed for 18 h. After cooling and acidification by ethanolic 6M-HCl to pH 3–4, the hydrochlorides formed were separated by filtration with suction and an additional portion of the salts was then obtained by evaporation of solvents under vacuum. Combined portions were then treated with 50 ml of 40% NaOH to release the bases which were subsequently continuously extracted with pentane, for 20 h. The extract was dried over sodium hydroxide, the solvent removed by distillation, and the distillation residue was sublimed at 120–130°C to

give 678 mg (82%) of 3,7-diazabicyclo[3,3,1]nonane, m.p. 203–205°C (refs<sup>14,15</sup> record the compound as liquid boiling 154–156°C/1 Torr, without giving analytical data). The mass spectrum shows  $[M]^+$  *m/e* 126, relative intensity 68%. The IR spectrum (CCl<sub>4</sub>): 3300–3350 cm<sup>-1</sup>  $\nu(\text{NH}_{\text{assoc.}})$ , 1470 cm<sup>-1</sup>  $\delta(\text{NH})$ , and 1062 cm<sup>-1</sup>, presumably  $\nu(\text{C-N})$ . The <sup>1</sup>H NMR spectrum (CCl<sub>4</sub>): multiplet 8 H at 3.02 $\delta$ (N—CH<sub>2</sub>—C), singlet 2 H at 1.96  $\delta$ , the residence of which is dependent on the concentration of measured solution, (C—NH—C), and two broad signals 2 H at 1.79  $\delta$  and 2 H at 1.45  $\delta$ , which on decoupling with respect to the above mentioned methylene signals are converted to two triplets of the A<sub>2</sub>X<sub>2</sub> system ( $J_{\text{HH}} \approx 4$  Hz) and can be then assigned to the CH—CH<sub>2</sub>—CH grouping. The above spectral characteristics are in agreement with

the presence of conformationally nonhomogeneous structure

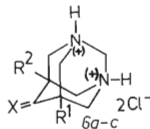
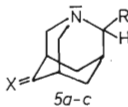
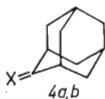


in the compound obtained *via* reduction and hydrolytic cleavage of the methylene bridge N—CH<sub>2</sub>—N in the starting ketone *1b*. For that reason 585 mg of the product was reacted<sup>14</sup> with 1.58 g of methylene iodide in 23 ml of methanol for 3 h. Crude, sublimed product was chromatographed on 140 g of aluminium oxide (Brockmann activity II—III, column was 26 cm long) with an ethanol—chloroform mixture (2:98, 25 ml)—fractions being collected. Fractions 8–16, which according to thin layer chromatography (detection by iodine vapours) contained only substance *3b*, yielded after acidification with ethanolic hydrogen chloride the dihydrochloride of substance *3b*. This was reacted with 60% NaOH and worked-up as reported<sup>14</sup> to give 415 mg (64.8%) of the pure derivative *3b*, m.p. 264–266°C (after sublimation at 110–120°C), refs<sup>14–16</sup>



- 1a, X = CH<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = H  
 b, X = O, R<sup>1</sup> = R<sup>2</sup> = H  
 c, X = O, R<sup>1</sup> = R<sup>2</sup> = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>

- 3a, A = N, R = H  
 b, A = CH, R = H  
 c, A = CH, R = OH



- 4a, X = O  
 b, X = CH<sub>2</sub>

- 5a, X = O, R = H  
 b, X = O, R = OH  
 c, X = H<sub>2</sub>, R = H

- 6a, X = CH<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = H  
 b, X = O, R<sup>1</sup> = R<sup>2</sup> = H  
 c, X = O, R<sup>1</sup> = R<sup>2</sup> = H

record m.p. 264—265°C. The mass spectrum shows  $[M]^+$   $m/e$  138, relative intensity 100%. The IR spectrum ( $\text{CCl}_4$ ): no maxima above  $3000\text{ cm}^{-1}$ , 2920, 2900, and  $2852\text{ cm}^{-1}$   $\nu$  (CH and  $\text{CH}_2$ ), 1450, 1300, 1280, and  $1270\text{ cm}^{-1}$   $\delta$  (CH and  $\text{CH}_2$ ).

In another experiments general Caglioti's procedure was used to reduce ketone *1b*. A mixture of 456 mg of substance *1b* and 600 mg of tosylhydrazine dissolved in 7.6 ml of ethanol was refluxed for 4 h and then it was evaporated to dryness. The residue was chromatographed on 160 g of aluminium oxide (activity III, the column was 31 cm long, 4% ethanol in chloroform was used as eluent, the extract was cut to 25 ml — fractions, the composition of which was followed by thin layer chromatography, detection by iodine vapours). The evaporation of fractions 18—25 afforded 480 mg of the tosylhydrazone of substance *1b*. The compound was dissolved in 20 ml of tetrahydrofuran, 730 mg of lithium aluminiumhydride was added and the mixture was refluxed for 10 h. After cooling and decomposition by 3.2 ml of 4% NaOH, the inorganic salts were separated by filtration with suction, washed twice with 5 ml of hot ethanol and combined filtrates were acidified with ethanolic hydrogen chloride. Evaporation of the solvents under vacuum followed by crystallization of the residue afforded 93 mg (14.7%) of the dihydrochloride *6b*, m.p. 266—268°C.

