Notes

The Structural Identification of Dicondensed Products Derived from the Reaction of Excess Fischer's Base with Salicylaldehydes

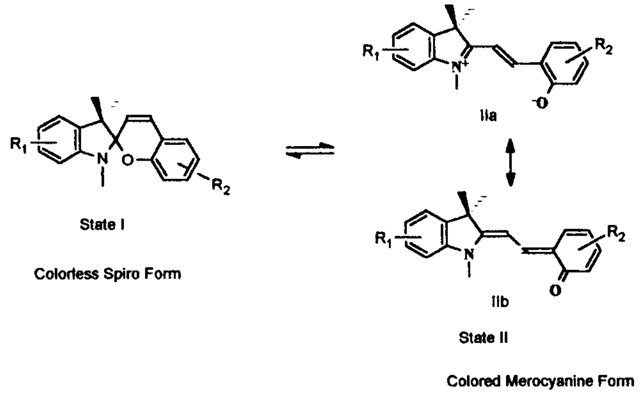
Sam-Rok Keum[†]*, Peter M. Kazmaier[‡]*, Kap-Soo Cheon[§], Richard A. Manderville[§], and Erwin Buncel[§]

[†]*Department of Chemistry, Korea University, Jochiwon, Chung-Nam, South 339-700, Korea*
[‡]*Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1*
[§]*Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

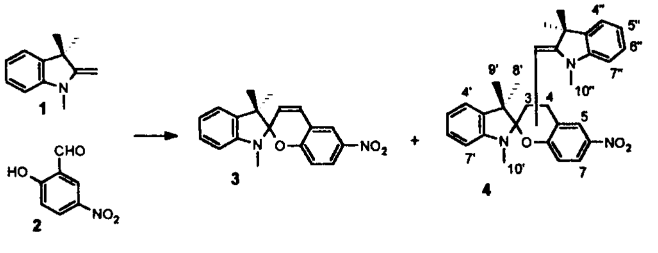
Received October 25, 1995

The thermochromism and photochromism of spiropyrans (Scheme 1) has received wide attention because of the potential practical applications of these materials to a variety of optoelectronic devices.[1] Spiropyran **3**, *i.e.* 1,3,3-trimethyl-6-nitrospiro(indolino-2,2'-benzopyrans), typlifies this class of compounds and has featured in a number of recent studies.[2] However, the synthesis of **3** involves some aspects which have not been fully elucidated.

Thus the reaction of Fischer's base **1** and the salicylaldehydes **2** in 1 : 1.3 molar ratio yields mainly monocondensed products **3** but when excess Fischer base is used both the mono- and dicondensed products, e.g. **4** are formed (Scheme 2).



Scheme 1.



Scheme 2.

While the dicondensed product has provoked considerable discussion[3~7] in the past, the structure could not be assigned unequivocally. Interest in these dicondensed heterocycles as additives in silver halide emulsion[8,9] and as components of thermal papers[10,11] provides further motivation for the unequivocal structure assignment of these compounds.

On going research focus in our laboratories has been in the development of new optoelectronic materials. Thus a particular interest pertaining to these dicondensed adducts, containing two indoline units, is the possibility that these structures could function as optical switches.

Experimental

Materials. Fischer's base (2-ethylene-1,3,3-trimethylindoline) and salicylaldehyde were available from Aldrich Chemical Co. and were used without further purification. A mixture of 5-nitrosalicylaldehyde and excess (4-5 fold) Fischer's base in ethanol was refluxed for 8 hours. The yellow precipitate was filtered from the hot methanolic solution and washed thoroughly with cold diethyl ether. Purification was carried out either by recrystallization from aceton or by precipitation from chloroform/diethyl ether. The mp was 162-165 ℃ and the yield was 65%. The product was identified by ^{1}H NMR and mass spectroscopy and gave a satisfactory analysis.

Measurements. The ^{1}H NMR and ^{1}H nOe spectra were recorded using 10 weight percent solution in aceton-d$_6$ on a Bruker 400 MHz spectrometre at ambient temperature.

Results and Discussion

The synthesis of the dicondensed indolinobenzospiropyran according to Scheme 2 could be readily accomplished. Predominance of the dicondensed product, **4** could be achieved by using a 4 to 5-fold excess of Fischer base over the salicylaldehyde.

