Benzo[*b*]cyclohepta[*e*][1,4]thiazines and Their Diazine Analogues. III.[1] π-Electronic Structures of 5*H*, 11*H*$^+$-Cyclohepta[*b*]quinoxalinium Ions and Their O- and S-Analogues

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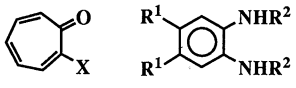
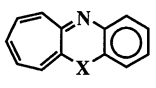
π-Electronic structures of 5*H*,11*H*$^+$-cyclohepta[*b*]quinoxalinium ions and their O- and S-analogues were elucidated by means of ^{1}H and ^{13}C NMR spectra, electronic spectra, and theoretical calculations. Consequently, it was shown that these compounds had very stable aromatic characters with positive resonance energies and that the 6π-tropylium-6π-benzonoid form plays an important role for the π-conjugation structure.

On of the authors (T.N.) and his co-workers[2] reported more than thirty years ago that the reaction of 2-chloro- and 2-methoxytropone (**1a,b**) with *o*-phenylenediamine (**2a**) gave 5*H*-cyclohepta[*b*]quinoxaline (**3a**), which they named "benzo[*b*]tropazine".

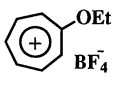


1a X=Cl
b X=OMe

2	R^1	R^2
a	H	H
b	Me	H
c	H	Me



3a X=NH
b X=NMe
c X=O
d X=S



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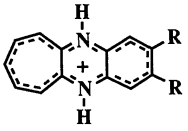
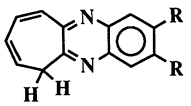
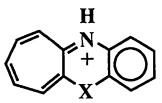
In 1971, Fukunaga[3a] reported that the reaction of ethoxytropylium tetrafluoroborate (**4**) with **2a** and its dimethyl derivative (**2b**) gave greenish-black crystals of **5a** and **5b**, which upon basification produced free compounds **6a** and **6b** that reverted to **5a,b** quantitatively



5a R=H
b R=Me



6a R=H
b R=Me



7a X=NH
b X=NMe
c X=O
d X=S

upon acidification. He proposed that the structure of **6** was the quinoxaline form (namely an isomer of **3a**), and that the salt **5** existed as a resonance-stabilized, peripheral anti-Hückel 16π-electron system based on the evidence of detailed NMR studies of **3a** and its related compounds.[3b] He also suspected that our colorless compound[2] reported as "purified" benzotropazine should have been a dimer of his 6*H*-cyclohepta[*b*]quinoxaline **6a**, but he did not study the structure of the dimer any further. On the other hand, according to our study, benzo[*b*]cyclohept[*e*][1,4]oxazine **3c** and its S-analogue **3d**[5,6] gave the red-colored cations **7c** and **7d**, respectively, under acidic conditions. Later, we also confirmed[1] that compound **3a** existed as a tautomeric form **6a**, and on acidification **6a** was converted into a dark-green salt **7a** which showed intense long-wavelength absorption bands at 500—800 nm; no such bands were observed in the spectra of **7c** and **7d** in acid.

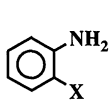
From the standpoint of synthetic and theoretical interest, we recently started the re-investigation of the electronic structures and reactivities of various troponoids and azulenoid compounds. In a previous paper, we reported[7] that the fundamental skeleton of the tropones possessing a unique heptagonal structure may be predicted to be aromatic with positive resonance energies[8] conforming to Gimarc's topological charge stabilization rule (TCS rule).[9] We also found that naturally occurring tropolones nicely fit the theory that conformity to the TCS rule provides a stable molecular system.

In order to clarify the π-electronic structures of the neutral species **3a**—**d** and their cationic species **7a**—**d**, we now wish to describe here a detailed study of their NMR spectra, electronic spectra, and theoretical considerations. Resonance energies, circuits resonance energies, and ring currents of these compounds were also estimated by the use of Aihara's method.[8] The HMO theory is assumed to be in its simplest form. Streitwieser evaluated the heteroatom parameters for the amine nitrogen, the imine nitrogen, the ether oxygen, and the ketone oxygen.[10] In this paper, we adopted these values with some other heteroatom parameters.[11,12]

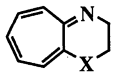
Results and Discussion

NMR Spectra. The ^{1}H NMR spectra of **3b** and its O- and S-analogues were compared with the spectra of some related compounds such as aromatic amines **2a,c** and **8a,b**, 1*H*-2,3-dihydrocycloheptapyrazines **9a,b** and their thiazine analogue **9c**, and their cations **10a**—**c**,[13] *N*-methylated cations **11a,b**[13] and **12a**—**c**,[1,6,14] quinoxaline (**13**) and phenazine (**14**).

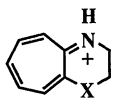
The average chemical shift (δ_{av}) values of protons on the seven-membered and benzene rings and the differences ($\Delta\delta_{av}$) of the average chemical shift values be-



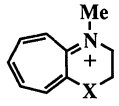
8a X=OH
b X=SH



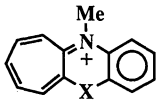
9a X=NH
b X=NMe
c X=S



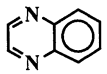
10a X=NH
b X=NMe
c X=S



11a X=NMe
b X=S



12a X=NMe
b X=O
c X=S



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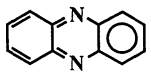

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tween the neutral species and the corresponding cationic species are listed in Table 1.