**Solvents.** Ethanol and methanol were dried with magnesium<sup>17</sup>, dioxane and cyclohexane were purified in the usual way<sup>18,19</sup>.

#### Spectroscopic Measurements

Unless stated otherwise, the spectra of  $4 \cdot 10^{-4}\text{ M}$  solutions of studied compounds were recorded with Optica Milano CF 4 NI spectrometer, using 1 cm thick cells. Characteristic data for absorption maximum were read with the accuracy  $\lambda_{\text{max}} \pm 2\text{ nm}$  and  $\epsilon \pm 10$ . Examples of absorption curves are shown in Figs 3 and 4, spectral characteristics are given in Tables II and III. The infrared spectra were recorded with Perkin-Elmer 325 instrument, the  $^1\text{H}$  NMR spectra were taken on Varian XL-100 and the mass spectra on LKB 9000 instruments (direct inlet, source 70 eV, temperature 230°C).

#### Calculations

Fifty six MO's of EHT models of substances *1b* and *6b* (dication) and 58 MO's of compounds *1a* and *4a* were computed using standard segmented program on ICL-4-50 and Tesla 270 digital

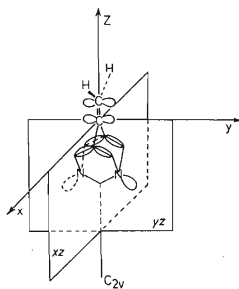


FIG. 2  
Octant Projection of Molecule *1a*

computers (one calculation took 30–90 min). The procedure reported by Hoffmann<sup>20,21</sup> was employed. The orientation of the models of molecules in coordinate system is shown in Fig. 2. The ideal geometry with bond angles of  $109^{\circ}28'$  and bond lengths  $N^+-H$  1.02 Å,  $C-H$  1.09 Å,  $C=O$  1.22 Å,  $C=C$  1.34 Å,  $C-C$  and  $C-N$  1.54 Å was adopted. The values of ionization potentials  $I_s$  and  $I_p$  for states  $s$  and  $p$ , as well as Slater exponents were taken from literature<sup>22–24</sup> and are listed in Table I. Diagonal matrix elements  $H_{ij}$ , approximated by ionization potentials of corresponding states, were used to calculate nondiagonal elements  $H_{ij}$  according to the relation<sup>21</sup>

$$H_{ij} = 0.875 S_{ij} (H_{ii} + H_{jj})$$

where  $S_{ij}$  denotes the corresponding overlap integral.

## RESULTS AND DISCUSSION

### *Spectroscopic Verification of Interaction of Chromophors*

Irrespective of any theoretical aspect, we first attempted to verify empirically the presumed interaction in systems *1a–c* by studying in more detail their absorption spectra in the 200–400 nm region.

*Structural disposition.* The necessity of rigid spatial arrangement of nitrogen  $n$ -chromophors— $\bar{N}$ — and of  $\pi$ -carbonyl chromophor  $>C=O$  for formation of long-wavelength absorption band of intensity  $\epsilon \approx 10^3$  in the case of compounds *1b* and *1c* has been convincingly shown earlier<sup>6–8</sup>. We have therefore centered on investigation of finer aspects of this interaction, in particular, the extent of spectroscopic mani-

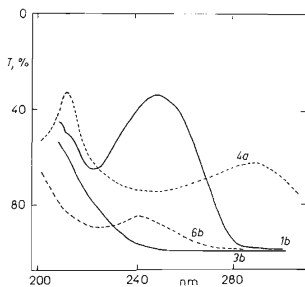


FIG. 3

Ultraviolet Absorption Spectra in Ethanol  
Full line, conc.  $4 \cdot 10^{-4}$ ; dashed line,  
conc.  $3.25 \cdot 10^{-3}$  M.

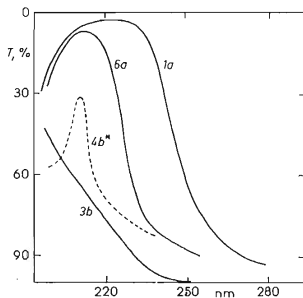


FIG. 4

Ultraviolet Absorption Spectra in Ethanol  
Full line, conc.  $4 \cdot 10^{-4}$  M; dashed line,  
conc.  $3.32 \cdot 10^{-3}$  M.

festation of *a*) partial interaction in the arrangements  $\text{O}=\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CO}_2\text{C}_2\text{H}_5$  (in compound *1c*),  $\text{O}=\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\bar{\text{N}}-$  and  $-\bar{\text{N}}-\text{CH}_2-\bar{\text{N}}-$  (in compounds *1b* and *1c*), *b*) the effect of the replacement of the carbonyl chromophor  $>\text{C}=\text{O}$  in compound *1b* by the olefinic chromophor  $>\text{C}=\text{CH}_2$  (compound *1a*).

