Thermal and Photochemical Behaviour, Structure and Bonding of the Stereoisomers of 6,7,8,9,14a,14b-Hexahydrodipyrido[1,2-*a*:2′,1′-*c*][1,4]diazocine

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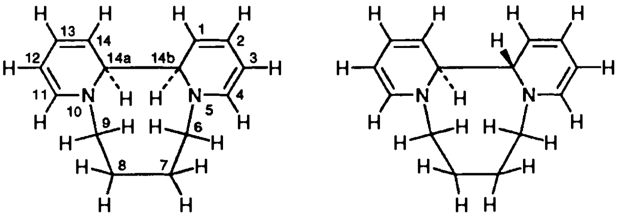
The *meso* and (±) isomers of the title compound have been prepared by reduction of 1,1′-(butane-1,4-diyl)dipyridinium dibromide with sodium amalgam. The *meso* form converts thermally into the (±) form, which reverts photochemically into the *meso* form through the diradical intermediate. The diradical generated by photolysis was characterized by EPR and absorption spectroscopy. MNDO calculations indicate that the energetically most favourable *meso* and (±) conformers possess an extremely long C–C single bond of *ca.* 1.60 Å at the position joining the two 1,2-dihydropyridine rings, the latter being lower in energy than the former by 5.7 kcal mol^{-1}.† The available experimental facts are reasonably accounted for by the theoretical results.

A number of investigations of pyridinyl radicals have been made and the chemistry of the radicals has been established through systematic studies of their physicochemical properties.[1-4]

In connection with the pyridinyl radicals, the non-conjugated pyridinyl diradicals of the type $\mathrm{Py^{\bullet}{-}[CH_2]_n{-}Py^{\bullet}}$ are intriguing from both theoretical and experimental viewpoints in the sense described below. Our recent study reveals that the pyridinyl diradicals, for $n = 2$ and 3, are in equilibrium with the corresponding cyclomers of *meso* and (±) forms formed by intramolecular cyclization, where the equilibrium overwhelmingly tends toward the cyclomers in the dark.[5-7] Among other things, of special interest is the fact that the *meso* and (±) cyclomers exhibit high responses to heat and light. In brief, the *meso* form is thermally converted into the (±) form and, inversely, the (±) form is photochemically converted into the *meso* form through the diradical intermediate.

In order to understand the chemistry of the pyridinyl diradicals, it is essential to prepare higher members of the diradical systems and to examine systematically the thermal and photochemical behaviour of the cyclomers. In this paper, we report the preparation of the *meso* and (±) stereoisomers of 6,7,8,9,14a,14b-hexahydrodipyrido[1,2-*a*:2′,1′-*c*]diazocine (Fig. 1) and the physicochemical properties, together with those of the photolytically generated diradical ($n = 4$). Moreover, we examine the structural and bonding features specific to the cyclomers on the basis of the semiempirical MNDO and INDO/S calculations.[8-10]



meso (±)

Fig. 1 Structures of the *meso* and (±) cyclomers and numbering of atomic positions

Experimental

General.—Standard vacuum techniques were used in the preparation and purification of the diradical, cyclomers, and solvents. UV–VIS spectra were measured on a Hitachi H220S spectrophotometer, EPR spectra were recorded on a Varian Model E-109E EPR spectrometer, and ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. Light irradiation was carried out using a high pressure Hg lamp (500 W) equipped with UV-35 glass filter, which is transparent at wavelength longer than 350 nm.

Materials.—1,1′-(butane-1,4-diyl)dipyridinium dibromide was prepared by treating 1,4-dibromobutane with a large excess of pyridine without solvent at 50 °C for 20 min. A solid product was filtered off and recrystallized from methanol to yield colourless crystals, m.p. 247–248 °C (Found: C, 44.6; H, 4.9; N, 7.3. Calc. for $C_{14}H_{18}Br_2N_2$: C, 44.95; H, 4.85; N, 7.49%).