Noting the differences of the average chemical shifts of the rings between solvents, the signals in CD_3CN shifted slightly to a lower field compared with those in $CDCl_3$, but this difference was smaller than 0.1 ppm. Under acidic conditions, the chemical shifts moved with the acid concentration, but this change in 20% CF_3COOD nearly agreed with those in CF_3COOD, and its difference as compared with that of the BF_4^- salt in CD_3CN was smaller than 0.1 ppm, suggesting that there were no problems in discussing $\Delta\delta_{av}$.[15]

In order to clarify the relationship between the NMR chemical shifts and π-electron distributions, the π-electron densities of **3a**—**d** and the related compounds were calculated by the MNDO method.[16] There is a quantitative relationship between NMR chemical shifts and electron distributions in aromatic molecules, as reported by many authors.[17] The suggested equations for protons (1) and for carbons (2) seem to have gathered the most support, where the $\Delta\delta$ values are the chemical shift changes and ρ_π is the change in charge.

$$\Delta\delta_H = 10.7\,\rho_\pi \quad (1)$$

$$\Delta\delta_C = 160\,\rho_\pi \quad (2)$$

The $\Delta\delta_{av}$ values of aromatic diamines **2a**—**c** were shown to be larger than those of **8a,b**. The relative values were related to the basicity of these amines.[18] In the NMR spectra of 1*H*-2,3-dihydrocyclohepta[*b*]-pyrazines (**9a,b**)[13] and their S-analogue **9c**,[13] the δ_{av} values of the protons on the seven-membered ring became slightly smaller compared with those of the benzene ring of the aromatic amines **2a**—**c** and **8a,b**. The $\Delta\delta_{av}$ value of **9c** was slightly larger than those of diamines **9a,b** which have higher basicity. The $\Delta\delta_{av}$ values of *N,N'*-dimethyl (**11a**)[13] and *N*-methyl cation (**11b**)[13] are nearly equal to those of the cationic species **10a** and **10c**. The π-electron densities of compounds **9**—**11** are shown in Fig. 1.

The π-electron distributions of the troponeimine part of **9** and **11** were similar to each other, whereas the π-electron densities on the nitrogen atom at position 1 of **10** were more negative than those of **9** and **11**. The sum of the π-electron densities of the seven-membered ring carbons of the cationic species were smaller than those of the neutral species. Though the δ_{av} values of the benzene ring of free compound **6a** were similar to those of quinoxaline **13** and phenazine **14**, these values were demonstrated to be shifted to a lower magnetic field compared with those of *N*-methyldiazine **3b** and its O-(**3c**) and S-analogues (**3d**). These results suggested that, as the π-conjugated system of **6a** differed from those of

Table 1. ^{1}H NMR of Cyclohepta[*b*]quinoxalines and Their O- and S-Analogues and Their Related Compounds

Compd	Protons	δ_{av}		$\Delta\delta_{av}$	Compd	Protons	δ_{av}		$\Delta\delta_{av}$
		Neutral (1)	Acidic (2)	(2)−(1)			Neutra (1)	Acidic (2)	(2)−(1)
2a	H_{3-6}	6.54[a)]	7.28[c)]	0.74	**3c**	H_{1-4}	6.61[a)]	6.80[a,s)]	0.10
2b	$H_{3,6}$	6.37[a)]	7.23[c)]	0.86		H_{6-10}	5.83	7.14	1.31
2c	$H_{3,6}$	6.70[b)]	7.75[d)]	1.05	**12b**	H_{1-4}	6.61[g)]	6.97[a,s)]	0.36
8a	H_{3-6}	6.60[e)]	7.15[f)]	0.55		H_{6-10}	5.83[g)]	7.36	1.53
8b	H_{3-6}	6.90[a)]	7.40[c)]	0.50	**3d**	H_{1-4}	6.96[a)]	6.95[a,s)]	−0.01
13	$H_{2,3}$	8.86[a)]	9.31[c)]	0.45		H_{6-10}	6.22	7.13	0.91
	H_{5-8}	7.97	8.31	0.34	**12c**	H_{1-4}	6.96[g)]	7.31	0.35
14	H_{1-4}	8.06[e)]	8.45[f)]	0.39		H_{6-10}	6.22[g)]	7.68	1.46
9a	H_{5-9}	6.32[b)]	7.33[c)]	1.01	**6a**	H_{1-4}	7.96[b)]		
9b	H_{5-9}	6.35[b)]	7.32[c)]	0.97		H_{7-10}	6.62		
11a	H_{5-9}	6.35[g)]	7.23[a)]	0.88	**7a**	H_{1-4}		6.32	
9c	H_{5-9}	6.45[b)]	7.61[c)]	1.16		H_{6-10}		6.13	
10c	H_{5-9}	6.45[g)]	7.55[a)]	1.10	**6b**	H_{1-4}	7.36[b)]		
3b	H_{1-4}	6.47[a)]	6.57[a,s)]	0.10		H_{7-10}	6.33		
	H_{6-10}	5.33	6.38	1.05	**5b**	H_{1-4}		5.94[a,s)]	
12a	H_{1-4}	6.47[g)]	6.81[a,s)]	0.34		H_{6-10}		6.00	
	H_{6-10}	5.33[g)]	6.71	1.38					

Solvent: a) CD_3CN. b) $CDCl_3$. c) CD_3CN+CF_3COOD. d) $CDCl_3$+CF_3COOD (6:1). e) CD_3CN+$CDCl_3$ (1:1). f) CD_3CN+$CDCl_3$+CF_3COOD (2:2:1). g) Value for the neutral species of the parent compounds. s) The BF_4^- or SO_3F^- salt.

