Table III. Kinetic Data for the Cyclization Reaction (1) and for the Corresponding Intermolecular Model Reaction (2) in 99% Aqueous Me_2SO at 25.0 ± 0.2 °C

Compd	10^3k_{intra}, s^{-1} [a]	$10k_{inter}$, $M^{-1}\ s^{-1}$ [b]	10^2EM, M [c]	Log EM
10	9.04 ± 0.11	2.95 ± 0.03	3.06	−1.51
11	3.56 ± 0.04	1.53 ± 0.04	2.33	−1.63
12	7.22 ± 0.13	4.68 ± 0.20	1.54	−1.81
13	1.59 ± 0.04	1.07 ± 0.06	1.49	−1.83
14	1.59 ± 0.01	0.84 ± 0.01	1.90	−1.72

[a] Average from three independent runs. [b] Average from four to six independent runs. [c] Calculated as k_{intra}/k_{inter}.

size of the rigid moiety of the reacting molecule. Furthermore, they provide additional, independent evidence on the insensitiveness to structural effects of the ease of large-ring formation in general. We have shown[1] that available EM values related to the formation of rings with more than 12 members and belonging to five different reaction series exhibit remarkable insensitiveness to structural effects. Log EM data cluster around an average value of −1.54, with a standard deviation 0.23. Table III now shows that the present values fit well into the same picture. Inclusion of these data into the existing set provides a new average value of −1.57 ± 0.22.

In conclusion, on the basis of the experimental evidence collected in this and in previous work, we believe that the operation of the rigid group effect on large-ring formation can be definitely ruled out, and that, in particular, no "magic" properties must be attributed to the *o*-phenylene unit.

Acknowledgment. Professor Illuminati's helpful suggestions are greately acknowledged.

Registry No.—7, 7125-23-7; 8, 63163-48-4; 1,12-dibromododecane, 3344-70-5; 1,3-benzenediol, 108-46-3; 1,4-benzenediol, 123-31-9; 2,7-naphthalenediol, 582-17-2; 1,5-naphthalenediol, 83-56-7.

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Structural Elucidation with Nuclear Magnetic Resonance Spectroscopy. Diels–Alder Adducts of 1-Aminoanthracene and Maleic Anhydride: Restricted Rotation about the Aryl C(1)–N Bond and Intrinsic Asymmetry about the Imide (N_{sp^2}–C_{sp^3}) System

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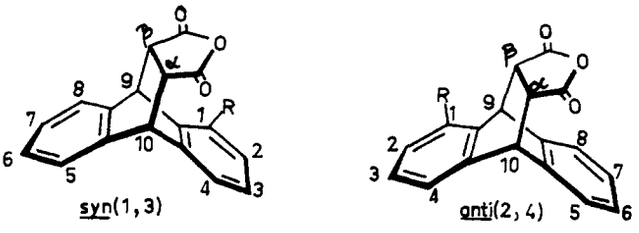
Diels–Alder reaction of 1-acetamidoanthracene and maleic anhydride yields a mixture of two isomeric adducts: syn (~35%) and anti (~65%). The configurations of both the adducts have been assigned with the help of NMR spectra of their imide derivatives. Restricted rotation and nonplanar conformation about the aryl C(1)–N bond have been demonstrated in the C(1)–$N(COCH_3)_2$ derivatives of the isomeric adducts. The steric effect of the C(1) substituent on the intrinsic asymmetry of the imide (N_{sp^2}–C_{sp^3}) system has been observed.

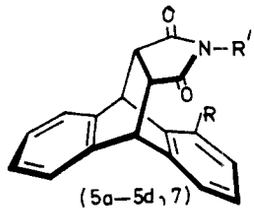
The characteristic feature of anthracene behaving as a diene and its ability to undergo Diels–Alder reaction with various dienophiles is a well-documented phenomenon. The Diels–Alder reaction, where there is possibility of the formation of more than one product, has been extensively investigated. The formation of two isomeric adducts syn[1a] and anti[1a] and their dependence on the nature of the 2 substituent in the Diels–Alder reaction of C(2) substituted anthracene and maleic anhydride have been demonstrated.[1b] Isolation of the two corresponding isomeric adducts in the case of C(2)-substituted anthracene and maleic anhydride and their characterization with the help of spectroscopic methods have been reported.[2] Substitution of anthracene in the 1 position, rather than the 2 position, may have a larger steric effect on the reacting centers, and the present investigations have been un-

