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REGULAR ARTICLE

Atropisomerism about the C(1)-N single bond in *N,N*-disubstituted-1-aminoanthracenes: isolation of conformational diastereomers

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Abstract. Restricted rotation about the C(1)-N single bond in *N*, *N*-disubstituted 1-aminoanthracenes has been investigated. The synthesis, isolation and characterization of diastereomers arising out of the hindered rotation about the C_{SP^2}-N_{SP^2} single bond has been demonstrated. With unsymmetrical substituents on the Nitrogen atom, preferred conformations about the C(1)-N bond were observed.

Keywords. Diels-Alder reaction; steric interaction; restricted rotation; atropisomerism; conformational diastereomers.

1. Introduction

Atropisomers are conformers which interconvert slowly enough because of steric and electronic constraints that they can be isolated.[1–3] The result of the restricted rotation about a single bond can be such that an apparent single compound can actually be a mixture of two compounds or, an achiral compound can be a racemic mixture. Atropisomerism may give rise to geometrical isomers, diastereoisomers, or enantiomers. It offers new ways of thinking about stereochemistry, dynamic processes, and about the relationship between structure and activity in both the biological and stereoselective sense. The conformational restriction has been used by scientists to study the compounds having structurally crowded features that cause decreased freedom of intramolecular motion, particularly of rotation around chemical bonds.

The restricted rotation about N-Ar single bond of *N*-phenyleimide has been utilised for stereoselective synthesis,[4] molecular recognition[5] and self assembly[6] and for the preparation of functionalised polymers.[7] The importance of both the rotational barrier and the spatial disposition of substituents on the *N*-phenyl group has been investigated in these works. The restricted rotation about a single bond is generally due to the combined effects of steric hindrance and electronic repulsion. The effect of electronic repulsion on the control system of the rotational barrier has been studied by preparing 4′-substituted 2-benzylamino-*N*-(2′-methylphenyl) succinimides **1** (Scheme 1).[8] The compound exists as two isomers **1a** and **1c**. The two isomers are easily distinguished from each other by ^{1}H NMR chemical shifts of the 2′-methyl group. The two isomers exist in the ratio 1:1.

Stereoisomerism due to restricted rotation about single bonds, i.e. atropisomerism is a well-known and widespread phenomenon among the biaryls and have been exploited in the form of the binaphthyl class of chiral auxiliaries.[9,10] Biaryls are commonly used as chiral ligands and chiral auxiliaries.[9,11] Clayden *et al.*,[12] have reported that atropisomerism which arises due to restricted rotation about single bonds of the non-biaryl compounds results into the formation of new chiral centres with stereoselectivity that can exceed 99:1.

Various methods have been developed for the diastereo- and enantioselective synthesis of atropisomeric molecules resulting from rotational barrier about single bonds.[13,14] The potential of the axial chirality of non-biaryl atropisomeric molecules as a source of asymmetric induction has been exploited.[15–17]

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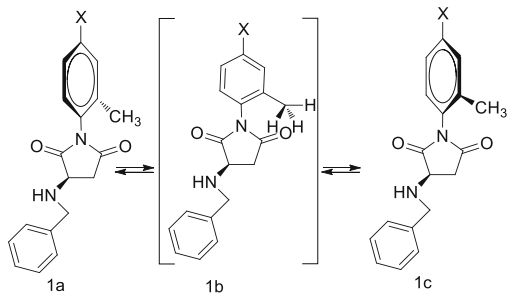


X- NEt_2, OMe, Me, H, Cl, F, CO_2Me, NO_2

Scheme 1. Rotational isomerization of **1b** to **1a** and **1b**.

We wish to report here the stereochemical outcome of the Diels-Alder reaction of 1-*N*, *N*-disubstituted aminoanthracenes with symmetrical dienophiles. It has been observed that introduction of the bridge at the 9,10-positions results in the restricted rotation of the aryl C(1)-N single bond, paving the way for the isolation of conformational diastereomers.