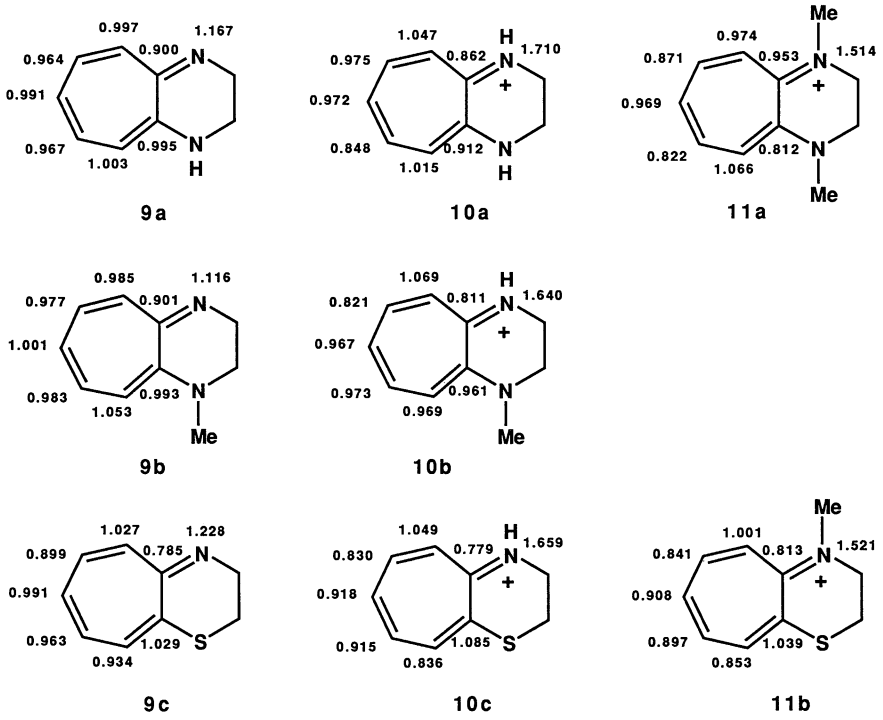


Fig. 1. π-Electron densities of **9**, **10**, and **11** by the MNDO method.

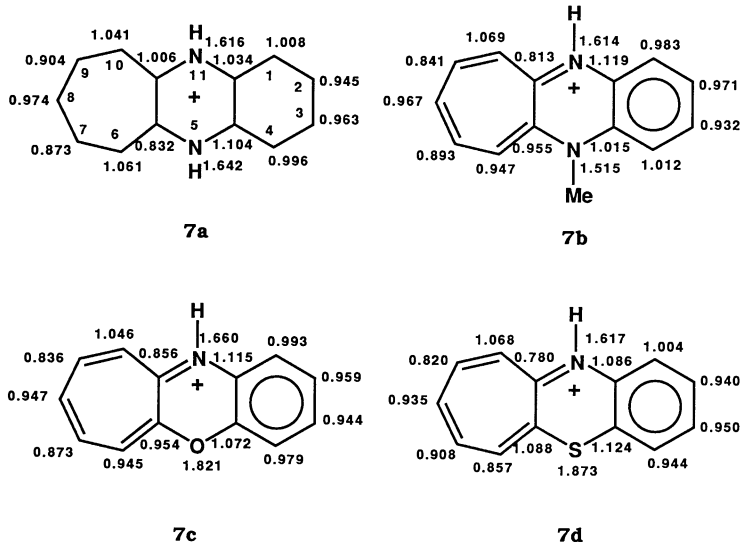


Fig. 2. π-Electron densities of 7 by the MNDO method.

3b—**d**, compound **6a** be removed from discussion of the π-electronic systems of **3a**—**d** and **7a**—**d**. The δ_{av} values of the protons on the benzene and seven-membered rings of $5H,11H^{+}$-cyclohepta[*b*]quinoxalinium ion (**7a**) appeared upfield by 0.5—0.6 and 1.0 ppm, respectively, compared with those of the O-(**7c**) and S-analogues (**7d**). The latter values were approximately proportional to differences in their π-electron density (Fig. 2). Although it was not possible to interpret their chemical shift changes in terms of the change in charge, the π-electron density of **7a** was larger than those of **7c** and **7d**. The $\Delta\delta_{av}$ between **7a** and **7c** or **7d** were calculated to be 0.36 ppm from Eq. 1. The δ_{av} values of **3b** and **7b** were smaller than those of **3c,d** and **7c,d**.

The $\Delta\delta_{av}$ values of the protons on the benzene ring of **3b**—**d** were much smaller than those of the aromatic amines **2a**—**c**, whereas the $\Delta\delta_{av}$ values of the seven-membered protons of **3b**—**d** were larger than those of **2a**—**c** and were similar to those of dihydropyrazines **9a,b**. In the NMR spectra of **3b**—**d**, the signals of the protons

on the benzene ring shifted slightly to a lower field, whereas the signals of the seven-membered ring protons shifted largely to a lower field under acidic conditions. The π-electron densities of **6a,3**, and **12** are shown in Fig. 3. The correlation coefficients between the calculated $\Delta\delta_H$ values and the observed $\Delta\delta_{av}$ values of the seven-membered rings in the N-, O-, and S-analogues were 0.92, 0.99, and 0.97, respectively.

The δ_{av} and $\Delta\delta_{av}$ values of the ^{13}C chemical shifts of **3b—d**, **7a—d**, and **12a** are listed in Table 2, where the $\Delta\delta_{av}$