Preparation of Cyclomers.—Cyclomer formation from 1,1′-(butane-1,4-diyl)dipyridinium dibromide was carried out by the following procedure. A solution of the dibromide (0.05 mmol in 20 cm^3 of water) was added dropwise to a suspension of 3% sodium amalgam in hexane (with stirring) under a nitrogen atmosphere at 0 °C. The hexane layer gradually turned pale yellow. After stirring for about 1 h, the organic layer was dried (magnesium sulfate) and filtered and the solvent was replaced by 2-methyltetrahydrofuran (MTHF) or CD_3CN *in vacuo* for spectral measurements. Here care was taken in handling the product in the tube to maintain the temperature below 25 °C in the dark.

Results and Discussion

Characterization and Properties of Cyclomers.—A solution of the reduction product shows no EPR signal at room temp. but exhibits a well-resolved ^{1}H NMR spectrum. This indicates that the reduction product is a diamagnetic compound formed by two-electron reduction of the dipyridinium dication. In solution, however, the reduction product is usually considered to exist as two different stereoisomers (Fig. 1), so that we identified them independently with the aid of spectroscopy through the following procedures. When the reduction product was warmed in CD_3CN at 80 °C, the ^{1}H NMR spectrum changed gradually, showing a thermal conversion, and finally gave only the spectrum of one isomer shown in Fig. 2(*b*). In contrast to the thermal conversion, light irradiation of the resulting solution at 0 °C caused a conversion in the reverse direction, with the result that the ^{1}H NMR spectrum exhibits

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† 1 kcal = 4.184 kJ.

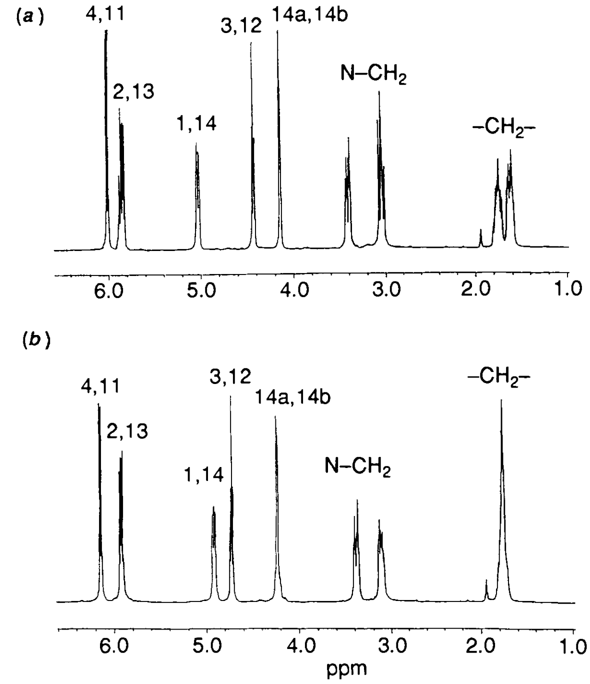

Fig. 2 ^{1}H NMR spectra of (*a*) *meso* and (*b*) (±) cyclomer at room temp. in CD$_3$CN

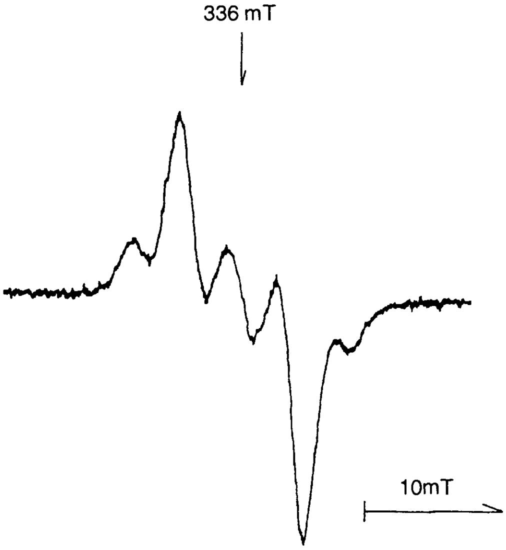

Fig. 3 Triplet EPR spectrum of the diradical generated by the photodissociation of the *meso* and (±) cyclomers at −196 °C in MTHF

the almost pure form of another isomer as shown in Fig. 2(*a*). Interestingly, the thermal and photochemical conversions are completely reversible in the degassed, sealed solution under the above conditions. This suggests strongly that the compound of interest should exist in two sterically isomeric forms.