2. Experimental

2.1 *Materials and Physical measurements*

The melting points were recorded on 'Veego' melting point apparatus and are uncorrected. IR spectra were recorded in KBr on a Shimadzu FT-IR 8400. The ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz Jeol ECS-400 (or 100 MHz for ^{13}C NMR) spectrometers using either residual solvent signals as an internal reference or from internal tetramethylsilane on the δ scale ($CDCl_3\delta_H$, 7.24 ppm, δ_C 77.0 ppm and for DMSO-$d_6\delta_H$, 2.52 ppm, δ_C 41.23 ppm). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Abbreviations for ^{1}H NMR multiplicities are as follows: s-singlet; d-doublet; dd-doublet of doublet; bs-broad singlet; m-multiplet. The compounds were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as a solvent mixture, followed by crystallization from different solvents.

2.2 *Synthesis of dienes*

2.2a *N-(anthracen-1-yl)-N-benzylacetamide* **5**: To a solution of 1-acetamidoanthracene (500 mg) in DMSO (4 mL) was added Na_2CO_3 (220 mg) and the mixture was stirred at room temperature for 10 min. Then benzyl chloride (0.3 mL) was added dropwise. The reaction mixture was then heated at 80−90 °C for 5 h. Then the reaction mixture was cooled and water was added and extracted with ethyl acetate. The organic layer was washed with water and dried over Na_2SO_4 and concentrated to get the crude product. The product was then purified by silica gel column chromatography. The pure *N*-(anthracen-1-yl)-*N*-benzylacetamide was eluted as colourless solid at 8% ethyl acetate in hexane. Yield: 79% (550 mg); M.p.: 150−153 °C; $C_{23}H_{19}NO$: Anal. Found: C, 84.85; H, 5.84; N, 4.27 Calc.: C, 84.89; H, 5.89; N, 4.30; IR (cm^{-1}): 3024, 3003, 2952, 2837, 1726, 1708, 1654,1271; ^{1}H NMR (δ, ppm in $CDCl_3$): 8.51 (s, 1H), 8.33 (s, 1H), 7.97–8.04 (m, 3H), 7.5–7.55 (m, 2H), 7.2–7.33 (m, 6H), 6.92–6.93 (d, J = 5.4 Hz, 1H), 4.31 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 171.2, 139.3, 137.8, 129.7, 129.5, 128.2, 128.0, 127.4, 127.3, 127.0, 126.5, 126.2, 126.0, 125.2, 124.1, 47.2, 21.2.

2.2b *N-acetyl-N-(anthracen-1-yl) benzamide* **7**: To a suspension of 1-acetamidoanthracene (500 mg) in 5% NaOH (5 mL) was added few drops of THF. Then benzoyl chloride (0.5 mL) was added and the reaction mixture was stirred at room temperature for 5 h. The solid material formed was filtered, washed with water and dried. Then it was recrystallized from ethanol to get *N*-acetyl-*N*-(anthracen-1-yl) benzamide as off-white solid. Yield: 85% (620 mg); M.p.: 175−178 °C; $C_{23}H_{17}NO_2$: Anal. Found: C, 81.37; H, 5.02; N, 4.11 Calc.: C, 81.40; H, 5.05; N, 4.13; IR (cm^{-1}): 3093, 2994, 2868, 1703, 1679, 1418, 932; ^{1}H NMR (δ, ppm in $CDCl_3$): 8.44–8.47 (d, J = 8.1 Hz, 2H), 7.97–8.01 (m, 3H), 7.65–7.67 (m, 2H), 7.22–7.52 (m, 7H), 2.45 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 175.0, 172.8, 139.9, 133.0, 131.4, 131.2, 130.0, 129.7, 129.2, 129.1, 128.5, 128.3, 127.9, 126.7, 126.2, 125.1, 124.0, 123.7, 121.4, 22.4.

