^{3}**3-Enol** for the short-lived transient from **1-Me**, and we expect it is probably an evolving mixture of the two.

Several conclusions may be drawn. Most importantly, the role of conformational control of interterminal distance in determining intersystem crossing rates of Norrish II 1,4 biradicals is indeed small and does contrast with experiments in which the interterminal distance is varied by varying the number of intervening bonds[3,4] or with cases in which through-space interaction dominates.[3,5] It seems likely that through-bond effects dominate the spin–orbit coupling interaction in the present case. Second, there is no special role of the cyclopropyl spacer in intersystem crossing; its special role is in facilitating the adiabatic scission thermochemically. Since ^{3}**2** is formally a cyclopropylcarbinyl biradical of the sort proposed in triplet state di-π-methane reactions,[18] we suggest that the dynamic behavior of such biradicals will not be exceptional, but can be understood on the basis of intersystem crossing and thermochemical kinetics of simpler biradical models. Third, the adiabatic opening of **2-Me** would suggest that triplet state cyclopropyldicarbinyl biradical formation from olefin triplet precursors is likely also adiabatically reversible when thermodynamically acceptable.

We will report separately the findings for another series of 1,4-biradicals which demonstrates a similar absence of conformational dependence.[19]

Acknowledgment is made to the Robert A. Welch Foundation (Grant AT-532) and the National Science Foundation for financial support. Laser flash photolysis was performed at the Center for Fast Kinetics Research at The University of Texas at Austin, supported by Grant RR-00886 of the Biotechnology Branch of the Division of Research Resources of the National Institutes of Health and by the University of Texas. S.C.G. thanks Kurukshetra University, India, for granting sabbatical leave.

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(18) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718. Zimmerman, H. E.; Armesto, D.; Mercedes, G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367.

(19) Caldwell, R. A.; Sink, R. M. Manuscript in preparation.

Chiral Azophenolic Acerands: Color Indicators To Judge the Absolute Configuration of Chiral Amines†

Takahiro Kaneda,* Keiji Hirose, and Soichi Misumi

The Institute of Scientific and Industrial Research
Osaka University, Mihogaoka
Ibaraki, Osaka 567, Japan

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Chiral azophenolic acerands[1e] **1–3**[2] are particularly interesting molecules because of their two different functions, enantiomer differential complexation established by Cram and his co-workers[3] and guest-selective coloration,[1] in the same molecule. These chromoacerands provide a good model to examine enantiomeric amine-selective coloration, the observation of which must be the first step toward developing color indicators to judge the absolute configuration of chiral amines on the basis of host–guest saltexing.[1e] We report here the first successful approach to such color indicators.[4]

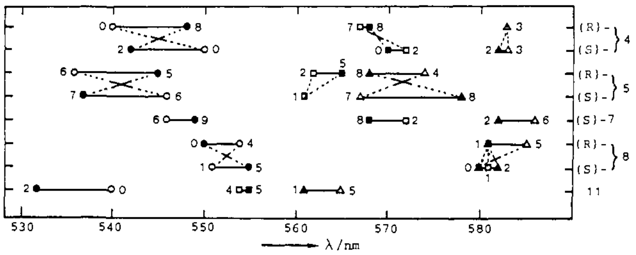


Figure 1. Absorption maxima for the colored salts of **1–3** with chiral amines in ethanol. The number next to the symbol is the units digit for the value of λ_{max}: (△), salt of (*RR*)-**1**; (▲), (*SS*)-**1**; (○), (*RRRR*)-**2**; (●), (*SSSS*)-**2**; (□), (*RR*)-**3**; (■), (*SS*)-**3**.