The dicondensed product was then obtained from the reaction of excess molar ratio of Fischer's base and nitrosalicylaldehyde in ethanol. The yellow precipitate was filtered from the hot solution and washed thoroughly with cold diethyl ether. Purification was carried out either by recrystalization from acetone or by precipitation from chloroform/diethyl ether.

Four isomeric structures (**4a-4d**) have been proposed for the dicondensed product. Koelsch and Workman[3] assumed the structure of the product was **4a**. This conjecture was supported by the infrared studies of Schiele and Arnold.[4] Bertelson[5] then pointed out that structure **4b** must also be considered as a possibility. Hinnen *et al.*[6~7] later preferred **4c** or **4d** based on ^{1}H NMR consideration.

The problem of unequivocal structure assignment of the dicondensed product requires that the correct structure must be selected from 14 possible isomers. This problem can be broken down into 3 segments. First, isomeric structures **4a-4d** must be considered and the constitutional isomer must be selected. Second, since the dicondensed compound con-

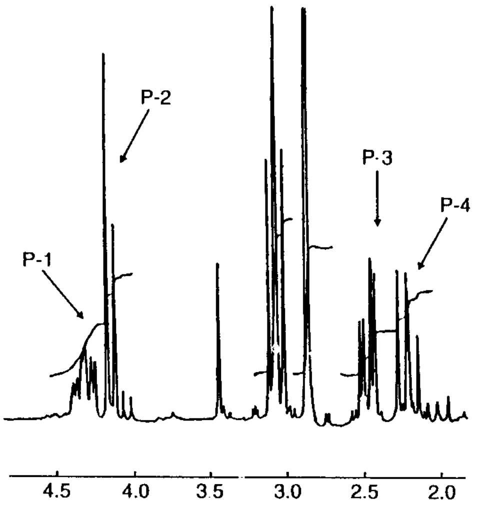
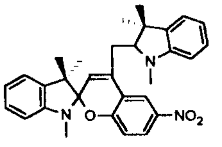
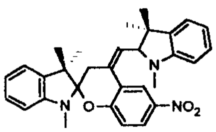


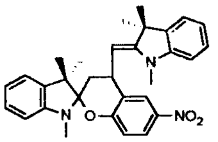
Figure 1. Proton spectrum of P-1 tc P-4 in $CDCl_3$.



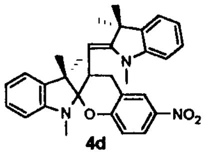
4a



4b



4c

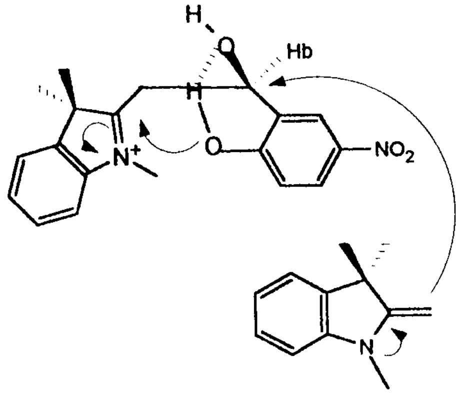


4d

tains two chiral centres, the stereochemical relationship of these centres must be established. Finally, in the case of structures **4b**, **4c** and **4d**, the geometry around the olefinic bond must be ascertained. We have found that 400 MHz ^{1}H NMR and ^{1}H nOe studies of these compounds have provided an unequivocal means for completing their structural assignment.

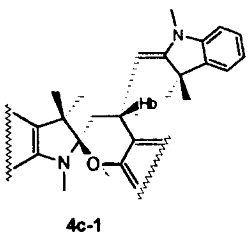
Structures **4a-4d** can be clearly distinguished by considering the four protons Ha, Ha′, Hb and Hc. In contrast to the earlier 60 MHz investigations,[1,6] we have observed that at 400 MHz, these four protons are well separated (P-1 to P-4) as shown in Figure 1. By inspection, structures **4a** and **4b** can immediately be eliminated from consideration. The olefinic proton in **4a** must occur at 5.60-5.93 ppm based on Hinnen *et al.*'s investigation[6] of 59 structures of this type, while, based on Simon's rule,[12] the olefinic proton in **4b** must occur at approximately 6 ppm. This is not consistent with the chemical shifts of P1 and P2. The case against **4a** and **4b** is confirmed by analysis of the coupling data. From the chemical shifts, P-1 and P-2 represent Hb and Hc. P-2 is coupled to P-1 and shows a single coupling of 10.1 Hz and so P-2 must be Hc. P-3 and P-4 show a large geminal coupling of 14.3 Hz and are coupled to Hb with coupling constants of 14.3 Hz and 4.87 Hz respectively.