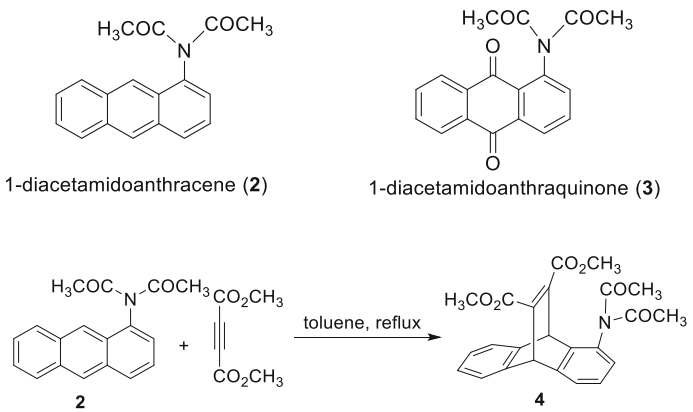
2.3 *General procedure for the Diels-Alder reaction of 1-N-disubstituted anthracenes with dimethylacetylenedicarboxylate*

To a 100 mL round bottom flask, the diene (1 equiv.) was dissolved in toluene. To it was added dimethylacetylenedicarboxylate (3 equiv.) dropwise at room temperature. The reaction mixture was then refluxed for 6 h. TLC showed completion of the reaction and two new products were observed. Then the reaction mixture was cooled and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography. The two isomers were eluted at different solvent systems.

2.3a *(9R,10S)-dimethyl 1-(N-acetylacetamido)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate* **4**: Colorless solid; Yield: 82% (620 mg); M.p.: 178−181 °C; $C_{24}H_{21}NO_6$: Anal. Found: C, 68.71; H, 5.02; N, 3.31 Calc.: C, 68.73; H, 5.05; N, 3.34; IR (cm^{-1}): 3010, 2958, 1714, 1695, 1631, 1471, 1274, 1058, 758; ^{1}H NMR (δ, ppm in $CDCl_3$): 6.61–7.12 (m, 7H), 5.38 (s, 1H), 5.12 (s, 1H), 3.59 (s, 3H), 3.58 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 171.3, 170.7, 167.0, 166.5, 141.3, 131.4, 131.0, 129.2, 129.1, 126.7, 126.2, 125.1,123.9, 53.0, 52.8, 45.1, 37.4, 22.7, 21.0.

The total yield of both isomers **6a** and **6b**: 78% (560 mg).

2.3b *(9R, 10S)-dimethyl 1-(N-benzylacetamido)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate*



Scheme 2. Diels-Alder reaction of 1-diacetamidoanthracene with DMAD.

6a: Colorless solid; M.p.: 169−171 °C; $C_{29}H_{25}NO_5$: Anal. Found: C, 74.46; H, 5.37; N, 3.03 Calc.: C, 74.50; H, 5.39; N, 3.00; IR (cm^{-1}): 3060, 3024, 2970, 2835, 1776, 1710, 1653, 1587, 1477, 1383, 1189; ^{1}H NMR (δ, ppm in $CDCl_3$): 6.98–7.51 (m, 11H), 6.46–6.51 (m, 1H), 4.98 (s, 1H), 4.74 (s, 1H), 4.30 (s, 2H), 3.49 (s, 3H), 2.94 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 175.7, 167.4, 165.3, 143.5, 139.3, 138.6, 134.9, 129.1, 126.4, 125.3, 125.0, 52.3, 49.3, 45.8, 44.9, 37.8, 22.5.

2.3c *(9R, 10S)-dimethyl 1-(N-benzylacetamido)-9,10-dihydro-9, 10-ethenoanthracene-11,12-dicarboxylate*
6b: Colorless solid; M.p.: 192−195 °C; $C_{29}H_{25}NO_5$: Anal. Found: C, 74.48; H, 5.33; N, 3.01 Calc.: C, 74.50; H, 5.39; N, 3.00; IR (cm^{-1}): 3052, 3025, 2948, 2863, 1729, 1714, 1649, 926; ^{1}H NMR (δ, ppm in $CDCl_3$): 6.94–7.56 (m, 11H), 6.41–6.58 (m, 1H), 4.94 (s, 1H), 4.79 (s, 1H), 4.28 (s, 2H), 3.41 (s, 3H), 3.28 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 175.5, 166.8, 165.2, 143.5, 139.3, 138.6, 134.9, 130.8, 129.1, 126.4, 125.3, 125.1, 125.0, 52.9, 52.4, 46.8, 44.3, 37.8, 26.4.

