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Tetrakis(1,3-benzodithiol-2-ylidene)cyclopentyl Cations with Light Absorption in a Near Infrared

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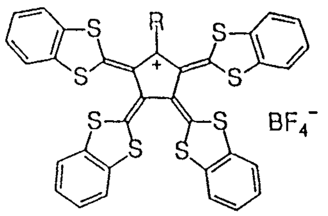
The titled cations exhibited remarkably long wavelength absorptions reaching to a near infrared above 750 nm. The cause of this deep coloration has been clarified, which is ascribed to such a stabilization of electronically-excited biradicalic structures beyond expectation, as to participate in the ground states of the cations albeit in a very small amount (10^{-3} - 10^{-2}%).

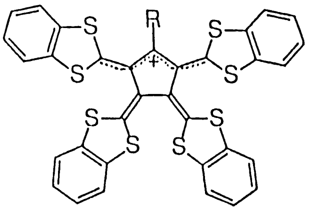
The search for deeply colored organic compounds with light absorption in a near infrared above 750 nm (NIR), is of current interest in various new applications as dye lasers and as materials for storing information with the help of diode lasers.1) The deep coloration is closely related to an electronic transition between the highest occupied and lowest unoccupied molecular orbitals in a very small energy separation. To that purpose closed-shell organic molecules have been endowed with extension of π electron conjugation or with increase of intramolecular charge-transfer (CT) contribution in the electronic transition.2) However, the longest wavelength absorption maxima are not shifted up to NIR as a result of bond fixation in the former case and of limitation of the contribution in the latter case. We have now observed remarkably long wavelength absorptions reaching to NIR in tetrakis(1,3-benzodithiol-2-ylidene)cyclopentyl cation ($\underline{1a}^+$), and its methyl- and phenyl-substituted derivatives ($\underline{1b}^+$ and $\underline{1c}^+$). The evidence that this deep coloration is due to very low-energy electron-



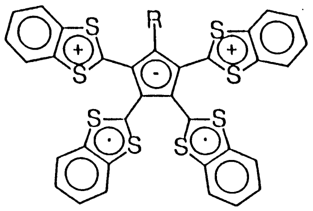
$\underline{1a}^+$: R=H
$\underline{1b}^+$: R=Me
$\underline{1c}^+$: R=Ph

ically-excited biradicalic structures of the cations, is given from ESR.

The tetrafluoroborate salts of $\underline{1a}^{+}$, $\underline{1b}^{+}$, and $\underline{1c}^{+}$ ($\underline{1a}^{+}\cdot BF_4^{-}$: mp 240-241 °C; $\underline{1b}^{+}\cdot BF_4^{-}$: 158-159 °C (dec); $\underline{1c}^{+}\cdot BF_4^{-}$: 182-183 °C (dec))[3] were obtained in yields of 88, 40, and 65%, respectively, by the reaction of tetrakis(1,3-benzodithiol-2-ylidene)cyclopentanone[4] with LAH, CH_3Li, and PhLi (3 equiv.) in THF at -70 °C and then by treatment with an excess of $HBF_4\cdot Et_2O$. In the ^1H NMR spectrum of $\underline{1a}^{+}\cdot BF_4^{-}$ the protons on the benzo groups at the nearer position to the cation site appeared at fairly low field (δ 8.7-7.9), while the chemical shifts of the protons on the remoter benzo groups were almost in a normal range (7.9-7.4),[5] suggesting delocalization of the positive charge over the bis(1,3-benzodithiol-2-ylidene)methine moiety as shown in A. Surprisingly, these salts were colored greenish blue to black. In the electronic spectra the longest wavelength absorption maxima with high intensity reach to NIR: 925 nm (log ε=3.97) for $\underline{1a}\cdot BF_4^{-}$, 825 (4.15) for $\underline{1b}^{+}\cdot BF_4^{-}$ and 836 (4.12) for $\underline{1c}^{+}\cdot BF_4^{-}$.[6] This can not be easily understood as much as one only considers an usual π-π* electronic transition due to such a short π electron conjugated system as A. The much more stabilized electronically-excited structure must be considered.