The examination of relative role of partial interactions in the sence of aspect *a*) was made possible by confrontation of spectral data in Table II and III. An interaction of partial chromophors in the  $\text{O}=\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CO}_2\text{C}_2\text{H}_5$  and  $\text{C}_2\text{H}_5\text{O}_2\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CO}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CO}_2\text{C}_2\text{H}_5$  groupings does not manifest itself through stronger absorp-

TABLE I  
Data Used in LCAO-EHMO Calculations

Atom	$I_s$ , eV	$I_p$ , eV	Slater exponent
H	-13.6	—	1.0
C	-21.01	-11.27	1.625
N	-26.92	-14.42	1.95
N <sup>+</sup>	-30.52	-15.62	1.95
O	-36.07	-18.53	2.275

TABLE II  
Longest Wavelength Electronic Absorption Bands of 1,3-Diazaadamantanoid Compounds *1a-c* (conc.  $4 \cdot 10^{-4}\text{M}$ )

Derivative	Solvent	$\lambda_{\text{max}}$ , nm	$\epsilon$ , $\text{cm}^2 \text{mol}^{-1}$
<i>1a</i>	ethanol <sup>a</sup>	224	3 600
<i>1b</i>	water	248	1 700
<i>1b</i>	ethanol <sup>b</sup>	250	1 400
<i>1b</i>	dioxane	255	1 700
<i>1c</i>	water	254	1 700
<i>1c</i>	methanol	260	1 700
<i>1c</i>	ethanol	258	1 700
<i>1c</i>	acetonitrile	258	2 000
<i>1c</i>	dioxane	262	2 200
<i>1c</i>	cyclohexane	260	1 900

<sup>a</sup> Unicam SP 800 spectrometer, conc.  $4.1 \cdot 10^{-3}\text{M}$ ; <sup>b</sup> conc.  $5.1 \cdot 10^{-4}\text{M}$ .

tion in the values of molar extinction coefficients higher than tens in the region of wavelengths above 220 nm. This follows from the fact that diketo tetraester 2 does not show the higher intensity in this region. Second argument in favour of this assumption is the fact<sup>7</sup> that removal of ester groups from *Ic* does not lead to the disappearance of absorption band at 250–260 nm with the intensity  $\epsilon \approx 10^3$ , as evident from comparison of the data given in Tables II and III. The strong band with  $\lambda_{\max}$  212 nm found for methanolic solution of substance 2 could have been attributed to the interaction of the ester with keto chromophor, more plausible seems, however, to ascribe it to the keto chromophor itself, since analogous absorption can be observed also with substances *Ib* and *Ic*. The interaction in the  $\text{—}\overline{\text{N}}\text{—}$   $\text{—}\text{CH}_2\text{—}\overline{\text{N}}\text{—}$  grouping is spectroscopically little significant, as it is shown by minimum absorption of urotropine (*3a*) and of 1,3-diazaadamantane (*3b*), in which cases the molar extinction in this region amounts only to several tens (Fig. 3). These facts led us to conclude that, in agreement with earlier assumption<sup>6,7</sup>, the formation of long-wavelength band with  $\epsilon \approx 10^3$  is mainly due to the interaction in the  $\text{O}=\text{C}\text{—}$

TABLE III  
Electronic Spectral Characteristics of Model Compounds

Substance	Solvent	$\lambda_{\max}$ , nm <sup>a</sup>	$\epsilon$ , cm <sup>2</sup> mol <sup>-1</sup>	$c \cdot 10^4$ , M
2	methanol	269	100	11
3a	ethanol <sup>b</sup>	209	200	36
		248	40	
3b	ethanol	210 <sup>c</sup>	~400	4
3b	cyclohexane	242 <sup>c</sup>	~300	4
3c	ethanol	212 <sup>c</sup>	~700	4.4
4a	ethanol <sup>b</sup>	209	70	33
		290	30	
4a	methanol	287	50	4
4a	cyclohexane	294	80	4
4b	ethanol	(205)	(600)	1
5a	ethanol	235 <sup>d</sup>	900 <sup>d</sup>	31
5b	ethanol	217 <sup>d</sup>	1 080 <sup>d</sup>	
5c	ethanol	(205)	(600)	4
6a	ethanol <sup>b</sup>	212	2 800	41
6b	ethanol <sup>b</sup>	243	10	32.4
6c	ethanol	262	10	4

<sup>a</sup> Values in parentheses refer to final absorption (without maximum); <sup>b</sup> determined with Unicam SP 800 instrument; <sup>c</sup> data for inflex; <sup>d</sup> taken from ref.<sup>11</sup>.