The total yield of both isomers **8a** and **8b**: 81% (580 mg).

2.3d *(9R, 10S)-dimethyl 1-(N-acetylbenzamido)-9,10-dihydro-9, 10-ethenoanthracene-11,12-dicarboxylate*
8a: Colorless crystal; M.p.: 203−205 °C; $C_{29}H_{23}NO_6$: Anal. Found: C, 72.32; H, 4.76; N, 2.85 Calc.: C, 72.34; H, 4.81; N, 2.91; IR (cm^{-1}): 3003, 2952, 2922, 2837, 1726, 1708, 1654, 1452, 1271, 1059; ^{1}H NMR (δ, ppm in $CDCl_3$): 7.90-8.05 (m, 3H), 7.48-7.88 (m, 6H), 7.19-7.46 (m, 3H), 5.57 (s, 1H), 5.48 (s, 1H), 3.89 (s, 3H), 3.47 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$): 176.6, 172.8, 167.2, 166.3, 143.0, 136.2, 132.1, 132.0, 131.6, 130.5, 128.7, 128.3, 128.0, 127.5, 127.2, 126.2, 126.1, 126.0, 124.3, 120.5, 52.1, 48.8, 45.1, 36.0, 22.6.

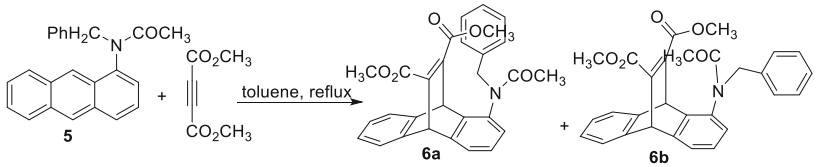
2.3e *(9R, 10S)-dimethyl 1-(N-acetylbenzamido)-9,10-dihydro-9, 10-ethenoanthracene-11,12-dicarboxylate*
8b: Colorless crystal; M.p.: 219−221 °C; $C_{29}H_{23}NO_6$: Anal. Found: C, 72.31; H, 4.79; N, 2.87 Calc C, 72.34; H, 4.81; N, 2.91; IR (cm^{-1}): 3084, 2951, 2887, 2837, 1723, 1702, 1684, 1656, 1416, 1293; ^{1}H NMR (δ, ppm in $CDCl_3$): 7.90–7.95 (m, 3H), 7.52–7.58 (m, 3H), 6.99–7.38 (m, 6H), 5.60 (s, 1H), 5.47 (s, 1H), 3.75 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (δ, ppm in $CDCl_3$):175.2, 172.3, 166.8, 165.6, 141.7, 132.5, 131.7, 130.9, 128.4, 127.9, 126.6, 125.8, 125.5, 125.2, 123.8, 119.6, 119.4, 107.7, 51.9, 51.6, 45.1, 35.8, 22.5.

3. Results and Discussion

Hindered rotation and non-planar conformation about the C(1)-N bond in 1-diacetamidoanthrane (**2**) and 1-diacetamidoanthraquinone (**3**) have been reported.[17] The two acetyl methyls appear as a singlet in both **2** and **3** because the two acetyl methyls have a similar environment (C_S symmetry) in the non-planar conformation.

If the C_S symmetry is destroyed, the two *N*-substituents will have different environments and hence will be non-equivalent in the ^{1}H NMR spectrum. This is exactly observed when a bridge was introduced at the C(9) and C(10) positions by reacting 1-diacetamidoanthracene with dimethylacetylenedicarboxylate (DMAD) as shown in Scheme 2.

The creation of a C(9)-C(10) bridge by the Diels-Alder reaction of 1-diacetamidoanthracene with DMAD causes steric hindrance resulting into the restricted rotation about the aryl C(1)-N bond. This also provides dissimilar magnetic environments to the two *N*-acetyl groups. Hence, the two acetyl groups become non-equivalent in the Diels-Alder adduct. This is confirmed by the ^{1}H NMR spectrum of the product **4**. The two acetyl methyl groups appear as two different singlets at 2.05 δ and 2.10 δ. The probability of *N*-aryl resonance due to delocalization of nitrogen lone pair onto the aromatic ring is very unlikely because planar arrangement about the C(1)-N bond will result into high steric crowding as the *N*-atom is attached to two carbonyl groups.