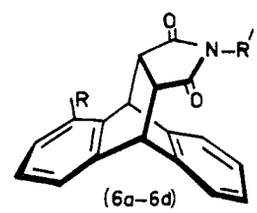


1, 2, R = $NHCOCH_3$
3, 4, R = $N(COCH_3)_2$

dertaken to probe the nature of the Diels–Alder reaction of 1-aminoanthracene and maleic anhydride

In this paper, we report the isolation of two isomeric adducts, *syn*-**1** and *anti*-**2**, from the Diels–Alder reaction of 1-acetamidoanthracene and maleic anhydride. The proposed structures of the two isomeric adducts have been demonstrated by converting them into their diacetyl derivatives **3** and **4** and into the imide derivatives **5a–d** and **6a–d**. Conversion to imides increases the solubility in $CDCl_3$ in which the NMR spectra were recorded. The mutual magnetic interaction of R and R′ has been carefully taken into account for the configurational assignment. As expected, no remarkable interaction of R and R′ has been observed in the spectra of the anti adduct, while the syn adduct exhibits a significant interaction between them. Further spectral studies of these compounds have revealed a phenomenon of restricted rotation about the aryl C(1)–$N(COCH_3)_2$ bond and the steric effect of the C(1) substituent (R) on the conformation of the imide group (R′).





5a, 6a, R′ = $N(COCH_3)_2$; R = $N(COCH_3)_2$
5b, 6b, R′ = $CH_2C_6H_5$; R = $N(COCH_3)_2$
5c, 6c, R′ = $CH(CH_3)_2$; R = $N(COCH_3)_2$
5d, 6d, R′ = CH_2CH_3; R = $N(COCH_3)_2$
7, R′ = $CH(CH_3)_2$; R = $NHCOCH_3$

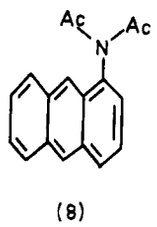
Experimental Section

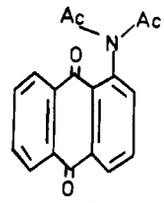
All the melting points (°C) are uncorrected. NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal reference on a Varian A-60D spectrometer at 45 °C. δ (ppm) values were recorded from Me_4Si in the NMR data (s, singlet; br s, broad singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet). IR spectra were recorded using Nujol mull techniques on a Perkin-Elmer 257 spectrophotometer, and the characteristic absorptions ν_{max} (cm^{-1}) were noted: m, medium; s, strong; w, weak. The elemental analyses (C and H) of the compounds (**1–4, 5a–d, 6a–d,** and **7–9**) were within acceptable experimental limits and were submitted for review.

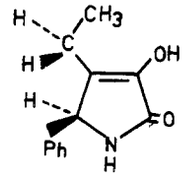
Preparation of Compounds. 1-Aminoanthracene was prepared by the reduction of 1-aminoanthraquinone by zinc dust and alkali as in the case of 2-aminoanthracene from 2-aminoanthraquinone.[1b] 1-Aminoanthraquinone (10 g) was stirred with 10% sodium hydroxide (100 mL) and zinc dust (8 g) at room temperature for about 30 min. It was slowly heated and the temperature of the reaction mixture was maintained at 85–90 °C. Zinc dust (10 g) was then introduced into the reaction mixture in two equal instalments at an interval of 30 min each, and heating was continued with constant stirring for 24 h at 90 °C.[2b] The solid material from the reaction mixture was collected and washed several times with water. Soxhelet extraction with acetone and then recrystallization from ethanol gave 1-aminoanthracene (6 g, 70%) as greenish-yellow plates, mp 126–127 °C (lit.[3] mp 127 °C).

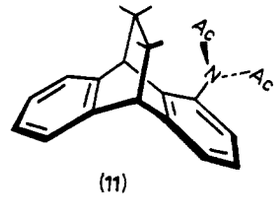
1-Acetamidoanthracene. 1-Aminoanthracene (3 g) was stirred with an excess of acetic anhydride (20 mL) at room temperature for 3 h. A solid material appeared and was collected, washed with water, and recrystallized from ethanol. 1-Acetamidoanthracene appeared as greenish-yellow needles (3.2 g, 91%), mp 210 °C (lit.[3] mp 212 °C).

