October, 1987] © 1987 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 60, 3789—3790 (1987) 3789

Effects of $CH_3\cdots O$ Hydrogen Bond on the Rotamer Populations in 9-(Alkoxymethyl)-1,4-dimethyltriptycenes

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(Received March 24, 1987)

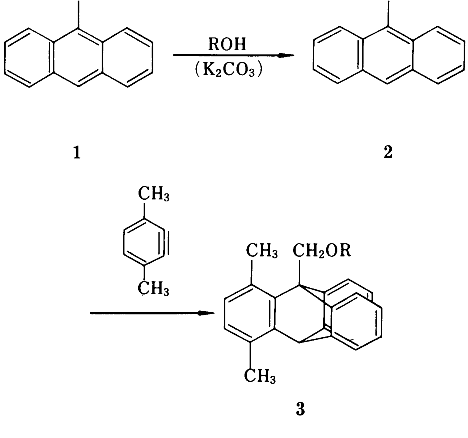
Synopsis. Rotamer populations in 9-(alkoxymethyl)-1,4-dimethyltriptycenes, where the alkyl is an ethyl, a methyl, or a 2,2,2-trifluoroethyl, were examined by ^1H NMR spectra. The populations of the *sc* isomer decreased as the alkyl group becomes electronegative. The population ratio, *sc*/*ap*, of the methyl compound was almost the same with that for 1,4-dimethyl-9-(phenoxymethyl)triptycene to indicate that the populations of the rotamers in this and related series of compounds are determined on a delicate balance of various factors such as van der Waals repulsive and charge-transfer attractive interactions.

As an extension of the investigation on the factors affecting the rotamer populations, we have prepared 9-(methoxymethyl)-1,4-dimethyltriptycene to find that the population ratio, *sc*/*ap*, was 0.45 at −49.6 °C. The result was surprising because the corresponding 9-(phenoxymethyl) compound gave the ratio of 0.44 at −49.4 °C:[1)] Though the electron-density of the phenolic oxygen is supposed to be lower than that of methanol-oxygen, the rotamer populations in these compounds were almost the same. The results may imply that, though the basicity of the oxygen atom in the methoxy compound is higher than that of the phenoxy compound, the van der Waals radius of the methoxy-oxygen is larger than the phenoxy-oxygen to counterbalance the attractive $CH_3\cdots O$ interactions with the van der Waals repulsion, since high electron-density of an atom means a large steric size. Thus we felt it would be worthwhile to examine the electronic effects on the rotamer populations in 9-(alkoxymethyl)-1,4-dimethyltriptycenes to find whether the effects again would support the existence of the $CH_3\cdots O$ hydrogen bond. This paper reports the results of such an investigation.

Syntheses of the compounds in question were carried out in analogous ways to those reported previously:[1)] 9-(Chloromethyl)anthracene (**1**) was treated with the corresponding alcohol, in the presence of a base if necessary, and the resulting 9-(alkoxymethyl)anthracene (**2**) was treated with 3,6-dimethylbenzyne to produce the desired 9-(alkoxymethyl)-1,4-dimethyltriptycene (**3**). As alkyl groups, other than a methyl, an ethyl and a 2,2,2-trifluoroethyl were chosen, the former giving a more basic oxygen and the latter giving a less basic oxygen than the methoxy-oxygen.

The rotamer populations were determined by 400 MHz ^1H NMR spectra at low temperatures. Assignment of the conformations was straightforward from the methylene signals (see Scheme 1).[1)] The results are shown in Tables 1 and 2. The population of the *sc* form was divided by 2 to accommodate the fact that there are two (+ and −) equivalent conformations for the *sc* form.

The results clearly indicate that, as the alkyl group becomes electronegative and consequently the proton affinity of the oxygen atom in the 9-substituent decreases, the population ratios (*sc*/*ap*) become small and the free energy differences between the *sc* and the *ap* rotamers become large. The results are consistent with the presence of the $CH_3\cdots O$ hydrogen bond, if we compare the populations in the 9-(alkoxymethyl)-1,4-



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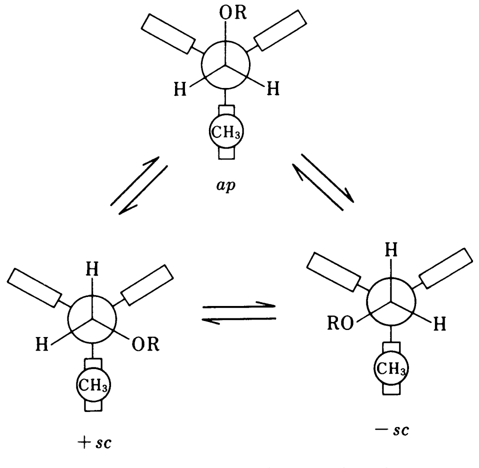

Scheme 1. Rotational circuit.

Table 1. Rotamer Populations in 9-(Alkoxymethyl)-1,4-dimethyltriptycenes in $CDCl_3$ at Various Temperatures

Alkyl	Population ratio[a)] (Temperature/°C)
CH_3CH_2	0.346 (−49.5) 0.354 (−39.6) 0.372 (−9.7)
CH_3	0.225 (−49.6) 0.240 (−39.6) 0.269 (−29.6) 0.278 (−19.7) 0.304 (−9.7)
CF_3CH_2	0.149 (−49.5) 0.163 (−39.6) 0.175 (−29.6) 0.188 (−19.7)

a) +(or −) *sc*/*ap*: see text.