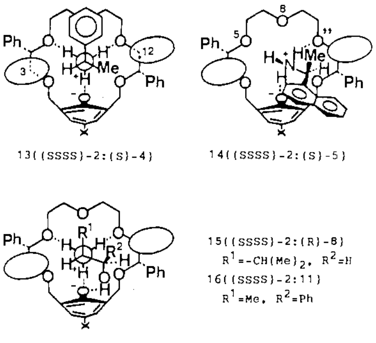
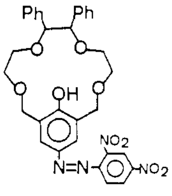
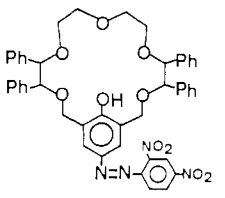


Figure 2. Predicted structures of the saltexes consisting of **2–4**, **–5**, **–8** and **–11** combinations, where X = 2,4-dinitrophenylazo group. The Ph groups at C_3 and C_{12} are shown as ellipses.

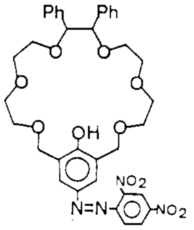
Thirteen chiral amines **4–12** including four enantiomeric pairs of alkyl- and ethanolamines **4–6** and **8** were used as potential guests. These colorless species were treated in ethanol with three enantiomeric pairs of yellow indicators **1–3** to give 39 diastereomeric sets of purple-colored ammonium phenolates, whose visible spectra were determined.[5] The absorption maxima for



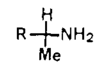
1



2

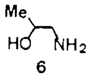


3

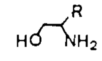


4: R = Ph

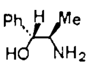
5: =



6



7: R = Me
8: = $CHMe_2$
9: = CH_2Ph
10: = Ph



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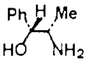

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† Dedicated to Professor Donald J. Cram, UCLA, on the occasion of his 70th birthday.

(1) For metal-ion-selective coloration: (a) Kaneda, T.; Sugihara, K.; Kamiya, H.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 4407–4408. (b) Sugihara, K.; Kaneda, T.; Misumi, S. *Heterocycles* **1982**, *18*, 57–61. (c) Tanigawa, I.; Tsuemoto, K.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1984**, *25*, 5327–5330. (d) Kaneda, T.; Umeda, S.; Tanigawa, H.; Misumi, S.; Kai, Y.; Morii, H.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 4802–4803. For amine-selective coloration: (e) Kaneda, T.; Ishizaki, Y.; Misumi, S.; Kai, Y.; Hirao, G.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 2970–2972. (f) Kaneda, T.; Umeda, S.; Ishizaki, Y.; Kuo, H.-S.; Misumi, S.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.*, in press. For reviews: (g) Misumi, S.; Kaneda, T. *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **1987**, *44*, 29–47. (h) Kaneda, T. *J. Synth. Org. Chem., Jpn.* **1988**, *46*, 96–107.

(2) Hirose, K. Ph.D. Thesis, Osaka University, 1988. Acerands **1–3** were synthesized via quinone intermediates by a method similar to that described previously.[1] The synthetic work will be reported elsewhere.

(3) (a) Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2692–2693. (b) Cram, D. J.; Helgeson, R. C.; Sousa, L. R.; Timko, J. M.; Newcomb, M.; Moreau, P.; de Jong, F.; Gokel, G. W.; Hoffman, D. H.; Domeier, L. A.; Peacock, S. C.; Madan, K.; Kaplan, L. *Pure Appl. Chem.* **1975**, *43*, 327–349.

(4) For the first report on this subject, see: Hollmann, G.; Vögtle, F. *Chem. Ber.* **1984**, *117*, 1355–1363.

(5) The stock solutions of an enantiomeric pair of the indicators were prepared carefully so that their concentrations (ca. 10^{-5} M) were exactly the same. Commercially available chiral amines were used without further purification after checking the rotation. An indicator/amine molar ratio of 1:10^3 was employed for all cases. The acerands dissociate to some extent in ethanol, so that two absorption bands due to the phenol and the phenolate appear at 390 and 587 for **1**, 397 and 555 for **2**, and 393 and 582 nm for **3**, respectively.