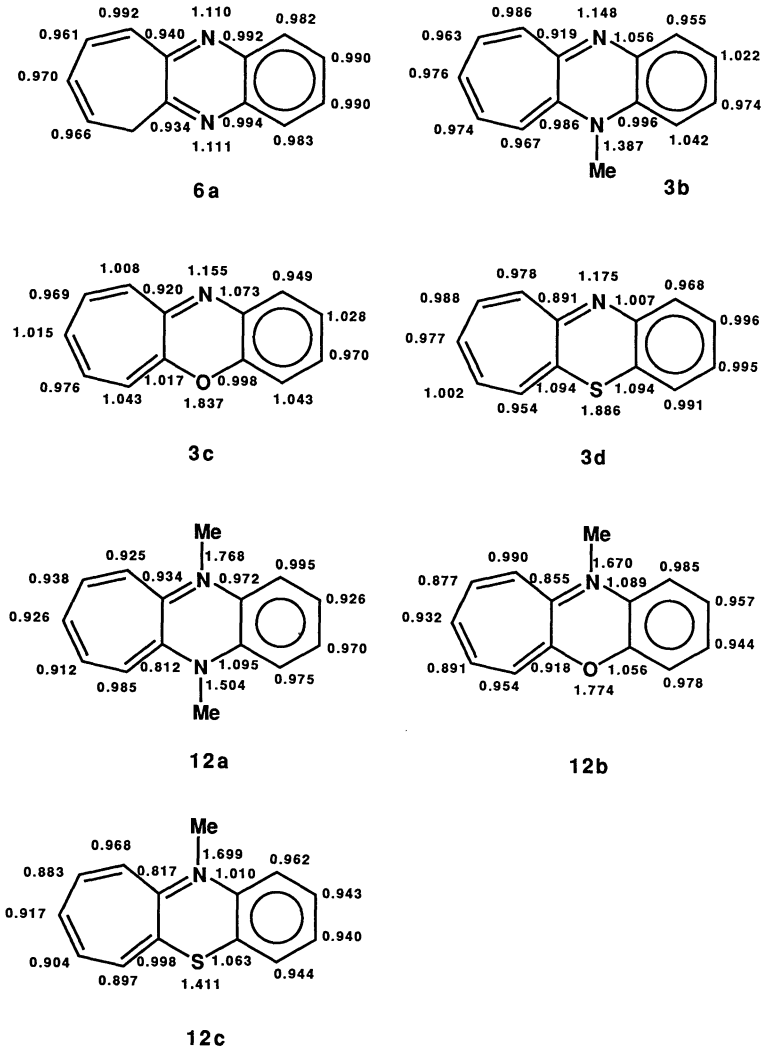


Fig. 3. π-Electron densities of **6**, **3**, and **12** by the MNDO method.

Table 2. ^{13}C NMR of Cyclohepta[*b*]quinoxalines and Their O- and S-Analogues (100 MHz in CD_3CN)

	δ_{av} Benzene ring (1)	δ_{av} Seven-membered ring (2)	$\Delta\delta_{av}$ (2)−(1)	$\Delta\delta_C^{calcd}$
7a	125.8	141.5	15.7	8.4
7b	126.7	141.6	14.9	12.6
12a	126.4	141.9	15.5	11.2
7c	127.8	144.5	16.7	14.1
7d	127.5	144.7	17.2	13.8
3b	129.1	136.8	7.7	6.6
3c	130.0	138.8	8.8	2.8
3d	129.0	138.8	9.8	4.2

$\Delta\delta_C^{calcd}$ values were calculated from Eq. 2.

values were the differences between the δ_{av} of the seven-membered and benzene ring carbons. The $\Delta\delta_{av}$ of **7a,b** and **12a** were similar in magnitude to their O- and S-analogues. The cationic species had larger $\Delta\delta_{av}$ values than the neutral species.

From the above-cited NMR spectral data, the heteroatoms of **3b—d** and related compounds were closely related to the seven-membered ring rather than the benzene ring. The cationic species had the smallest values for π-electron densities compared with their neutral species. The change in charge seemed to be one of the reasons for its lower field shifts.

Resonance Energies and Circuit Currents. Resonance energies, circuit resonance energies, and circuit currents of **3**, **7**, and **12** were calculated by Aihara's graph theory of aromaticity.[8] Geometrically unidentical π-electron circuits are shown and numbered in Fig. 4. The results are listed in Table 3. Compounds **3**, **7**, and **12** could be regarded as aromatics with positive resonance energies. The cationic species possessed larger resonance energies than the neutral species. From the calculated circuit resonance energies of each ring, the circuit resonance energies of r_1 and r_3 showed positive values, while the values of r_2, r_4, r_5, and r_6 were very small or negative. Consequently, compounds **3a,b** and **7a,b** were stabilized as the 6π-tropylium-6π-benzenoid form similar to the O- and S-analogues, but not as a 16π-peripheral system as was suggested by Fukunaga.[3]

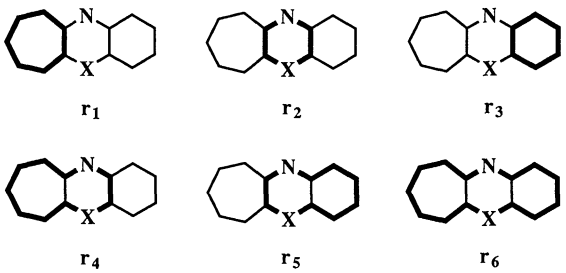


Fig. 4. Geometrically unidentical π-electron circuits.

The calculated circuit currents are also shown in units of I_0 in Table 3. The plus and minus signs in the Table indicate diatropism and paratropism, respectively. Large diatropism was predicted to arise from r_1 and r_3, while large paratropism was predicted to arise from r_4 and r_6. As for compound **3b**, the diatropism effect due to the 6π-tropylium structure (i.e., structure r_1: $0.997I_0$) and the 6π-benzenoid part (i.e., structure r_3: $0.881I_0$) was the main contributor to the magnetic effect, although a small contribution came from the diatropism effect of the heterocyclic part (i.e., structure r_2: $0.094I_0$, r_5: $0.175I_0$) and the paratropism effect due to the peripheral 16π-structure (i.e., structure r_6: $-0.155I_0$). Such a tendency was also found for the O- and S-analogues. Thus, theoretical considerations suggested that the 6π-tropylium-6π-benzenoid form played a crucial role in the stabilization of 5*H*,11*H*$^+$-cyclohepta[*b*]quinoxalinium ions and their O- and S-analogues, and the downfield shifts of the seven-membered ring protons were due to its large diatropism.

Electronic Spectra of 3 and 7. In the electronic spectra of **7a—d**, the bands in the visible region showed large red shifts with increased intensities compared with those of the corresponding neutral species **3a—d**, as mentioned previously.[1,4,6] Compounds **3b** and **3c** showed four electronic absorption bands in the long wavelength region (500—800 nm). It is interesting to note that the cationic species, **7a**, **7b**, and the free *N*-methyl compound **3b**, had almost the same deep green color and very similar absorption bands. For example, **7b** showed long wavelength absorption bands at 564, 616, 670, and 752 nm (log ε 3.01, 2.91, 2.83, and 2.34). On the other hand, compounds without a benzene ring, such as **9a—c**, **10a—c**, and **11a,b**, did not show these absorption bands in the same region.[13] These absorption bands were thus closely related to the π-electronic structure of the benzene ring.

We have also calculated the electronic transition of these compounds by the CNDO/S-CI method.[19] The coefficient distribution of the three highest occupied and the three lowest unoccupied π orbitals are shown in Fig.