TABLE IV

Significant EHMO's of Substances *1a*, *1b*, *4a*, and *6b* as Linear Combinations of *p*-AO's of Individual Atom Centers

Substance	EHMO order <sup>a</sup>	Symmetry	Type	Energy eV	Linear combination of <i>p</i> -AO's <sup>b</sup>
<i>1a</i>	27	SA	$\sigma^*$	-2.02	$-0.57 N_x(1, 3) - 0.44 C_x(4, 8, 9, 10) - 0.10 C_x(5, 7) \mp 0.28 C_z(4, 9) (8, 10)$
	28	AS	$(n\sigma\pi^*)$	-7.58	$0.87 C_y(6) - 0.75 C_y(6') + 0.10 C_y(4, 8, 9, 10) - 0.11 C_z(8, 9) + 0.11 C_z(4, 10) - [0.05 N_y(1, 3)]$
	29	AS	$(n\sigma\pi)$	-12.08	$-0.25 C_y(6) - 0.54 C_y(6') + 0.31 N_y(1, 3) + 0.29 C_y(5, 7) - 0.19 C_y(4, 8, 9, 10) \mp 0.12 N_z(1, 3)$
	31	SS	$(n\sigma)$	-12.46	$0.34 C_z(5, 7) + 0.31 N_z(1, 3) - 0.30 C_z(6) + 0.23 C_z(6') - 0.19 C_z(4, 8, 9, 10) \mp 0.18 N_y(1, 3) \pm 0.11 C_y(8, 9) (4, 10)$
	32	AS	$(n\sigma\pi)$	-13.02	$-0.45 C_y(6) - 0.45 C_y(6') - 0.32 N_y(1, 3) - 0.18 C_y(5, 7) + 0.15 C_y(4, 8, 9, 10)$
	33	AA	$\sigma$	-13.03	$\pm 0.33 C_y(5, 7) \mp 0.32 C_y(4, 9) (8, 10)$
	37	SA	$\sigma$	-14.26	$\mp 0.25 C_z(5, 7) \pm 0.15 C_y(4, 8) (9, 10)$
	38	AS	$(n\sigma\pi)$	-14.45	$\pm 0.31 N_z(1, 3) \pm 0.20 C_z(4, 10) (8, 9) - 0.18 C_y(6) - 0.11 C_y(6') - 0.16 N_y(1, 3) - 0.11 C_y(4, 8, 9, 10)$
	39	SS	$(n\sigma)$	-14.64	$\mp 0.36 N_y(1, 3) \pm 0.15 C_y(8, 9) (4, 10) + 0.13 C_z(4, 8, 9, 10) + 0.11 C_z(5, 7)$
	<i>1b</i>	25	SA	$\sigma^*$	-1.97
26		AS	$(n\sigma\pi^*)$	-8.88	$-0.98 C_y(6) + 0.36 O_y(6') - 0.12 C_y(4, 8, 9, 10) + 0.11 C_y(5, 7) \mp 0.13 C_z(4, 10) (8, 9) + [0.09 N_y(1, 3)]$
28		AS	$(n\sigma\pi^*)$	-12.57	$0.44 N_y(1, 3) + 0.32 C_y(5, 7) - 0.21 C_y(4, 8, 9, 10) + 0.21 C_y(6) - 0.11 O_y(6') \mp 0.13 N_z(1, 3)$
29		SS	$(n\sigma)$	-12.83	$\pm 0.22 N_y(1, 3) \pm 0.10 C_y(4, 10) (8, 9) - 0.41 N_z(1, 3) - 0.32 C_z(5, 7) + 0.19 C_z(4, 8, 9, 10)$
30		AA	$\sigma$	-13.03	$\mp 0.34 C_y(5, 7) \pm 0.33 C_y(4, 9) (8, 10)$

TABLE IV  
 (Continued)