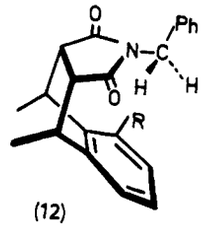
Reaction of 1-Acetamidoanthracene and Maleic Anhydride. A mixture of 1-acetamidoanthracene (2 g) and maleic anhydride (2 g) was heated under reflux in dry benzene (15 mL) for 8 h, with constant stirring. The adduct appeared as a white insoluble substance in benzene, while the excess maleic anhydride went into solution. The solid material was collected (~2.5 g) and traces of maleic anhydride were removed by sublimation at 110 °C. When subjected to fractional crystallization from acetone (25 mL), the first product *syn*-**1** appeared almost completely in about 24 h. The second product *anti*-**2** was recovered from the filtrate by evaporation and recrystallized from a benzene–petroleum ether mixture. From isolation and spectral analysis, the mixture was found to comprise about 35% of the syn adduct and ~65% of the anti adduct (total yield ~90%).

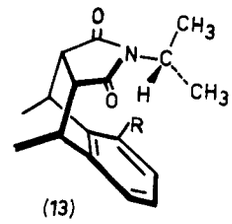












***syn*-1-Acetamido-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydride (1):** mp 282–284 °C; IR 3250 (m, NH), 1865 (m), 1780 (s), 1665 (m), 1600 (w), 1540 (w).

***anti*-1-Acetamido-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydride (2):** mp 268–270 °C; IR 3380 (m, NH), 1865 (m), 1780 (s), 1685 (m), 1600 (w), 1540 (w).

***syn*-1-Diacetamido-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydride (3)** was obtained by heating under reflux 450 mg of the adduct **1** with an excess of acetic anhydride (15 mL) for 3 h, and was recrystallized from a benzene–*n*-hexane mixture. The *anti*-1-diacetamido adduct **4** was also obtained similarly.

Compound 3: mp 215–217 °C; IR 1860 (w), 1840 (w), 1780 (s), 1720 (s), 1700 (m), 1615 (w), 1590 (w); NMR 2.20 (s, 3 H), 2.40 (s, 3 H), 3.40 (t, 2 H), 4.92 (m, 2 H), 6.90–7.40 (m, 7 H).

Compound 4: mp 242–243 °C; IR 1860 (w), 1830 (w), 1770 (s), 1700 (s), 1580 (w); NMR 1.78 (s, 3 H), 2.78 (s, 3 H), 3.56 (t, 2 H), 4.71 (m, 1 H), 4.96 (m, 1 H), 6.95–7.60 (m, 7 H).

Preparation of 5a and 6a. The isomeric adducts **1** and **2** were treated with hydrazine hydrate (equimolar) in ethanol with constant stirring at room temperature, and the respective *N*-aminoimides obtained were acetylated with acetic anhydride in the presence of a few drops of pyridine to give **5a** and **6a.** Both the compounds were recrystallized from ethanol.

5a: mp 260–262 °C; IR 1780 (w), 1700 (s), 1590 (w), 1500 (w); NMR 1.33 (s, 3 H) 1.63 (s, 3 H), 2.50 (s, 3 H), 2.70 (s, 3 H), 3.43 (t, 2 H), 4.95 (m, 2 H), 6.95–7.51 (m, 7 H).

6a: mp 220–221 °C; IR 1770 (w), 1690 (s), 1600 (w), 1510 (w); NMR 0.95 (s, 3 H), 1.81 (s, 3 H), 2.50 (s, 3 H), 2.71 (s, 3 H), 3.48 (t, 2 H), 4.75 (m, 1 H), 5.10 (m, 1 H), 7.00–7.60 (m, 7 H).