Table 3. Resonance Energies, Circuit Resonance Energies, and Circuit Currents of Title Compounds

	Resonance energies and circuit resonance energies (in β units)							Circuit currents (in benzene, I_0 units)					
	RE	r_1	r_2	r_3	r_4	r_5	r_6	r_1	r_2	r_3	r_4	r_5	r_6
3c	0.310	0.118	0.011	0.198	−0.019	0.005	−0.015	1.037	0.051	0.893	−0.488	0.084	−0.802
3d	0.256	0.113	0.019	0.196	−0.014	0.009	−0.020	0.993	0.085	0.880	−0.610	0.157	−1.043
3a	0.299	0.116	0.017	0.197	−0.024	0.008	−0.020	1.023	0.078	0.886	−0.610	0.136	−1.023
3b	0.291	0.113	0.021	0.196	−0.026	0.010	−0.022	0.997	0.094	0.881	−0.676	0.175	−1.155
7c	0.446	0.175	−0.002	0.216	−0.006	−0.001	−0.004	1.544	−0.007	0.970	−0.151	−0.018	−0.230
12b	0.420	0.173	−0.001	0.215	−0.007	−0.001	−0.005	1.527	−0.005	0.967	−0.168	−0.014	−0.258
7d	0.426	0.168	0.001	0.213	−0.008	−0.000	−0.006	1.478	0.004	0.958	−0.201	−0.003	−0.313
12c	0.420	0.166	0.002	0.212	−0.009	0.000	−0.007	1.463	0.008	0.954	−0.222	0.004	−0.349
7a	0.446	0.175	−0.002	0.216	−0.006	−0.001	−0.004	1.544	−0.007	0.970	−0.151	−0.018	−0.230
7b	0.421	0.168	0.001	0.213	−0.009	−0.000	−0.007	1.476	0.003	0.957	−0.221	−0.004	−0.343
12b	0.434	0.172	−0.000	0.214	−0.007	−0.001	−0.006	1.511	−0.002	0.963	−0.187	−0.010	−0.289

RE: Resonance energy (in β units).

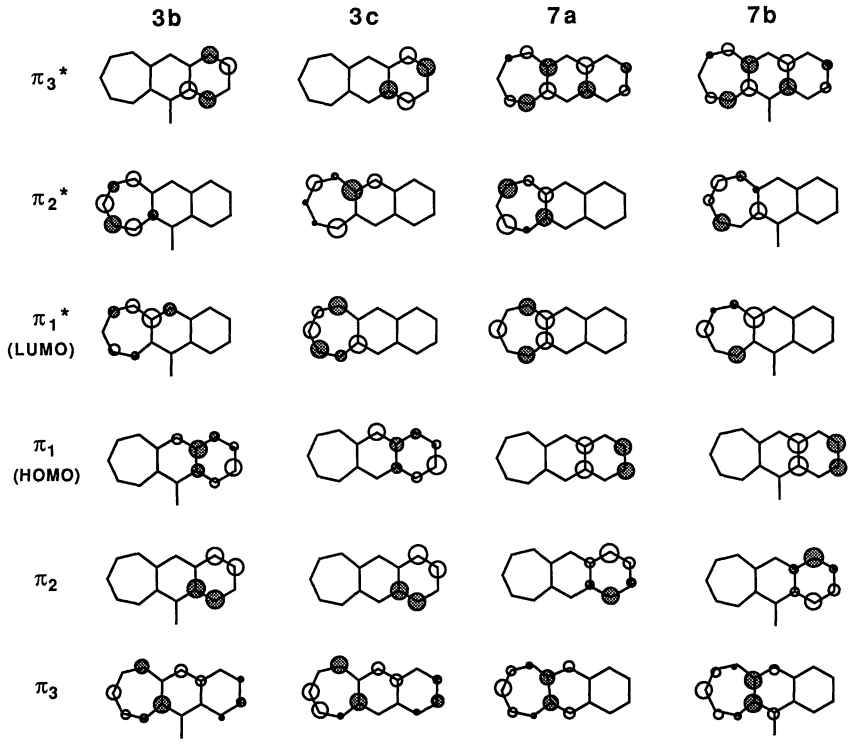


Fig. 5. Topology of the frontier orbitals of **3b**, **c** and **7a**, **b** (CNDO/S-CI calculations). Sizes of circles are roughly proportional to the coefficient values.

Table 4. Electronic Transitions (eV) in the Long Wavelength Region of Compounds **3b**, **7a**, and **7b**

3b			7a			7b		
E[a)]	f	Nature	E[a)]	f	Nature	E[a)]	f	Nature
2.36	0.001	$\pi_1 \rightarrow \pi_3^*$	2.02	0.004	$\pi_1 \rightarrow \pi_2^*$	2.05	0.037	$\pi_1 \rightarrow \pi_1^*$
2.58	0.298	$\pi_1 \rightarrow \pi_1^*$	2.12	0.050	$\pi_1 \rightarrow \pi_1^*$	2.26	0.006	$\pi_1 \rightarrow \pi_2^*$
3.09	0.007	$\pi_1 \rightarrow \pi_2^*$	2.36	0.015	$\pi_2 \rightarrow \pi_2^*$	2.35	0.009	$\pi_2 \rightarrow \pi_1^*$
3.32	0.045	$\pi_3 \rightarrow \pi_2^*$	2.42	0.000	$\pi_2 \rightarrow \pi_1^*$	2.44	0.000	$\pi_1 \rightarrow \pi_5^*$
3.41	0.029	$\pi_2 \rightarrow \pi_1^*$	2.51	0.011	$\pi_2 \rightarrow \pi_2^*$	2.54	0.004	$\pi_3 \rightarrow \pi_2^*$
3.53	0.056	$\pi_1 \rightarrow \pi_4^*$	2.65	0.001	$\pi_3 \rightarrow \pi_2^*$	2.55	0.000	$\pi_2 \rightarrow \pi_2^*$
3.59	0.036	$\pi_4 \rightarrow \pi_1^*$	2.70	0.009	$\pi_3 \rightarrow \pi_1^*$	2.65	0.022	$\pi_3 \rightarrow \pi_1^*$
3.85	0.197	$\pi_1 \rightarrow \pi_5^*$	3.49	0.000	$\pi_1 \rightarrow \pi_3^*$	3.49	0.004	$\pi_1 \rightarrow \pi_4^*$
4.05	0.193	$\pi_2 \rightarrow \pi_2^*$	3.87	0.067	$\pi_2 \rightarrow \pi_6^*$	3.82	1.170	$\pi_4 \rightarrow \pi_2^*$

a) E (eV) is the energy of the transitions; f (dimensionless) is the oscillator strength.