Scheme 3. Diels-Alder reaction of *N*-(anthracen-1-yl)-*N*-benzylacetamide (**5**) with DMAD.

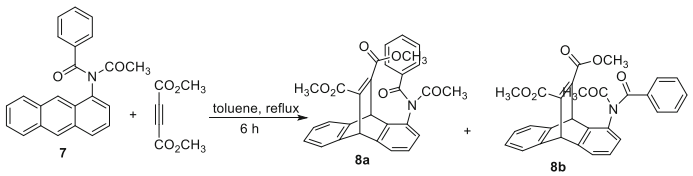
Hence, the formation of a partial double-bond about the C(1)-N bond cannot be the reason for the observed results. The carboxylate methyl groups appear as singlets at 3.58 δ and 3.59 δ. The singlet peaks at 5.12 δ and 5.38 δ are for the protons at C(9) and C(10) positions. The aromatic protons appear in the range 6.61–7.12 δ. The non-equivalence of the two acetyl groups was further confirmed from the ^{13}C NMR spectrum of **4**. They appear as two different peaks at 22.7 δ and 21.0 δ. This observation confirms that the introduction of C(9)-C(10) bridge in 1-diacetamidoanthracene affect the free rotation about the aryl C(1)-N bond. This provides a different magnetic environment to the two *N*-acetyl groups and hence they become non-equivalent. The product **4** exhibits IR absorption at 3010 and 2958 cm^{-1} which are characteristics of the aromatic, aliphatic groups, respectively. The peaks at 1714, 1695 cm^{-1} are for the two carboxylate carbonyl groups.

3.1 *Variable-Temperature ^{1}H NMR Studies*

In order to evaluate the barrier to rotation ($\Delta G\pm$) about the C(1)-N bond, the compound **4** was subjected to variable temperature ^{1}H NMR studies. The two singlets for the two *N*-acetyl methyl groups (2.05 δ and 2.10 δ) remain unchanged at elevated temperature (110 °C, toluene—d_8) and there is no sign of coalescence even at 180 °C (Nitrobenzene—d_5). Using the Gutowsky–Holm approximation, a lower limit of $\Delta G\pm$ more than 23 kcal mol^{-1} is estimated[18] which is the required energy barrier to the rotation for the rotational isomers to be separated as stable species at room temperature.[19]

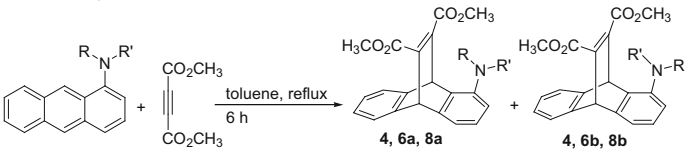
If the substituents at C(1)-N position are different, then we can expect two stereoisomers, i.e. atropisomers. So in order to study this, we focussed on the Diels-Alder reaction of unsymmetrically substituted aminoanthracenes with DMAD (Scheme 3). For this, *N*-(anthracen-1-yl)-N-benzylacetamide (**5**) was prepared by acetylation of 1-aminoanthracene followed by benzylation and used as diene. The Diels-Alder reaction was carried out by refluxing the diene and the dienophile in toluene for 9 hours. The starting materials were consumed and gave two new spots on thin layer chromatography which were separated by silica gel column chromatography using ethyl acetate and hexane as eluent. The isomers were confirmed by ^{1}H NMR and ^{13}C NMR spectra of the adducts.