The connectivity and coupling constants obtained by the decoupling experiments are consistent only with structures **4c** and **4d**. For example **4a** predicts that Hb and Hc are not coupled while **4b** would have only one vicinal coupling.

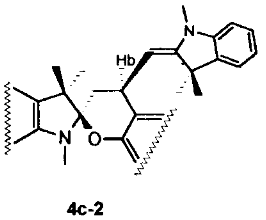


Scheme 3.

In order to unequivocally distinguish between **4c** and **4d** and to determine which diastereomer has formed, it was necessary to measure nuclea Overhauser interactions (nOe's). The two methyl groups on ring A appear characteristically at 1.31 (8′-methyl) and 1.33 (9′-methyl) ppm respectively.[2a] Irradiation of the 8′-methyl group gave an observable nOe on the signals at 2.47 (p-3), 4.15 (p-2) and 7.07 ppm (H-4′ in ring A) respectively, and hence P-3 must be assigned to Ha. The observation that Ha is proximate to the 8′-methyl group rules out structure **4b**. This conclusion is supported by the observed chemical shift of Hb (4.32) which is indicative of conjugation with both an olefinic bond and an aromatic moiety, structural features which are found in **4c** but not **4d**. The regiochemistry about the enamine double bond is established by the observation of strong nOe between the ring B N-methyl group and the enamine proton Hc. The only remaining assignment concerns the relative configurations of the stereoisomers involved. These isomers are epimeric about C-4. From examination of geometries of these diastereomers by PCMODEL[13] and Dreiding mechanical models, it is apparent that the ring system is quite rigid and that in **4c-1** proton Hb is spatially closed to the 9′-CH_3 group (1.33 ppm) while in **4c-2** this is not the case. Since irradiation at the 9′-methyl resonance provides a large nOe at Hb, **4c-1** represents the correct configuration of the dicondensed product. That is to say, the relative configuration of the product is RS/SR, thus completing the assignment.



4c-1



4c-2

Having established the structure of the dicondensed product, it is possible to rationalize the formation of this compound as shown in Scheme 3. A plausible mechanism for its formation involves the capture of the hydroxy adduct of the Schiff base, aldehyde condensation product. This hypothesis is supported by the observation that under the conditions of the reaction, the spiropyran product is not converted to the dicondensed product.

Acknowledgment. This work was supported in part by research grant in part from the Korea Science and Engineering Foundation (941-300-006-2) and in part from the Ministry of Education of the Republic of Korea Under the Basic Science Research Program (BSRI-96-3406) (S.R.K.). This work was also supported by research grant from the Natural Sciences and Engineering Research Council of Canada (E.B. and P.M.K.).