A



B

The ESR measurement gave a valuable information on the electronically-excited structure. In the solid ESR spectra of the $\underline{1}^{+}$ salts, for instance, as shown in Fig. 1a for $\underline{1a}^{+}\cdot BF_4^{-}$ the comparatively strong and apparently two-overlapped signal was observed near g=2. The temperature (T) dependence of the signal intensity (I) was investigated in the range of 15 to 300 K (see Fig. 1b). The observed I-T curve does not follow a Curie law at all. The analysis was well performed by assuming involvement of a low-energy biradical singlet in equilibrium with its thermally-accessible counterpart triplet along with an impurity monoradical. By use of an equation relating between I and T, i.e., $I=N_m g^2 \mu_B^2 \cdot 1/2(1+1/2)/3kT + N_b g^2 \mu_B^2 \cdot 1(1+1)/3kT \{1+1/3\exp(\Delta E/kT)\}$, where N_m and N_b are amounts of monoradical and biradical, respectively, μ_B is Bohr magneton, k is Boltzmann constant, ΔE is an energy separation between the low-energy singlet and its thermally-accessible counterpart triplet, N_b and ΔE were determined. Such a treatment also was performed for $\underline{1b}^{+}\cdot BF_4^{-}$ and $\underline{1c}^{+}\cdot BF_4^{-}$. The results are summarized in Table 1. The amounts of biradicals involved are 2.1 x 10^{20} for $\underline{1a}^{+}\cdot BF_4^{-}$, 2.1 x 10^{19} for $\underline{1b}^{+}\cdot BF_4^{-}$, and 1.2 x 10^{19} molecules/mol for $\underline{1c}^{+}\cdot BF_4^{-}$,[7] and the contents

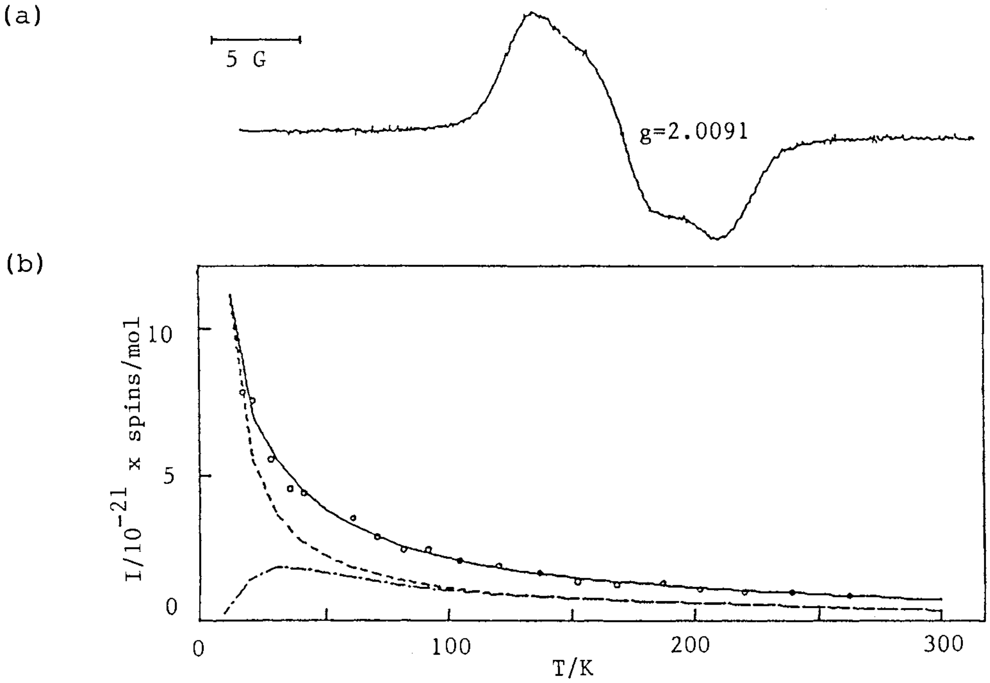


Fig. 1. (a) The solid ESR spectrum of $\underline{1a}^+\cdot BF_4^-$ at 298 K: the magnetic field of the absorption center is 3300 G and the microwave frequency used is 9.305 GHz. (b) The temperature (T) dependence of the signal intensity (I) and the separation to each contribution due to a thermally-accessible triplet (——·——) and due to an impurity monoradical (----): (o) the observed I at each temperature and (——) the calculated I-T curve.