In the ^{1}H NMR spectrum of **6a**, one of the two carboxylate methyl groups appear more upfield (2.94 δ) than the other. This corresponds to the CH_3 group that lies in the shielding zone of the phenyl ring of the benzyl group. The shielding effect is probably due to CH/ π interaction between the methyl protons and the π electrons of the phenyl ring. Such effect is absent in the case of the other carboxylate group as it is far from the phenyl ring and hence it appears more downfield (3.49 δ) in the ^{1}H NMR spectrum. The acetyl methyl group appears as a singlet at 2.24 δ. The singlet peak at 4.30 δ corresponds to the benzylic methylene group. The protons at C(9) and C(10) positions appear as a singlet at 4.74 δ and 4.98 δ. The aromatic protons appear in the range 6.46–7.51 δ. This observation is further confirmed by the ^{13}C NMR spectrum. The acetyl carbonyl group appears at 175.7 δ. The spectrum showed two different groups for the two carboxylate carbonyl groups at 167.4 δ and 165.3 δ. The carboxylate methyl groups appear at 52.3 δ and 49.3 δ. Here, one of the carboxylate appears more upfield at 49.3 δ than the other one. This shows that it experiences shielding effect of the phenyl ring. In the IR spectrum, the aromatic, aliphatic groups appear at 3060, 3024, 2970, 2835 cm^{-1}. The two carboxylate group are shown by the carbonyl peaks at 1776, 1710 cm^{-1}. The acetyl carbonyl group appears at 1653 cm^{-1}. In the case of **6b**, since the benzyl group is far from the C(9)-C(10) bridge, the carboxylate methyl group does not experience any shielding effect like that of **6a**. Hence, the two -CO_2CH_3 groups appear very near as two singlets at 3.28 δ and 3.34 δ in the ^{1}H NMR spectrum. The singlet at 2.11 δ is for the acetyl methyl group. In the ^{13}C NMR spectrum of **6b**, the carbonyl group appears at 175.5 δ. The peaks at 166.8 δ and 165.3 δ correspond to the two carboxylate carbonyl groups. Here, since the carboxylate methyl group do not fall in the shielding zone of the phenyl ring, the two methyl groups appear almost in the same range at 52.9 δ and 52.4 δ. This observation shows that the formation of C(9)-C(10) bridge results in the restricted rotation of the aryl C(1)-N bond. The groups attached to the N-atom being different give rise to the two atropisomers **6a** and **6b**.



Scheme 4. Diels-Alder reaction of **7** with DMAD.

Table 1. Diels-Alder reaction of *N*, *N*-disubstituted-1-aminoanthracenes with DMAD[a].



Substrate	Time (h)	Adduct	Ratio (**a:b**)	Total yield (%)[b]
R = R′- $COCH_3$	6	**4**	-	82
R- CH_2Ph, R′- $COCH_3$	9	**6**	65:35	78
R- COPh, R′- $COCH_3$	6	**8**	56:44	81

[a]Reaction conditions: Diene (1 equiv.), DMAD (3 equiv.) in toluene (5 mL) at 120 °C for 6 h.
[b]isolated yields.

In order to further prove the formation of atropisomers, the Diels-Alder reaction between *N*-acetyl-*N*-(anthracen-1-yl) benzamide (**7**) and DMAD was carried out. The reaction was carried out by refluxing the reaction mixture in toluene for 6 hours. In this case, also, thin layer chromatography showed the formation of two new spots. They were separated by silica gel column chromatography. Here also, from the ^{1}H NMR and ^{13}C NMR spectrum, it was found that the two spots were the atropisomers **8a** and **8b** which was resulted from the restricted rotation about the aryl C(1)-N single bond (Scheme 4). In both the cases of **6** and **8** also, the possibility of having a planar arrangement about the C(1)-N bond which may lead to the partial double bond formation is ruled out as the *N*-atom is attached to two bulky groups. In amide systems like the most widely investigated *N*, *N*-dimethylformamide and related derivatives, the methyl signals are different because of restricted rotation about the N-CO bond, but conformers cannot be physically isolated. Physical isolation of **6a** and **6b** and also **8a** and **8b** which are conformational diastereoisomers are interesting examples of atropisomerism about the Aryl C-N bond.