Table 2. Thermodynamic Parameters for the Equilibrium, $ap \rightleftharpoons sc$, in 9-(Alkoxymethyl)-1,4-dimethyltriptycenes in $CDCl_3$ and Related Data

Alkyl	ΔH°	ΔS°	PA[b]
	kcal mol^{-1}[a]	cal mol^{-1} K^{-1}	kcal mol^{-1}
CH_3CH_2	0.21±0.05	−1.2±0.2	190.3
CH_3	0.88±0.16	1.0±0.7	184.9
CF_3CH_2	0.87±0.05	0.1±0.2	174.9

a) 1 cal≑4.184 J. b) Proton affinity of the corresponding alcohols obtained from the gas phase equilibrium.[2)]

dimethyltriptycene series.

As was discussed previously, the 9-(alkoxymethyl) group in these compounds is placed in a space where other neighboring groups are in close proximity. Therefore, the repulsive interactions between the alkoxy-oxygen and the 1-methyl group is especially severe in the *sc* conformation, where the attractive $CH_3 \cdots O$ interaction is also possible. We believe that the bulkiness effects of the methoxy-oxygen compensate the stabilization by the $CH_3 \cdots O$ hydrogen bond in 9-(methoxymethyl)-1,4-dimethyltriptycene to make the apparent rotameric populations of the compound about the same with that of 1,4-dimethyl-9-(phenoxymethyl)triptycene.

We conclude that the $CH_3 \cdots O$ hydrogen-bond effects on the rotamer populations do exist in this series but care should be exercised in comparing the population ratios of rotamers in different series of compounds, if the molecules are in congested states.

Experimental

Determination of Population Ratios. The ^{1}H NMR spectra at low temperatures were obtained with the use of a JEOL GX-400 NMR spectrometer. The indicated temperatures were calibrated with a thermocouple. For the determination of populations, the integrated intensities were obtained by cutting the chart papers and weighing them for several times. The peaks for the integration were those due to 9-methylene protons.

9-(Ethoxymethyl)anthracene. A solution of 0.15 g (0.66 mmol) of 9-(chloromethyl)anthracene[3)] in 20 mL of ethanol was stirred for 10 h at room temperature. The mixture was poured into water and extracted with dichloromethane. The solvent was evaporated, after drying over magnesium sulfate, to afford 0.14 g (90%) of practically pure 9-(ethoxymethyl)anthracene. This compound was directly used for the syntheses of the corresponding triptycene. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded: 1.27 (3H, t, J=6.0 Hz), 3.70 (2H, q, J=6.0 Hz), 5.43 (2H, s), 7.1—8.6 (8H, m), 8.43 (1H, s).

9-[(2,2,2-Trifluoroethoxy)methyl]anthracene. A mixture of 0.20 g (0.88 mmol) of 9-(chloromethyl)anthracene, 1.30 g (13.0 mmol) of 2,2,2-trifluoroethanol, and 0.12 g (0.86 mmol) of potassium carbonate in 40 mL of acetone was refluxed for 3 d. The precipitate was filtered off and the product was taken up into dichloromethane by shaking the filtrate with a mixture of water and dichloromethane. The organic layer was washed with aqueous sodium hydroxide and dried over magnesium sulfate. Evaporation of the solvent afforded 0.20 g of the crude product which was recrystallized from dichloromethane-hexane. The mother liquor was submitted to preparative TLC (silica gel, 2:1 hexane-dichloromethane) to afford a further crop. The desired product was obtained in 0.16 g (62%) yield. This compound was directly used for the triptycene synthesis. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded: 3.89 (2H, q, J=9.0 Hz), 5.66 (2H, s), 7.3—8.6 (8H, m), 8.48 (1H, s).

9-(Methoxymethyl)-1,4-dimethyltriptycene. To a boiling solution of 0.46 g (2.1 mmol) of 9-(methoxymethyl)anthracene[3)] in 20 mL of dichloromethane, were simultaneously added from two separatory funnels a solution of 2.23 g (13.5 mmol) of 3,6-dimethylanthranilic acid[4)] in 70 mL of acetone and that of 3.92 g (33.5 mmol) of isopentyl nitrite in 70 mL of dichloromethane in 3 h. The whole was refluxed for further 30 min and the solvent was evaporated. The residue was submitted to chromatography on alumina with a 4:1 hexane-dichloromethane eluent. The desired product, mp 219—220 °C, was obtained in 20% yield after recrystallization of the product from dichloromethane-hexane. Found: C, 88.50; H, 6.49%. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%. ^{1}H NMR ($CDCl_3$) δ=2.43 (3H, s), 2.52 (3H, s), 3.70 (3H, s), 5.03 (2H, br s), 5.56 (1H, s), 6.58 and 6.66 (2H, ABq, J=8.1 Hz), 6.8—7.8 (8H, m).

9-(Ethoxymethyl)-1,4-dimethyltriptycene. Mp 167.5—169 °C, was prepared in 84% yield similarly. Found: C, 88.24; H, 7.27%. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11%. ^{1}H NMR ($CDCl_3$) δ=1.33 (3H, t, J=6.3 Hz), 2.40 (3H, s), 2.50 (3H, s), 3.83 (2H, q, J=6.3 Hz), 5.03 (2H, br s), 5.54 (1H, s), 6.4—8.0 (10H, m).

1,4-Dimethyl-9-[(2,2,2-trifluoroethoxy)methyl]triptycene. Mp 151—152 °C, was prepared similarly in 41% yield. Found: C, 76.01; H, 5.67%. Calcd for $C_{25}H_{21}F_3O$: C, 76.13; H, 5.37%. ^{1}H NMR ($CDCl_3$) δ=2,44 (3H, s), 2.50 (3H, s), 4.18 (2H, q, J=9.0 Hz), 5.34 (2H, br s), 5,58 (1H, s), 6.4—7.6 (10H, m).

We thank Dr. Shigeru Murata, Institute for Molecular Science, for the measurement of the ^{1}H NMR spectra.

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