In Table 1 are summarized the NMR spectral data of the two cyclomers, together with their assignments. Analysis of the ^{1}H NMR spectra by means of the homonuclear double resonance and H–H COSY experiments reveals that both isomers have the structure of 6,7,8,9,14a,14b-hexahydrodipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazocine. This structural assignment is corroborated by ^{13}C NMR spectroscopy. That is, the appearance of the five ^{13}C NMR lines for each isomer in the range of 58–138 ppm can be interpreted as arising from two asymmetric dihydropyridine rings. By comparing the NMR spectra of the present cyclomers with those of the lower homologues (n = 2 and 3) and by reference to the fact that the (±) form is more stable than the *meso* form,[6,7] we assign here the stable isomer to the (±) cyclomer and the less stable isomer to the *meso* cyclomer. As will be mentioned below, this assignment is substantiated by the results of MNDO calculations.[8]

It is remarked that the ^{1}H NMR spectrum of the *meso* form differs from the (±) form in the following respect. The β-methylene protons appear as two distinct sets of multiplets for the *meso* form, while those appear as a broad multiplet for the (±) form (Fig. 2). This aspect will be interpreted below from the difference in the spatial arrangements of the protons. In this connection, it is noted that no modifications of these ^{1}H NMR spectra are observed upon heating the sealed solution up to 90 °C. This implies that the central hexahydro-1,4-diazocine ring in both cyclomers should be somewhat conformationally rigid at least on the NMR time scale.

Generation and Properties of the Diradical.—The solutions of *meso* and (±) cyclomers in MTHF show no EPR signal at −196 °C in the dark. However, irradiation of either solution of the *meso* or (±) cyclomer with light at $\lambda > 350$ nm leads to the appearance of an EPR signal as shown in Fig. 3. This signal is ascribed to the triplet transition of a two spin system generated by photolysis of a cyclomer. Analysis of the EPR spectrum reveals that the zero field parameters are $|D| = 0.015$ and $|E| \simeq 0$ cm^{-1}. The D value is consistent with the spin–spin dipolar interaction for an average separation of 5.6 Å, using the relation $D = -(3/2)g^2\beta^2r^{-3}$. The E value for the present triplet species is close to zero, in contrast to that for 1,1′-(ethane-1,2-diyl)dipyridinyl diradical (n = 2),[6] *i.e.*, $|E| = 0.0012 - 0.0017$ cm^{-1}. The zero E value implies that the molecular skeleton of the present diradical should be rather conformationally flexible in comparison with the diradical for n = 2 because of the presence of four methylene groups.

Fig. 4 shows the absorption spectra of the cyclomers and the diradical in MTHF, where the solid, dashed, and dotted lines refer to those of the *meso* and (±) cyclomers at room temp. and that of the diradical at −196 °C respectively. Light irradiation of the solutions of *meso* and (±) cyclomers changes their spectra into that of the dotted line and the intensity of this spectrum shows no change for a long period at −196 °C. Hence the appearance of the longest wavelength absorption band at 310 nm demonstrates clearly the photolytic generation of the diradical from both cyclomers. Raising the temperature of the system up to 0 °C after the diradical formation gives rise to a reformation of the *meso* cyclomer, since the spectral change is observed as given by the spectrum of solid line. Of course, the conversion of *meso* into (±) is achieved by further warming the resulting solution up to 80 °C. These light and thermal processes can be repeated many times on a given sample.

Structural and Bonding Features of Cyclomers.—To obtain the structural facts of the cyclomers, we carried out the full geometry optimizations with the MNDO method.[8] Here the molecular symmetry groups of the *meso* and (±) forms are assumed to belong to the point groups C_s and C_2, respectively. As a result, the heats of formation indicate that the (±) form is lower in energy than the *meso* form by 5.7 kcal mol^{-1}. This is consistent with the fact that the *meso* form converts thermally into the (±) form. Fig. 5 shows the geometrical parameters with respect to C–C and C–N bond lengths of the *meso* and (±) structures. It is seen that the two 1,2-dihydropyridine rings take nearly planar forms and a π conjugation is spread over each C=C–C=C–N moiety of the rings. The more striking aspect is the finding that the C–C single bond connecting the two 1,2-dihydropyridine rings is unusually long in comparison with the other C–C single bonds as well as the ones in ordinary