Substance	EHMO order <sup>a</sup>	Symmetry	Type	Energy eV	Linear combination of <i>p</i> -AO's <sup>b</sup>
	34	SA	$\sigma$	-14.45	$-0.34 C_x(2) \mp 0.29 C_z(5, 7) \pm 0.16 C_y(4, 8) (9, 10)$
	36	SS	$(n\sigma)$	-14.77	$\mp 0.22 C_x(5, 7) \pm 0.14 C_x(4, 9) (8, 10) \pm 0.13 N_y(1, 3) - 0.14 C_z(4, 8, 9, 10) - 0.30 N_z(1, 3)$
	38	AS	$(n\sigma)$	-15.03	$0.48 N_y(1, 3) - 0.20 C_y(5, 7) + 0.17 C_y(4, 8, 9, 10) \mp 0.10 N_z(1, 3)$
	46	AS	$\pi$	-18.84	$0.19 C_y(6) + 0.94 O_y(6')$
4a	27	SA	$\sigma^*$	-1.23	$-0.59 C_x(5, 7) - 0.42 C_x(4, 8, 9, 10) - 0.27 C_x(1, 3) - 0.39 C_x(2) \pm 0.18 C_z(4, 10) (8, 9)$
	28	AS	$(\sigma\pi^*)$	-8.93	$-0.98 C_y(2) + 0.37 O_y(2') - 0.12 C_y(4, 8, 9, 10) + 0.10 C_y(1, 3) \mp 0.14 C_z(4, 9) (8, 10)$
	31	AS	$(\sigma\pi^*)$	-12.29	$0.44 C_y(6) - 0.34 C_y(5, 7) - 0.24 C_y(1, 3) + 0.19 C_x(4, 8, 9, 10) - 0.15 C_y(2) + [0.08 O_y(2')]$
	33	AA	$\sigma$	-13.00	$\pm 0.22 C_x(5, 7) \mp 0.24 C_x(4, 9) (8, 10) \pm 0.22 C_y(1, 3) \pm 0.24 C_y(4, 10) (8, 9)$
	35	AS	$(\sigma\pi^*)$	-13.63	$0.29 C_y(6) + 0.23 C_y(1, 3) + 0.16 C_y(2) - 0.11 O_y(2') \pm 0.33 C_z(5, 7) \mp 0.22 C_z(4, 9) (8, 10)$
	36	SS	$\sigma$	-13.72	$\mp 0.24 C_y(5, 7) \pm 0.15 C_y(4, 9) (8, 10) - 0.42 C_z(6) - 0.27 C_z(1, 3) + 0.11 C_z(5, 7) + 0.11 C_z(2) - 0.12 O_z(2')$
	39	AS	$\sigma$	-14.49	$-0.28 C_y(5, 7) - 0.22 C_y(4, 8, 9, 10) + 0.19 C_y(6) + 0.16 C_y(1, 3)$
	48	AS	$\pi$	-18.83	$-0.18 C_y(2) - 0.93 O_y(2')$
6b	27	SA	$\sigma^*$	-1.96	$-0.56 N_x(1, 3) - 0.45 C_x(4, 8, 9, 10) - 0.16 C_x(6) \pm 0.29 C_z(4, 9) (8, 10)$
	28	AS	$(\sigma\pi^*)$	-8.93	$-0.99 C_y(6) + 0.37 O_y(6') - 0.12 C_y(4, 8, 9, 10) \pm 0.14 C_z(8, 9) (4, 10)$
	30	AA	$\sigma$	-13.03	$\mp 0.34 C_y(5, 7) \pm 0.33 C_y(4, 9) (8, 10)$
	31	AS	$(\sigma\pi^*)$	-13.13	$0.34 C_y(5, 7) - 0.28 C_y(4, 8, 9, 10) + 0.18 C_y(6) - 0.10 C_y(6') - 0.14 C_y(2)$

TABLE IV  
(Continued)

Substance	EHMO order <sup>a</sup>	Symmetry	Type	Energy	Linear combination of <i>p</i> -AO's <sup>b</sup>
32		SS	$\sigma$	-13.36	$\mp 0.10 C_y(4, 10) (8, 9) + 0.35 C_x(5, 7) -$ $- 0.24 C_z(4, 8, 9, 10) + 0.24 N_z(1, 3) -$ $- 0.14 C_z(6) + 0.14 O_z(6')$
35		SA	$\sigma$	-14.44	$- 0.34 C_x(2) - 0.17 C_x(5, 7) \pm$ $\pm 0.16 C_y(9, 10) (4, 8) \mp 0.29 C_z(5, 7)$
36		AS	$(\sigma\pi^*)$	-14.56	$0.16 C_y(5, 7) + 0.14 C_y(6) -$ $- 0.11 O_y(6') \pm 0.25 C_z(4, 10) (8, 9) \mp$ $\mp 0.19 N_z(1, 3)$
48		AS	$\pi$	-18.84	$0.19 C_y(6) + 0.94 O_y(6')$

<sup>a</sup> The highest level has the order 1; <sup>b</sup> as a rule, only expansion coefficients with absolute value higher than 0.1 are listed. The numbering of positions (cf. formulas 1, 4, and 6) is given in parentheses.

occur with 2-methylenadamantane (4*b*). On the other hand, the dihydrochloride 6*a* exhibits another maximum located at shorter wavelengths (212 nm). The absorption band of the free base 1*a* can again be assigned to complex chromophoric system containing four fragments ( $\text{---}\bar{\text{N}}\text{---})\text{CH}_2\text{---C---}(\text{C}=\text{CH}_2)$  which are spatially fixed in the way depicted in Fig. 1. The occurrence of similar long-wavelength absorption band in the case of compounds 1*a* and 1*b* indicates that for complex chromophore to be formed it is not necessary to have *n*-electrons of the oxygen atom of 1*b* in excitation state. The existence of intermolecular C—T transition, too, is highly unlikely, since the extinction curves of equimolar mixtures of substances 4*a* and 3*b*, and of 4*b* and 3*b*, do not show absorption maxima similar to these observed with single substances 1*a* and 1*b*.