5. They were similar to each other. Therefore, the calculated electronic transitions were predicted to have very similar absorption bands. The electronic transitions calculated for **3b**, **7a**, and **7b** are collected in Table 4. The free *N*-methyl compound **3d** showed two $\pi \rightarrow \pi^*$ electronic transitions at 2.58 and 3.09 eV, corresponding to $\pi_1 \rightarrow \pi_1^*$ and $\pi_1 \rightarrow \pi_2^*$, whereas its cation **7b** showed corresponding transitions at 2.05 and 2.26 eV, respectively.

From the coefficient distribution as shown in Fig. 5, these bands could be attributed to an intramolecular charge-transfer transition from the benzene ring part to the seven-membered ring part. CNDO/S calculations satisfactorily reproduced the red shift observed in the long wavelength region of the neutral spcies and their cationic species **7a**—**d**.

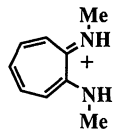
Molecular Geometries. The geometry optimizations of **3**, **6**, **7**, and **9**—**12** were carried out with optimization of all geometrical parameters with no assumptions whatsoever. In **3b**—**d** and related compounds, the C–C bonds of the benzene ring were 1.40—1.43 Å, the formular double bonds of the seven-membered ring were 1.35—1.39 Å, the C–C single bonds were 1.40—1.47 Å, except for the C-5a–C-10a bonds which were 1.45—1.49 Å. The C-10a–N-11 bonds were 1.31—1.37 Å, the C-11a–N-11 bonds were 1.40—1.44 Å. In the oxazines,

the C–O bonds were 1.35—1.38 Å.

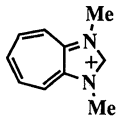
In the thiazines, the C–S bonds were 1.68—1.70 Å. CNDO/S calculations adopted these optimized values.

Concluding Remarks

Fukunaga[3b] compared the NMR and electronic spectra of compounds **6a**—**b**, **15**, and **16** with the reference compounds **5a,b**.

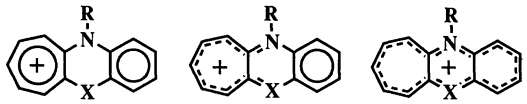


15



16

The ^{1}H NMR spectra of **5a**—**b** indicated large upfield shifts of the ring-proton signals compared with those of the benzene ring of **6** and the seven-membered ring protons of **15** by 1.2—1.9 ppm. Such a large upfield shift arose from the paramagnetic ring current effect. He believed that **5a,b** existed as a resonance-stabilized, peripheral 4nπ-electron system. We assumed three models (I—III) for the π-electronic structures of **7a**—**d**.



I **II** **III**

From the above-cited spectral data and theoretical calculations, we propose that the heteroatoms of **7a**—**d** are closely related to the seven-membered ring rather than the benzene ring. The positive charge is delocalized over the seven-membered ring (Type I). This suggests that contributions of the 10π-2-aminotroponiminium structure (Type II) and 16π-peripheral conjugation structure (Type III) are negligible. The electronic structures of **7a**—**d** can not be elucidated solely by II, because the electronic spectra of **10** and **11** do not show absorption bands in the long wavelength region. In view of these absorption bands that can be attributed to an intramolecular charge-transfer transition, the π-conjugation system of 5*H*,11*H*$^+$-cyclohepta[*b*]quinoxalinium ions and their O- and S-analogues are shown by the contribution of I. Therefore, we conclude that the title compounds are stabilized as a 6π-tropylium–6π-benzenoid system (I) and the appearance of their color is due to the intramolecular charge-transfer transition.

Experimental

General. NMR spectra were re-measured as CD_3CN and $CDCl_3$ solutions on JEOL JNM PS100 (100 MHz), GX 270 (270 MHz) and GX 400 (400 MHz) spectrometers with TMS as the internal standard. The UV-vis spectra were recorded with Shimadzu UV-202 or Hitachi 557 spectrometers.

Materials. Aromatic amines were purchased from Wako Pure Chemicals Ind. Benzo[*b*]cyclohepta[*e*][1,4]thiazines and the related compounds were prepared according to the reported methods.[1,4,6,13]

***o*-Phenylenediamine (2a):** ^{1}H NMR (CD_3CN) δ=6.54 (4H, s, ar-H) and 3.60 (4H, br, NH_2); (20% CF_3COOD–CD_3CN) δ=7.28 (4H, ar-H).

4,5-Dimethyl-*o*-phenylenediamine (2b): ^{1}H NMR (CD_3CN) δ=2.04 (6H, s, CH_3), 3.40 (4H, br, NH_2), and 6.37 (2H, s, ar-H); (20% CF_3COOD–CD_3CN) δ=2.27 (6H, s, CH_3) and 7.23 (2H, s, ar-H).

***N,N'*-Dimethyl-*o*-phenylenediamine (2c):** ^{1}H NMR ($CDCl_3$) δ=2.82 (6H, s, CH_3), 3.15 (2H, br, NH), and 6.70 (4H, s, ar-H); (10% CF_3COOD-$CDCl_3$) δ=3.40 (6H, s, CH_3) and 7.75 (4H, s, ar-H).

5-Methyl-5*H*-cyclohepta[*b*]quinoxaline (3b): ^{1}H NMR (400 MHz) (CD_3CN) δ=2.64 (3H, s, CH_3), 4.46 (1H, d, *J*=10 Hz, H-6), 5.21 (1H, t, *J*=10.7 Hz, H-8), 5.39 (1H, d, *J*=12 Hz, H-10), 5.80 (2H, m, H-7,9), 6.23 (1H, d, *J*=8 Hz, H-4), 6.47 (1H, d, *J*=8 Hz, H-1), 6.52 (1H, t, *J*=8 Hz, H-2), and 6.67 (1H, t, *J*=8 Hz, H-3); ^{13}C NMR (100 MHz) (CD_3CN) δ=34.8 (CH_3), 109.8 (C-6), 114.0 (C-4), 123.6 (C-8), 123.8 (C-2), 126.6 (C-1), 127.9 (C-3), 134.0 (C-10), 138.0 (C-7 or 9), 138.1 (C-9 or 7), 140.8 (C-4a), 141.3 (C-11a), 151.3 (C-5a), and 163.8 (C-10a).