Table 1 ^1H and ^{13}C NMR spectral data for the *meso* and (±) cyclomers in CD_3CN

	meso		(±)	
Position	δ	*J*/Hz[a]	δ	*J*/Hz
^1H NMR				
1,14	5.03 (dddd)[b]	9.77, 3.91, 1.46, 1.00	4.91 (dddd)	9.28, 3.20, 1.46, 1.00
2,13	5.83 (dddd)	9.77, 5.37, 1.40, 1.00	5.91 (dddd)	9.28, 5.37, 1.30, 0.98
3,12	4.43 (ddd),	6.83, 5.37, 1.46	4.72 (ddd)	7.32. 5.37, 1.46
4,11	5.99 (dddd)	6.83, 1.40, 1.00, < 1.0	6.13 (dddd)	7.32, 1.30, 1.00, 0.80
6,9	3.00–3.09 (m) 3.38–3.44 (m)		3.07–3.15 (m) 3.34–3.41 (m)	
7,8	1.57–1.68 (m) 1.71–1.82 (m)		1.69–1.83 (m)	
14a,14b	4.14 (ddd)	3.91, 1.00, < 1.0	4.23 (ddd)	3.20, 0.98, 0.80
^{13}C NMR				
1,14	92.8		94.8	
2,13	125.9		124.8	
3,12	111.8		108.4	
4,11	138.4		134.9	
6,9	52.3		52.8	
7,8	27.0		25.5	
14,14b	61.6		58.3	

[a] *J* values were obtained by simulation. [b] d = doublet and m = multiplet.

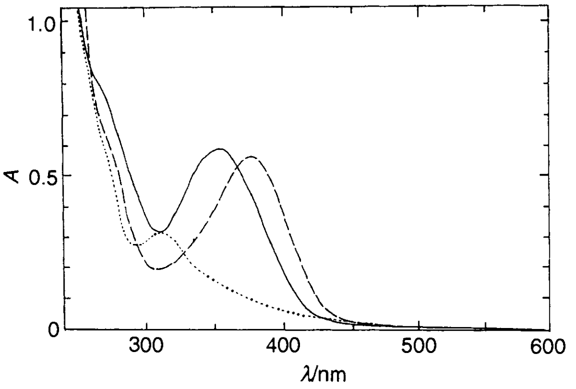

Fig. 4 Absorption spectra of the *meso* (———) and (±) (— — —) cyclomers at room temp. and the diradical (· · · ·) at −196 °C in MTHF

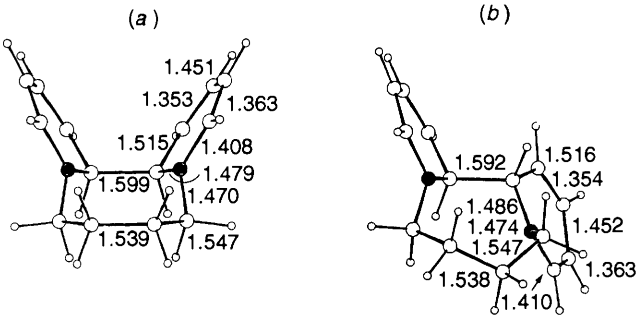

Fig. 5 Optimized geometrical structures of the (*a*) *meso* and (*b*) (±) cyclomers, where N atoms are indicated with black circles; bond distances are given in Å; heats of formation (*a*) 85.1, (*b*) 79.4 kcal mol^{-1}

saturated hydrocarbons. The bond lengths are 1.598 and 1.592 Å in the *meso* and (±) forms, respectively. It is thus obvious that the thermal and photochemical reactions accompanied by a facile bond cleavage should be responsible for the presence of a long C–C single bond in both cyclomers.