**Solvent effect.** The position of long-wavelength maximum for substances 1*b* and 1*c* is little solvent-dependent (Table II). On going from more polar solvents to protonic ones there occurs small blue shift (6–8 nm), so that the excited state can be regarded as being somewhat less polar than the ground state. In this respect the behaviour of the followed absorption band resembles that of the bands due to  $n \rightarrow \pi^*$  transitions of simple chromophores<sup>2</sup>, the intensity of the absorption remains, however, practically constant in our case. By measuring several solutions differing in concentration of the studied compounds, we have established deviations from Lambert–Beer law. Thus, for example, the molar extinction coefficient at the band maximum for ethanolic

solutions of compound *1b* at 250 nm attains for the concentrations:  $5 \cdot 1 \cdot 10^{-4} \text{M}$ ,  $1 \cdot 0 \cdot 10^{-4} \text{M}$ , and  $5 \cdot 1 \cdot 10^{-5} \text{M}$  the values  $\epsilon$  1420, 1560, and 1790. Summarizing, the observed effect of solvents support the assumption<sup>6,7</sup> that we deal here with the absorption of specific type which differs somewhat from that of the so far most widely used types of chromophors.

### *Theoretical Interpretation by Means of EHMO's*

In this part of the work we will attempt to explain character of electronic excitation in the compounds under study on the basis of one-electron approximation, particularly we will try to verify by calculations qualitative assumptions concerning the possibility of  $\sigma$ -coupling<sup>6</sup> and of splitting of energetic  $\pi$ -levels<sup>8</sup>. With this aim we evaluated above all the characteristics of frontier EHMO's which were calculated for substances *1a*, *1b*, *4a*, and *6b* (Table IV). The term "frontier MO" refers here not only to LUMO and HOMO, but also to other occupied orbitals differing by c. 2 eV from the former ones, the overall energetic difference in the spectrum of studied substances being 85 eV. The calculated LCAO expansion includes in the case of EHMO's frontier orbitals essentially only  $2p$  AO's, while the importance of  $2s$  and  $1s$  spheres (hydrogen) is insignificant. To make the interpretation of directional orientation of single EHMO's with respect to partial chromophor  $\text{>C=X}$  easier, the EHT calculation was made for octant arrangement (Fig. 2) and expansion coefficients of single AO's were expressed by means of its components in the direction of proper coordinates (Table IV).

*Symmetrical properties.* Substances *1a*, *1b*, *4a*, and *6b* belong to the same point group  $C_{2v}$  and all the EHMO's followed can conveniently be classified according to their symmetry with respect to the two, mutually perpendicular planes  $xz$  and  $yz$  (Fig. 2). Table II presents corresponding symbols S and A which denote symmetrical or antisymmetrical behaviour with respect to the mentioned symmetry elements; the first value relates to the plane of the double bond of the partial chromophor  $\text{>C=X}$ , i.e.  $xz$  plane. We started from working hypothesis that contributions to long-wavelengths absorption may be due to electronic transitions between bonding and antibonding levels of the same symmetry, which are further referred to as "allowed" transitions. These can be considered as the most probable ones and they can be therefore associated with strong absorption bands of substances *1a* and *1b*. From eigenvalues of one-electron EHT-hamiltonians presented in Table IV it is evident that only LUMO's of type  $\pi^*$  can be regarded as antibonding levels, since subsequent  $\sigma^*$  levels are energetically too distant. The symmetry of LUMO, which is in all cases of the AS type is then the decisive factor for the choice of appropriate bonding levels.

*Orbital interactions and electronic transitions.* In Fig. 5 are graphically represented qualitative correlation diagrams of interacting electronic levels in substances

*Ia* and *Ib*, drawn with regard to the results of EHT calculations. It is evident that in both cases there is distinct orbital interaction of two  $n$  levels with four  $\sigma$  levels (in the sense of the situation shown in Fig. 1) "through space", leading to components  $n_{SS}$  and  $n_{AS}$ , or to  $\sigma_{SS}$ ,  $\sigma_{SA}$ ,  $\sigma_{AS}$ , and  $\sigma_{AA}$ . Further interactions of symmetry "allowed" levels  $n_{AS}$  and  $\sigma_{AS}$  depend on their energetic difference from  $\pi_{AS}$  or  $\pi_{AS}^*$  levels. For the olefinic partial chromophore in substance *Ia*, the  $\pi_{AS}$  level lies between  $n_{AS}$  and  $\sigma_{AS}$ . As the result, the interaction of these three levels leads to formation of new mixed levels of the orbital type  $(n\pi\sigma)_{AS}$ , which correspond to MO's  $\varphi_{29}$ ,  $\varphi_{32}$ , and  $\varphi_{38}$  of EHT calculation. It can easily be seen that for studied type of ultraviolet absorption of substance *Ia*, the following singlet-singlet transitions has to be considered:  $\varphi_{29} \rightarrow \varphi_{28}$ ,  $\varphi_{32} \rightarrow \varphi_{28}$ , and perhaps also  $\varphi_{38} \rightarrow \varphi_{28}$ . These all are altogether of type  $(n\pi\sigma)^2 \rightarrow (n\pi^*\sigma)^0$ , i.e. between delocalized bonding states of  $n$ -electrons and antibonding  $\pi^*$ -states (Fig. 6). In the case of carbonyl chromophore in substance *Ib* the bonding  $\pi_{AS}$  level is energetically low lying ( $\varphi_{46}$ ) and then there occurs only