the phenolates appeared in the long wavelength region and varied from 532–586 nm for the same type of electronic transition. Similar observations have been reported for mono-[1f] and dibasic[1e] chromoacerands-amine systems. Significant differences (up to 11 nm) in λ_{max}'s between diastereomeric sets of the salts have been observed for several acerand-amine combinations (Figure 1). *When the guests were (S)-(−)-α-phenethylamine ((S)-**4**), (S)-(−)-1-(1-naphthyl)ethylamine ((S)-**5**),* D*-valinol ((R)-**8**), and (1R,2R)-(−)-norpseudoephedrine (**11**), indicator (SSSS)-**2** caused blue-shifts of the absorption bands compared with the enantiomer (RRRR)-**2**. A similar blue-shift was also observed with the (SS)-**1**:(R)-**5** combination.* As expected, utilization of (*RR*)-**1** and (*RRRR*)-**2** brought about the reverse results so that several "crossings" are noted in Figure 1.[6] These blue-shifts are the first observation of enantiomeric amine-selective coloration.

The second step of this work is to predict the structures of the colored saltexes in ethanol. From examination of CPK molecular models it is predicted, as described below, that the most stable geometries of the saltexes consisting of **2**–**4**, –**5**, –**8**, and –**11** combinations are **13**–**16** as shown in Figure 2. In other words, *(SSSS)-**2** shows better complementarity than the (RRRR)-isomer to (S)-**4**, (S)-**5**, (R)-**8**, and **11**, and (SS)-**1** fits (R)-**5** better than the (RR)-isomer does.* Here, the assumption is made that the phenolate oxygen atom participates in hydrogen bonding between the host and guest. This assumption seems to be quite reasonable in view of the high hydrogen bond-acceptor ability of the negatively charged oxygen and has been verified in the crystal structures of saltexes.[1e,f,7] Applying the well-known three-point binding model[3b] to the (*SSSS*)-**2**:**4** system gives the predicted geometry **13**[8] where the smallest substituent, hydrogen, occupies the most hindered area. Judging from the steric requirements of this model, the Ph group at C_3 in **13** must be more effective than the Ph group at C_{12} as a chiral barrier against the guest. However, the same binding model would be unfavorable for the **2**:**5** system because of the more bulky 1-naphthyl group, which should prefer to occupy the least hindered area in structure **14** as predicted from the two-point binding mode.[10] Applying the same binding model to **1**:**5** systems predicts better complementarity of (*R*)-**5** to (*SS*)-**1** rather than the (*RR*)-isomer. A slim ethanolamine skeleton would exactly fit a three-point binding model as shown in **15**[8] and **16**,[8] where an additional hydrogen bonding between the phenolate oxygen and the alcoholic OH group should stabilize these saltexes further. Another conformer produced by rotation about the C–C bond axis of the guest in **15** should be less stable due to steric hindrance between the phenyl group at C_3 and the R^2 group. Therefore, it is easily understandable from the predicted structures **15** and **16** that (*R*)-**8** and **11** which bear substituents R^1 and R^2 in less hindered positions should show better complementarity to (*SSSS*)-**2** than the (*RRRR*)-isomer.

The final step is to correlate the observed blue-shift with the difference in the structure or the host–guest complementarity between the two diastereomers. It is noted that *the indicator-species combinations for which better host–guest complementarity is predicted are those combinations which exhibit the blue-shift.* This is consistent with the following explanation for the blue-shift. Hydrogen bonding between the phenolate oxygen of the host and an N^+H hydrogen of the guest in **13**–**16** stabilizes the energy of the polar ground state more than that of the less polar excited state of the chromophore. Similar blue-shifts induced by metal[11] and ammonium ions have been reported in other dye systems.[1] Further, a parallel relationship between the blue-shift and thermodynamic stability in chloroform, which increases with the better host–guest complementarity, has been found.[1e,f]

Thus we have demonstrated that enantiomeric amine-selective coloration can be obtained. By synthesizing the indicator as an enantiomeric pair, we have overcome the troublesome problem that both enantiomers of the species to be analyzed are not always available. Utilization of the present acerands as color indicators to judge the absolute configuration of chiral amines depends on the reliability of the structures predicted for their ammonium saltexes.