We briefly explain the origin of bond elongation common to both cyclomers in terms of two interaction effects. One is a coulombic repulsion effect arising from a charge polarization.[11] In short, the C-14a and C-14b atoms are surrounded by the more electronegative nitrogen and sp^2 hybrid carbon atoms,[12] and they should be charged positively in the ground state. In fact, net atomic charges obtained by the MNDO calculations indicate that the C-14a atom carries the most positive charge, 0.194 and 0.190 (e) in the *meso* and (±) structures, respectively. This should induce an extra coulombic repulsion between the C-14a and C-14b atoms, leading to an elongation of the C–C single bond. The other is an orbital interaction effect.[13,14] Orbital analysis reveals that a through-bond interaction is operative between the two non-conjugated C=C–C=C–N π moieties *via* the C–C single bond in both cyclomers. In Fig. 6 we illustrate the through-bond interaction in the highest occupied molecular orbital (HOMO) and the next HOMO of the *meso* cyclomer with C_s symmetry. To sum up, the appearance of long C–C single bonds is attributable to the combined effects of these interactions.

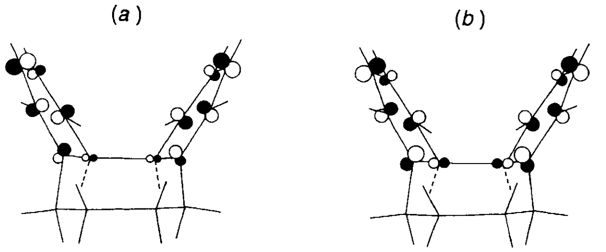

Fig. 6 Representation of the through-bond interaction in the (*a*) next HOMO and (*b*) HOMO of the *meso* cyclomer with C_s symmetry

As noted above, the distinction between the ^1H NMR spectra concerning the β-methylene protons in both cyclomers (Fig. 2) can be interpreted from the difference in the spatial arrangements of the protons. The geometrical structure of the *meso* form indicates that one of the β-methylene protons points toward the shielding region of the adjacent 1,2-dihydropyridine ring and, consequently, the proton NMR signal should appear in the upfield region compared with the remaining proton.[15]

Electronically Lowest Excited State of Cyclomers.—Assuming the geometrical structures in Fig. 5 and carrying out the INDO/S calculations including 55 singly excited configurations,[9,10] the lowest singlet transition energy is calculated to be 3.96 eV for the *meso* cyclomer and to be 4.00 eV for the (±) cyclomer, in fairly good agreement with the respective experimental values of 3.54 and 3.31 eV. In this connection, configuration analysis indicates that for both cyclomers the lowest excited singlet state is described mainly by two orbital jumps from the HOMO to the next lowest unoccupied molecular orbital (next LUMO) and from the next HOMO to the LUMO, in order of importance. Further, examination of these orbitals with regard to the C–C single bond reveals that in the (±) cyclomer the promotion of one electron from the HOMO to the next LUMO leads to a decrease in bonding electrons in the C–C single bond and, at the same time, to an increase in the net positive charge on both carbon atoms. It is thus expected that the orbital jumps involved in the lowest excited singlet state should contribute to the weakening of the C–C single bond. A similar analysis suggests that in the lowest excited singlet state the *meso* cyclomer also undergoes a photochemical bond fission at the long C–C single bond.

Conclusions

The present experiments clearly indicate that the cyclomers of *meso* and (±) forms of 6,7,8,9,14a,14b-hexahydrodipyrido[1,2-*a*:2′,1′-*c*][1,4]diazocine are sensitive to heat and light. That is, the *meso* form isomerizes thermally into the (±) form, which converts photochemically into the *meso* form. Besides, both cyclomers are photolized to yield the diradical at low temperature. The molecular orbital treatments reveal that the thermal conversion is responsible for the occurrence of an unusually long C–C single bond at the position connecting the two 1,2-dihydropyridine rings, in conjunction with the thermodynamic stability of the (±) cyclomer. Moreover, the facile C–C single bond cleavage on light irradiation is attributed to the bonding nature of the molecular orbitals involved in the lowest excited singlet state of the cyclomers, together with the electrostatic repulsive interaction. The effect of coulombic repulsion can be said to play an important role in the occurrence of photochemical bond fission. Actually, this will be shown to hold good for the lower homologues of the present cyclomers.[11]

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