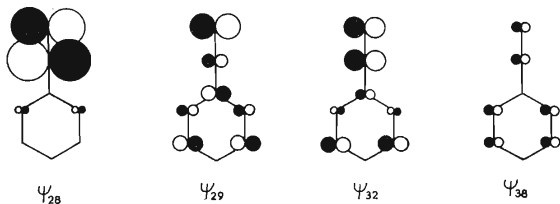


FIG. 6

Spectroscopically Significant EHMO's of 1,3-Diaza-6-methylenadamantane (*Ia*)  
Only directional components of  $2p_y$ AO's are represented.

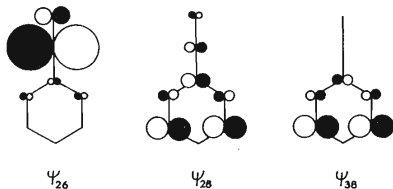


FIG. 7

Spectroscopically Significant EHMO's of 1,3-Diaza-6-adamantanone (*Ib*)  
Only directional components of  $2p_y$ AO's are represented.

interaction of energetically highest  $(n\sigma)'_{AS}$  component with close antibonding level  $\pi^*_{AS}$  to form one bonding and one antibonding level of mixed type  $(n\pi^*\sigma)_{AS}$ , (Fig. 7). For long-wavelength ultraviolet absorption of ketone *1b* it remains to consider the electronic transition between following delocalized MO's  $\varphi_{28} \rightarrow \varphi_{26}$ , and presumably also  $\varphi_{38} \rightarrow \varphi_{26}$ , of the type  $(n\pi^*\sigma)^2 \rightarrow (n\pi^*\sigma)^0$ , Fig. 5.

In the case of 2-adamantanone (*4a*) and of isoelectronic dication *6b* there occurs only the interaction of  $\sigma_{AS}$  with  $\pi^*_{AS}$  components, which leads to smaller mixing of bonding level of central  $\sigma$ -bonds with antibonding  $\pi^*$ -MO and to the formation of comparatively more delocalized bonding  $\sigma$ -levels mixed with  $\pi^*$ -level. Within the framework of EHT calculation of substance *4a* this situation is represented by MO's  $\varphi_{28}$ ,  $\varphi_{31}$ , and  $\varphi_{35}$ , and in the case of dication *6b* by MO's  $\varphi_{28}$ ,  $\varphi_{31}$ , and  $\varphi_{36}$  (Table IV). The electronic transitions responsible for the formation of long-wavelength absorption in both compounds *4a* and *6b* are in the main  $\varphi_{31} \rightarrow \varphi_{28}$ , *i.e.* essentially of the  $\sigma \rightarrow \pi^*$  type. Transitions of analogous type have been found also when strict symmetrical rules have not been applied to substances *4a* and *6a* because of low intensity of experimental absorption bands (Table V). This is, at least to some extent, surprising, since it is generally assumed that the longest wavelength absorption bands of ketones are due to  $n \rightarrow \pi^*$  transitions of carbonyl chromophors<sup>2,25,26</sup>. We believe that this problem, especially in the case of more complex carbonyl derivatives, still remains to further investigate.

From Table V it is evident that the above mentioned electronic transitions satisfactorily describe the relations in *positions* of absorption maxima in the electronic spectra of substances *1a*, *1b*, *4a*, and *6b*. Remarkable analogy arises also on examination of unsymmetrical band at 224 nm in the spectrum of exomethylene derivative *1a*, which can be easily separated to two, mutually overlapping bands (Fig. 8). Excitation energies found, 5.41 eV and 5.87 eV, are comparable with analogous data calculated for transitions  $\varphi_{29} \rightarrow \varphi_{28}$ , and  $\varphi_{32} \rightarrow \varphi_{28}$  (Table V). On the other hand, the long-wavelength band of 6-ketone *1b* at 250 nm is symmetrical and then comparable with the energy of the presumed single dominant transition  $\varphi_{28} \rightarrow \varphi_{26}$ . Even with taking into account the neglect of CI in our approach, these facts seem to support our theoretical assumptions, which are then in accordance with empirical conclusions drawn from experimental data, particularly that long wavelength absorption of substance *1a* and *1b* is due to excitation of  $n$  electrons of *nitrogen* atoms.\* Mutual splitting of levels (Fig. 5) and significant delocalization to the region of