References

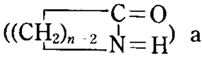
1. (a) Brown, G. H, editor, *Photochromism*; in Technique of Chemistry; Weissberger, A., Ed.; Wiley-Interscience: New York, U.S.A., 1971; Vol. 3. (b) Durr, H; Bouas-Laurent, H. *Photochromism-Molecules and Systems*; Elsevier: Amsterdam, 1990. (c) Daehne, S. Z. Wiss. *Photogr., Photochem.* **1969**, *62*, 183. (d) Arakwa, S.; Kondo, H.; Seto, J. *Chemistry Lett.* **1985**, 1805. (e) Tamaki, T.; Ichimura, K. *J. Chem. Soc., Chem. Comm.* **1989**, 1805.
2. (a) Keum, S. R.; Hur, M. S.; Kazmair, P. M.; Buncel, E. *Can. J. Chem.* **1991**, *69*, 1940. (b) Keum, S. R.; Lee, K. B.; Kazmair, P. M.; Buncel, E. *Magn. Reson. Chem.* **1992**, *30*, 1128. (c) Keum, S. R.; Yun, J. H.; Lee, K. W. *Bull. Kor. Chem. Soc.* **1992**, *13*, 351. (d) Keum, S. R.; Lee, K. W. *Bull. Kor. Chem. Soc.* **1993**, *14*, 16. (e) Keum, S. R.; Seok, M. K.; Lee, J. H. *Dyes and Pigments* **1994**, *25*, 21-29. (f) Keum, S. R.; Lim, S. S.; Min, B. H. *Bull. Kor. Chem. Soc.* **1995**, *16*, 1.
3. Koelsch, C. F.; Workman, W. R. *J. Am. Chem. Soc.* **1952**, *74*, 6288.
4. Schiele, C.; Arnold, G. *Tet. Lett.* **1968**, 245.
5. Bertelson, R. C.; Chapter 3 in ref. 1a.
6. Hinnen, A.; Audic, C.; Gautron, R. *Bull. Soc. Chim. Fr.* **1968**, 2066.
7. Balny, C.; Hinnen, A.; Mosse, M. *Tet. Lett.* **1968**, 5097.
8. Anon. Res. Discl. **1982**, *215*, 72; *Chem. Abstr.* *97*(18), 153836e.
9. Baralle, R. M.; Compere, M. A.; Pfaff, M. E.: Jordi, F. X.; Goumount, C. G. *Fr. Demande* **1982** FR 2491638 A1; *Chem. Abstr.* *97*(14): 118187x.
10. Ricoh Co., Ltd. Jpn. Tokkyo Koho **1980** JP55035277; *Chem. Abstr.* *95*(4): 33421c.
11. Samat, A.; Guglielmetti, R.; Metzger, J. *Fr. Demande* **1975** FR 2271938; *Chem. Abstr.* *85*(16): 114776t.
12. (a) Jackman, L. M.; Sternhell, S. *Applications of Nuclea Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: U. K., **1969**; pp 184-192. (b) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta.* **1966**, *49*, 164.

The Self-Association of ε-Caprolactam in Carbon Tetrachloride : A Near-Infrared Spectroscopic Study

Jooho Kim, Jeunghee Park†, Chang-Ju Yoon§,
and Young-Sang Choi*

Department of Chemistry, Korea University,
1 Anam-Dong, Seoul 136-701, Korea
†Department of Chemistry, Korea University,
Jochiwon, Chungnam 339-700, Korea
§Department of Chemistry, Catholic University,
Bucheon 422-102, Korea

Received October 28, 1995

The structure and hydrogen bonding behavior of lactams have attracted the interest of scientists for many years. Lactams have been used as models of the amide group in peptides and the self-association of the *cis*-lactams serves as model for the hydrogen bondingof the bases in nucleic acids. Several spectroscopic studies[1,2] have shown that the lactams  $((CH_2)_{n-2}\,\overset{C=O}{\underset{N=H}{|}})$ are of the *cis* configuration for ring size $n \leq 8$ and of the *trans* configuration for $n > 9$. The $n > 9$ lactams exist in both the *cis* and the *trans* configurations. The associated species are cyclic dimers for lactams having amide group in the *cis* form, while a chain dimers and a small fraction of higher oligomers are involved in the case of *trans* amide group. These studies also indicate that ε-caprolactam ($n = 7$) having only *cis* configuration exclusively forms cyclic dimers in the concentration ($c \leq 0.15$ M) and temperature range (293 K$\leq T \leq$333 K). It is known that at 293 K the model for cyclic dimerization breaks down at concentration distinctly larger than $c = 0.2$ M. Despite the attention addressed to self-association constant,[3~7] disagreement between the reported values for the dimerization constant of ε-caprolactam still exists. The purpose of present study is to exploit more thoroughly the use of near-IR spectrometry to determine the equilibrium constants and thermodynamic parameters for the dimerization reaction. We have chosen the first overtones of N-H stretching mode for this study. Earlier investigators have observed the absence of a first overtone band corresponding to the hydrogen-bonded inter-amide N-H stretching vibration of cyclic *cis*-lactam dimers in solution.[5] Thus the concentration dependence of a first overtones of monomeric free N-H stretching mode near 6720 cm^{-1} has been measured in order to find the equilibrium constant for the dimerization. *Ab initio* thermodynamic parameters of dimerization reaction have been calculated and compared with the experimental results.

ε-Caprolactam (Aldrich, 99%) was recrystallized and dried under reduced pressure for 24 hours. Carbon tetrachloride (J. T. Baker, HPLC grade) was dried over 3 Å molecular sieves. Densities of CCl_4 solutions were measured by pyconometer at various temperatures and used to calculate the concentration of solution. The samples were prepared in N_2 filled glove box.

The near-IR absorption spectra of ε-caprolactam have been obtained with Cary 17DX spectrophotometer, using 10 cm