The two isomers could be differentiated from the ^{1}H NMR and ^{13}C NMR spectra of the adducts. In this case, also, the formation of the C(9)-C(10) bridge in the Diels-Alder adducts results in the hindered rotation about the aryl C(1)-N bond. Since the groups attached to C(1)-N group are different, it gives rise to the two diastereomers **8a** and **8b**. In the ^{1}H NMR spectrum of **8a**, the singlet peak at 2.23 δ is for the acetyl methyl protons. The two carboxylate methyl groups are shown by the two singlets at 3.47 δ and 3.89 δ. In this, one of the carboxylate methyl groups which is near the *N*-benzoyl group appears more upfield at 3.47 δ. This is because the methyl group falls in the shielding zone of the phenyl ring. The protons at C(9) and C(10) positions appear as singlets at 5.48 δ and 5.56 δ. The aromatic protons correspond to the multiplet in the range 7.19–8.05 δ. In the ^{13}C NMR spectrum of **8a**, the acetyl and the benzoyl carbonyl groups appear at 176.6 δ and 172.8 δ. The two carboxylate carbonyl groups are shown by the peaks at 167.2 δ and 166.3 δ. Here the two carboxylate methyl groups appear as two different peaks at 52.1 δ and 48.8 δ. This is because one of the methyl groups fall in the shielding zone of the phenyl ring and hence appear more upfield at 48.8 δ. The IR spectrum of **8a** exhibits peaks at 3003, 2952, 2922, 2837 cm^{-1} corresponding to the aromatic and the aliphatic groups. The carbonyl peaks at 1726 and 1708 cm^{-1} are for the two carboxylate groups. The peak at 1654 cm^{-1} corresponds to the acetyl group. In the ^{1}H NMR spectrum of **8b**, the acetyl methyl protons appear as a singlet at 2.36 δ. The two carboxylate methyl protons appear as singlets almost in the same range at 3.754 δ and 3.757 δ. In the case of **8b**, none of the methyl protons experience any kind

of shielding effect as that of **8a** and hence appear at the same range in the ^{1}H NMR spectrum. This is further confirmed from the ^{13}C NMR spectrum. Here the peaks at 175.2 δ and 172.3 δ correspond to the acetyl and benzoyl carbonyl groups. The two carboxylate carbonyl groups are shown by the peaks at 166.8 δ and 165.6 δ. In the isomer **8b**, as the carboxylate methyl groups do not fall in the shielding zone, they appear almost in the same range at 51.9 δ and 51.6 δ. This is because the phenyl group is away from the carboxylate methyl groups and there is no CH/ π interaction. The protons at C(9) and C(10) positions appear as singlets at 5.47 δ and 5.60 δ. The aromatic protons appear as multiplet in the range 7.01–7.95 δ. The overall result of our studies are summarised in Table 1.

To confirm the structures of **6a, 6b** and **8a, 8b**, we would have liked the single crystal X-ray study of at least one of the compounds. However, in spite of several attempts, unfortunately, we could not get good crystals suitable for X-ray crystallography. Nevertheless, the NMR data are quite reasonable to establish the structures of the compounds.

From our studies, it has been observed that the formation of C(9)-C(10) bridge due to Diels-Alder reaction can bring about the restricted rotation about the aryl C(1)-N single bond. This results in the formation of atropisomers when the groups attached to the C(1)-N position are non-equivalent. In both the cases of **6** and **8**, the isomers **6a** and **8a** were observed as the major adducts. This may be because of the possible π–electron interaction between the ethylenic bridge and the aryl system making them more stable. The Diels-Alder reaction gave good yield in all the three cases.

4. Conclusions

In conclusion, we have demonstrated that the Diels-Alder reaction of 1-*N*, *N*-disubstituted anthracenes with dimethylacetylenedicarboxylate results in the restricted rotation of the aryl C(1)-N bond. This is attributed to the steric interaction between the C(9)- C(10) bridge and the substituents at C(1)-N position. It has also been proved that the introduction of the C(9)-C(10) bridge gives rise to atropisomers when the substituents at C(1)-N position are non-equivalent. The π-electron system of the phenyl ring stabilizes one of the adducts which was obtained as the major isomer in very good overall yield.

Supplementary Information (SI)

Supplementary Information is available at www.ias.ac.in/chemsci.

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