\* With the use of the transitions of this type also *blue* shift of the long wavelength absorption maximum of hydroxy derivative *5b* relative to desoxy derivative *5a* (Table III) can be accounted for. The presence of electronegative hydroxyl group in the vicinity of nitrogenous partial chromophor brings about a decrease of energy of the  $n$ -level, which results in the *increase* of excitaton energy.

central  $\sigma$ -bonds (Figs 6 and 7) agree with both alternative qualitative presumptions<sup>8,9</sup>, which are not then contradictory. At the same time it is also highly probable that the increased intensity observed with substances *Ia* and *Ib* is due to participation of

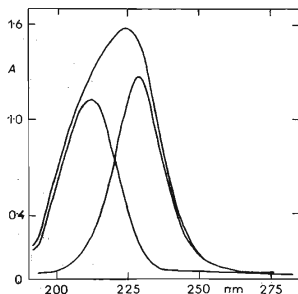


FIG. 8.  
Separation of Overlapping Bands in Ultraviolet Spectrum of 1,3-Diaza-6-methylenadamantane (*Ia*)  
A Absorbance.

TABLE V

Most Probable Electronic Transitions in EHT Models of Substances *Ia*, *Ib*, *4a*, and *6b* (CI Not Considered)

Substance	Transition $\varphi_i \rightarrow \varphi_j$		Energy eV	Experiment eV <sup>b</sup>
	<i>i-j</i>	type <sup>a</sup>		
<i>Ia</i>	29-28	$(n\pi\sigma)^2 \rightarrow (n\pi^*\sigma)^0$	4.50	5.41
	32-28	$(n\pi\sigma)^2 \rightarrow (n\pi^*\sigma)^0$	5.45	5.87
	38-28	$(n\pi\sigma)^2 \rightarrow (n\pi^*\sigma)^0$	6.87	— <sup>c</sup>
<i>Ib</i>	28-26	$(n\pi^*\sigma)^2 \rightarrow (n\pi^*\sigma)^0$	3.69	4.96
	38-26	$(n\sigma)^2 \rightarrow (n\pi^*\sigma)^0$	6.15	— <sup>c</sup>
<i>4a</i>	31-28	$(\pi^*\sigma)^2 \rightarrow (\pi^*\sigma)^0$	3.36	} 4.27
	34-28 <sup>d</sup>	$\sigma^2 \rightarrow (\pi^*\sigma)^0$	4.14	
	35-28	$(\pi^*\sigma)^2 \rightarrow (\pi^*\sigma)^0$	4.70	
	39-28	$\sigma^2 \rightarrow (\pi^*\sigma)^0$	5.56	} 5.93
	41-28 <sup>d</sup>	$\sigma^2 \rightarrow (\pi^*\sigma)^0$	5.74	
<i>6b</i>	31-28	$(\pi^*\sigma)^2 \rightarrow (\pi^*\sigma)^0$	4.20	} 5.1
	34-28 <sup>d</sup>	$\sigma^2 \rightarrow (\pi^*\sigma)^0$	5.05	
	36-28	$(\pi^*\sigma)^2 \rightarrow (\pi^*\sigma)^0$	5.63	— <sup>c</sup>

<sup>a</sup> Population number given by index; <sup>b</sup> position of absorption maxima; <sup>c</sup> beyond the scale of the instrument used (<200 nm); <sup>d</sup> symmetry forbidden transitions.

mixed levels of the types  $(n\pi\sigma)_{AS}$  and  $(n\pi^*\sigma)_{AS}$  representing "σ-coupling" in complex system of chromophors. Definitive confirmation of this assumption is to be expected from explicit consideration of configurational interaction on theoretical treatment.

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*Note added in proof:* After the present work had been submitted to publication, the more detailed quantum chemical study of α-aminocarbonyl chromophor was published (Levin Ch. C., Hoffmann R., Hehre W. J., Hudec J.: J. Chem. Soc., Perkin. Trans. II, 210 (1973)) in which four major types of spectroscopically significant interactions have been recognized. In view of the rigid conformation of the cyclic system in substances 1b and 1c in the sense of Fig. 1, especially the interactions "through bond coupling" has to be considered in our case, in agreement with our conclusions. In accordance with the mentioned authors, the one-electron approximation used in this work can be regarded as reasonable approach to interpretation of absorption anomalies, since one-electron terms in the expression for excitation energy  $\Delta E_{j \rightarrow i} = \epsilon_i - \epsilon_j - J_{ij} + 2K_{ij}$  can be assumed as dominant in the case of transitions of the  $n \rightarrow \pi^*$  type (cf. Ditchfield R., Del Bene J. E., Pople J. A.: J. Am. Chem. Soc. 94, 703 (1972)).

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