correspond to 0.034, 0.0036, and 0.0020%, respectively, of which the larger is comparable with that of a monoquinone of tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)thieno[3,2-b]thiophene,[8] while the smaller with that of cyclic bicalicene.[9] The ΔE value is very small (69-103 cal/mol) in each cation, implying that the two unpaired electrons in the biradical have almost no interaction with each other.

The electronically-excited structure of $\underline{1}^+$ is biradicalic and in low

Table 1. The values of N_b, content, and ΔE for the BF_4^- salts of $\underline{1a}^+$, $\underline{1b}^+$, and $\underline{1c}^+$

Cation	N_b molecules·mol^{-1}	Content %	ΔE cal·mol^{-1}
$\underline{1a}^+$	2.1×10^{20}	0.034	103
$\underline{1b}^+$	2.1×10^{19}	0.0036	99
$\underline{1c}^+$	1.2×10^{19}	0.0020	69

energy. The most conceivable structure is B, in which the two unpaired electrons are occupied in each of two 1,3-dithiole groups largely twisted from the central five-membered ring, and the positive and negative charges are stabilized by aromatic π electron conjugation of cyclopentadienide and 1,3-dithiolium ions, respectively. As this result the energy separation between the ground and electronically-excited structures becomes remarkably small, bringing the light absorption to NIR. The substitution effect of methyl and phenyl groups on the absorption shift to the shorter wavelength region and on the more decreased excited structure contribution compared with $\underline{1a}^+$, can reasonably be understood by considering much more stabilized ground structures of $\underline{1b}^+$ and $\underline{1c}^+$, even though there might be more or less different in the energy of the excited structures between these cations. In summary, the NIR absorption results from very much intramolecular CT from four powerful electron-donating 1,3-dithiole groups to a powerful electron-accepting carbocation. The present finding will give a new extension of CT consideration for developing of organic NIR compounds.

References

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2) A large number of neutral and ionic π radicals, and their dimers and solids are also known to exhibit light absorption in NIR.

3) The satisfactory elemental analyses were obtained.

4) T. Sugimoto, Y. Misaki, Y. Arai, Y. Yamamoto, Z. Yoshida, Y. Kai, and N. Kasai, J. Am. Chem. Soc., 110, 628 (1988).

5) The difference of chemical shifts between the protons on the two magnetically different benzo groups decreased gradually as going from $\underline{1a}^+\cdot BF_4^-$ to $\underline{1b}^+\cdot BF_4^-$ (δ 8.13-7.86(m, 4H), 7.86-7.51(m, 4H), 7.51-7.02(m, 8H)) and further to $\underline{1c}^+\cdot BF_4^-$ (8.01-7.00(m)).

6) The electronic spectra measured in CH_2Cl_2 are as follows: λ_{max} (log ε) 325(4.07), 383(4.03), 492(3.74), 610(4.18), 925 nm(3.97) for $\underline{1a}^+\cdot BF_4^-$; 321(4.33), 365(4.26), 601(4.37), 825(4.15) for $\underline{1b}^+\cdot BF_4^-$; 325(4.31), 398(4.20), 609(4.30), 690(4.09), 836(4.12) for $\underline{1c}^+\cdot BF_4^-$.

7) The amounts of impurity monoradicals were 3.8×10^{20}, 3.7×10^{19}, and 8.5×10^{18} molecules/mol for the corresponding cations, respectively.

8) T. Sugimoto, M. Sakaguchi, H. Ando, T. Tanaka, Z. Yoshida, J. Yamauchi, Y. Kai, and N. Kasai, unpublished results.

9) T. Sugimoto, M. Sakaguchi, H. Ando, Y. Arai, T. Tanaka, Z. Yoshida, J. Yamauchi, A. A. Bothner-By, and M. Lisicki, J. Am. Chem. Soc., 113, 3193 (1991).

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