Benzo[*b*]cyclohept[*e*][1,4]oxazine (3c): ^{1}H NMR (270 MHz) ($CDCl_3$) δ=5.37 (1H, d, *J*=9.5 Hz, H-6), 5.75 (1H, dd, *J*=10.5 and 8 Hz, H-8), 5.94 (1H, t, *J*=10.5 and 9.5 Hz, H-7), 5.97 (1H, d, *J*=12 Hz, H-10), 6.11 (1H, dd, *J*=12 and 8 Hz, H-9), 6.35 (1H, d, *J*=7.9 Hz, H-4), and 6.69 (3H, m, H-1,2,3); ^{13}C NMR (67.8 MHz) (CD_3CN) δ=114.1 (C-6), 115.1 (C-4), 125.5 (C-1), 126.6 (C-2), 128.2 (C-3), 129.2 (C-8), 134.7 (C-7 or 9), 136.8 (C-4a), 137.0 (C-10), 137.3 (C-9 or 7), 147.9 (C-11a), 158.1 (C-5a), and 161.2 (C-10a).

Benzo[*b*]cyclohept[*e*][1,4]thiazine (3d): ^{1}H NMR (400 MHz) (CD_3CN) δ=6.10 (1H, d, *J*=8 Hz, H-6), 6.13 (1H, d, *J*=12 Hz, H-10), 6.19 (1H, ddt, *J*=11, 7, and 1 Hz, H-8), 6.31 (1H, ddt, *J*=11, 8, and 1 Hz, H-7), 6.37 (1H, ddd, *J*=12, 7, and 1 Hz, H-9), 6.85 (1H, dd, *J*=7 and 1.5 Hz, H-4), 6.95 (1H, td, *J*=7 and 1.8 Hz, H-3), 7.00 (1H, dd, *J*=7 and 1.8 Hz, H-1), and 7.04 (1H, ddd, *J*=7 and 1.5 Hz, H-2); ^{13}C NMR (100 MHz) (CD_3CN) δ=126.6 (C-4), 127.6 (C-3), 128.2 (C-4a), 128.3 (C-1), 128.6 (C-2), 130.0 (C-10), 132.6 (C-8), 134.5 (C-6), 134.6 (C-11a), 134.7 (C-9), 135.3 (C-7), 144.4 (C-5a), and 160.3 (C-10a).

2,3-Dimethyl-5*H*,11*H*$^+$-cyclohepta[*b*]quinoxalinium Tetrafluoroborate (5b): ^{1}H NMR (270 MHz) (CD_3CN) δ=1.90 (6H, s, CH3), 5.55 (2H, d, *J*=11.0 Hz, H-10), 5.92 (1H, t, *J*=9.3 Hz, H-8), 5.94 (2H, s, H-1,4), and 6.50 (2H, dd, *J*=11.0 and 9.3 Hz, H-7,9).

2,3-Dimethyl-6*H*-cyclohepta[*b*]quinoxaline (6b): ^{1}H NMR (270 MHz) ($CDCl_3$) δ=2.48 (6H, s, CH3), 3.55 (2H, d, *J*=6.6 Hz, H-6,6), 6.06 (1H, dt, *J*=10.0 and 6.6 Hz, H-7), 6.25 (1H, dd, *J*=10.0 and 5.5 Hz, H-8), 6.77 (1H, dd, *J*=12.1 and 5.5 Hz, H-9), and 7.24 (1H, d, *J*=12.1 Hz, H-10).

5*H*,11*H*$^+$-Cyclohepta[*b*]quinoxalinium Tetrafluoroborate (7a): ^{1}H NMR (400 MHz) (CD_3CN) δ=5.65 (2H, d, *J*=11 Hz, H-6,11), 6.04 (1H, t, *J*=9.5 Hz, H-8), 6.11 (2H, m, H-1,4), 6.52 (2H, m, H-2,3), 6.60 (2H, dd, *J*=11 and 9.5 Hz, H-7,9), and 7.83 (2H, br, NH); ^{13}C NMR (100 MHz) (CD_3CN) δ=116.9 (C-1,4), 124.0 (C-6,10), 128.2 (C-2,3), 131.4 (C-8), 132.2 (C-4a,11a), 147.9 (C-7,9), and 157.7 (C-5a, 10a).

11*H*$^+$-5-Methylcyclohepta[*b*]quinoxalinium Tetrafluorobo-

rate (7b): ^{1}H NMR (400 MHz) (CD_3CN) δ=2.85 (3H, s, CH_3), 5.88 (1H, d, J=11 Hz, H-6 or 10), 5.93 (1H, d, J=11 Hz, H-10 or 6), 6.26 (1H, t, J=9.5 Hz, H-8), 6.39 (1H, dd, J=7.5 and 1.5 Hz, H-1 or 4), 6.43 (1H, d, J=8 Hz, H-4 or 1), 6.69 (1H, td, J=7.5 and 1.5 Hz, H-2 or 3), 6.77 (1H, td, J=7.5 and 1.5 Hz, H-3 or 2), 6.90 (1H, ddd, J=11, 9.5, and 1.5 Hz, H-7 or 9), 6.93 (1H, ddd, J=11, 9.5, and 1.5 Hz, H-9 or 7), and 8.48 (1H, br, NH); ^{13}C NMR (100 MHz) (CD_3CN) δ=37.0 (CH_3), 117.5 (C-1 or 4), 117.6 (C-4 or 1), 123.9 (C-6 or 10), 125.1 (C-10 or 6), 127.6 (C-2 or 3), 128.8 (C-3 or 2), 131.3 (C-8), 132.1 (C-4a), 136.7 (C-11a), 147.5 (C-7 or 9), 148.2 (C-9 or 7), 156.0 (C-5a), and 159.0 (C-10a).