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(6) Such crossings provide strong evidence for the reliability of the experiments.

(7) (a) Goldberg, I. *Acta Crystallogr.* **1975**, *B31*, 2592–2600. (b) Browne, C. M.; Ferguson, G.; McKervey, M. A.; Mulholand, D. L.; O'Conner, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703–2712.

(8) This structure is the same as that predicted by chiral twist theory,[9] a general rationalization for enantioselective complexation involving chiral 18-crown-6 analogues.

(9) Sutherland, I. O., private communication.

(10) The other two possible candidates involving O_5 or O_8 would be unfavorable because of the steric interactions between the Ph group at C_3 and the guest or absence for additional binding with the benzylic oxygens.

(11) (a) Dix, J. P.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 857–859. (b) For a review: Löhr, H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65–72.

Selective Alternating Copolymerization of Allene Derivatives through Macro Allyl Zwitterion

Jiro Mizuya, Tsutomu Yokozawa, and Takeshi Endo*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

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Recent investigations in our laboratory have focused on the features of the polymerization of substituted allenes, which are regarded as vinyl monomers bonded to another methylene carbon. We have recently reported that allene derivatives undergo radical polymerization to obtain polymers bearing *exo*-methylene groups attached to the polymer backbone.[1] In the course of research on the copolymerization of monosubstituted allenes, we found that an allene bearing an electron-donating group reacted with one bearing an electron-withdrawing group to give copolymer under mild conditions. Herein we report the spontaneous copolymerization of methoxyallene **1**[2] with cyanoallene **2**,[3] which yields 1:1 copolymer irrespective of the feed ratio of both allenes.

The reaction of **1** with **2** was carried out at 60 °C in bulk to afford the copolymer of **1** and **2**.[4] Some peculiar features of this copolymerization are as follows. (1) When an equimolar mixture of **1** and **2** was allowed to react, the rate of consumption of **1** and that of **2** was equal, and the copolymer consisted of **1** and **2** with the ratio 1:1 irrespective of the reaction time. (2) The number-average molecular weight ($\bar{M}_n$) of polymer obtained increased with conversion, especially the increase of $\bar{M}_n$ was accelerated in high conversion. (3) When **1** was allowed to react with 3 equiv of **2**, the rate of consumption of **1** and that of **2** was also equal, and the lack of **1** stopped completely the reaction even though 66% of **2** remained in the reaction mixture (Figure 1). In the reaction of 3 equiv of **1** with **2**, similar behavior was observed. (4) When the reaction was carried out in various feed ratios of **1** to **2**, the composition of the copolymers constantly remained as the ratio 1:1 irrespective of the feed ratio, while yields became maximum in the feed ratio 1:1 (Figure 2). Since the corre-

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(1) Yokozawa, T.; Tanaka, M.; Endo, T. *Chem. Lett.* **1987**, 1831. Mizuya, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Lett. Ed.*, in press.

(2) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Ed.* **1978**, *16*, 615.

(3) Kuritz, P.; Gold, H.; Disselnkotler, H. *Ann. Chem.* **1959**, 624.

(4) Four sealed polymerization tubes containing **1** (0.30 g, 4.3 mmol) and **2** (0.28 g, 4.3 mmol) were heated at 60 °C for 0.5, 1, 2, and 3 h, respectively. The polymers were purified by dissolution in dichloromethane, followed by precipitation with diethyl ether (the soluble polymers were converted into gel polymer during isolation). The precipitated materials and the ether layer were dried under reduced pressure [the yield and polymer composition (estimated from elemental analysis) show after isolation of the polymer, spectral data (^{1}H NMR and IR) of soluble polymer were measured, and Mn was estimated by GPC (based on Poly-St) before precipitation]: (0.5 h) conversion = 59%, yield = 3%, $\bar{M}_n = 2.0 \times 10^4$, 1:2 = 53:47; (1 h) 73%, 7%, 3.7×10^4, 51:49; (2 h) 81%, 13%, 4.7×10^4, 52:48; (3 h) 86%, 15%, 5.0×10^4, 51:49.

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