11*H*$^+$-Benzo[*b*]cyclohept[*e*][1,4]oxazinium Tetrafluoroborate (7c): ^{1}H NMR (400 NHz) (CD_3CN) δ=6.67 (1H, dd, J=8 and 1.5 Hz, H-1 or 4), 6.70 (1H, dd, J=7.5 and 1.5 Hz, H-4 or 1), 6.85 (1H, d, J=11.5 Hz, H-6 or 10), 6.89 (1H, td, J=7.5 and 1.5 Hz, H-2 or 3), 6.92 (1H, dd, J=10.3 and 1 Hz, H-10 or 6), 6.95 (1H, td, J=8 and 1.5 Hz, H-3 or 2), 7.09 (1H, ddd, J=10.3, 9, and 1Hz, H-8), 7.34 (1H, td, J=10.3 and 1.5 Hz, H-7 or 9), 7.49 (1H, dd, J=11.5, 9, and 1 Hz, H-9), and 9.40 (1H, br, NH); ^{13}C NMR (100 MHz) (CD_3CN) δ=117.4 (C-1 or 4), 118.5 (C-4 or 1), 126.4 (C-11a), 128.0 (C-2 or 3), 129.8 (C-6 or 10), 130.0 (C-10 or 6), 131.1 (C-3 or 2), 138.2 (C-8), 145.1 (C-7 or 9), 145.6 (C-4a), 149.0 (C-9 or 7), 157.6 (C-10a), and 161.5 (C-5a).

11*H*$^+$-Benzo[*b*]cyclohepta[*e*][1,4]thiazinium Tetrafluoroborate (7d): ^{1}H NMR (400 MHz) (CD_3CN) δ=6.76 (1H, d, J=11.5 Hz, H-6 or 10), 6.82 (2H, m, H-1,4), 7.07 (3H, m, H-2,3,8), 7.18 (1H, d, J=9 Hz, H-10 or 6), 7.22 (1H, td, J=9 and 1.5 Hz, H-7 or 9), 7.41 (1H, ddd, J=11.5, 9, and 1.5 Hz, H-9 or 7), and 9.55 (1H, br, NH); ^{13}C NMR (100 MHz) (CD_3CN) δ=120.4 (C-4), 121.2 (C-4a), 127.6 (C-1), 129.4 (C-6), 130.6 (C-2 or 3), 130.9 (C-3 or 2), 134.4 (C-11a), 140.5 (C-10), 142.2 (C-8 or 9), 144.2 (C-9 or 8), 145.7 (C-5a), 148.1 (C-7), and 162.9 (C-10a).

***o*-Aminophenol (8a):** ^{1}H NMR (50% $CDCl_3$-CD_3CN) δ=6.60 (s, ar-H); (1:2:2, CF_3COOD-$CDCl_3$-CD_3CN) δ=6.75—7.45 (m, ar-H).

2-Aminobenzenethiol (8b): ^{1}H NMR (CD_3CN) δ=4.0 (3H, br, NH and SH) and 6.50—7.40 (4H, m, ar-H); (20% CF_3COOD-CD_3CN) δ=7.20—7.70 (m, ar-H).

2,3-Dihydro-1*H*-cyclohepta[*b*]pyrazine (9a): ^{1}H NMR (270 MHz) (CD_3CN) δ=3.40 (4H, s, CH_2), 6.00 (1H, t, J=9.3 Hz, H-7), 6.15 (2H, d, J=11.5 Hz, H-5,9), and 6.46 (2H, dd, J=11.5 and 9.3 Hz, H-6,8); (20% CF_3COOD-CD_3CN) δ=3.59 (4H, s, CH_2), 7.13 (1H, t, J=10 Hz, H-7), 7.26 (2H, d, J=11 Hz, H-5,9), and 7.51 (2H, dd, J=11 and 10 Hz, H-6,8).

2,3-Dihydro-1-methyl-1*H*-cyclohepta[*b*]pyrazine (9b): ^{1}H NMR (270 MHz) (20% CF_3COOD+CD_3CN) δ=3.35 (3H, s, CH_3), 3.68 (2H, t, J=5.0 Hz, CH_2), 3.78 (2H, t, J=5.0 Hz, CH_2), 7.08 (1H, t, J=9.3 Hz, H-7), 7.21 (2H, d, J=11.0 Hz, H-5,9), 7.50 (1H, dd, J=11.0 and 9.3 Hz, H-8), and 7.58 (1H, dd, J=11.0 and 9.3 Hz, H-6).

5,11-Dimethyl-5*H*-cyclohepta[*b*]quinoxalinium Tetrafluoroborate (12a): ^{1}H NMR (400 MHz) (CD_3CN) δ=3.08 (6H, s, CH_3), 6.27 (2H, d, J=12 Hz, H-6,10), 6.56 (1H, t, J=9.5 Hz, H-8), 6.70 (2H, m, H-1,4), 6.93 (2H, m, H-2,3), and 7.22 (2H, dd, J=12 and 9.5 Hz, H-7,9); ^{13}C NMR (100 MHz) (CD_3CN) δ=37.6 (CH_3), 118.0 (C-1,4), 124.7 (C-6,10), 128.0 (C-2,3), 131.5 (C-8), 133.2 (C-4a, 11a), 147.9 (C-7,9), and 158.3 (C-5a, 10a).

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15) For example, the δ_{av} values of protons on the benzene and seven-membered rings of oxazine **3c** in CD_3CN are 6.61 and 5.83 ppm, whereas these values are 6.72 and 5.83 ppm in $CDCl_3$, respectively. The corresponding values for thiazine **3d** are 6.96 and 6.22 ppm in CD_3CN, whereas these values are 6.95 and 6.17 ppm in $CDCl_3$, respectively. The δ_{av} values of protons on the benzene and seven-membered rings of diazine **3b** in CD_3CN

are 6.47 and 5.33 ppm, whereas these values are 6.49 and 5.46 ppm in $CDCl_3$, respectively.

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