Preparation of 5b–d, 6b–d, and 7. The compounds **5b–d** and **6b–d** were obtained by condensing the anhydride adducts **1** and **2** with the corresponding primary amines, at 110–120 °C for 2 h. The adduct (500 mg) was mixed thoroughly with its equivalent of the primary amine and heated at 120 °C for 2 h. The product obtained was cooled, washed with water, and recrystallized from benzene. At first, 1-acetamido-9,10-dihydroanthracene-9,10-*endo*-α,β-succinimide of the corresponding adduct was obtained, which on acetylation gave the 1-diacetamido derivatives in quantitative (70–80%) yields. Compound **7** was obtained by condensing the adduct **1** with isopropylamine and recrystallized from a benzene–petroleum ether mixture. The 1-diacetamidoimides **5a–d** and **6a–d** were recrystallized from ethanol.

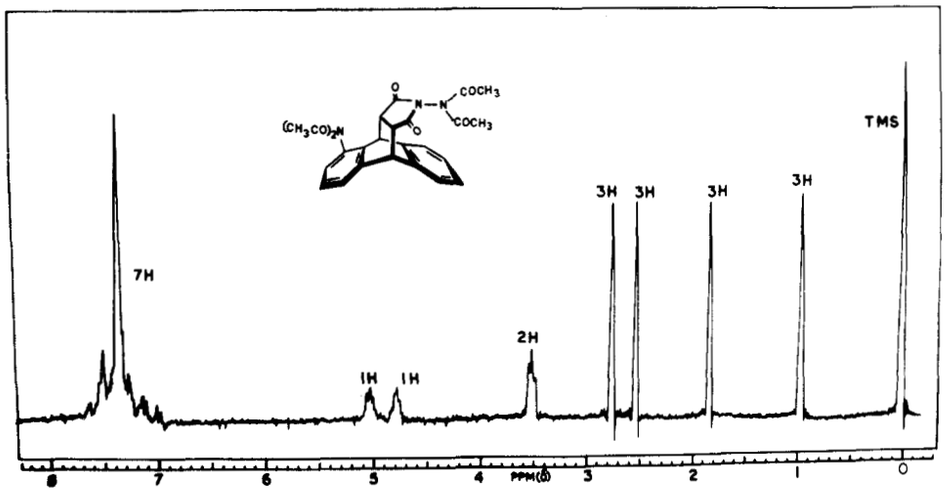


Figure 1. 60-MHz NMR spectrum of **6a** in $CDCl_3$ at 45 °C.

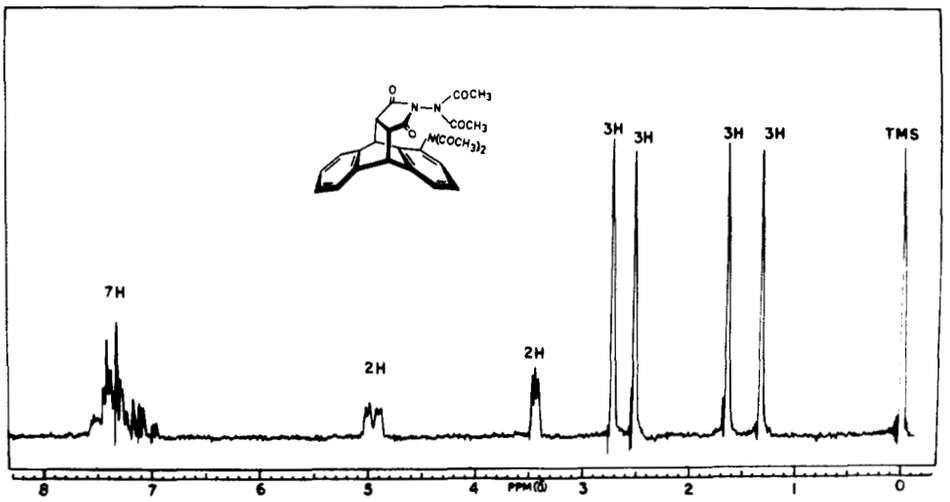


Figure 2. 60-MHz NMR spectrum of **5a** in $CDCl_3$ at 45 °C.

5b: mp 256–258 °C; IR 1780 (w), 1710 (s), 1610 (w), 1590 (w); NMR 1.97 (s, 3 H), 2.15 (s, 3 H), 3.16 (t, 2 H), 4.30 (m, 2 H), 4.66 (m, 1 H), 4.83 (m, 1 H), 6.70–7.40 (m, 12 H).

6b: mp 213–214 °C; IR 1780 (w), 1720 (s), 1660 (m), 1610 (w), 1600 (w); NMR 1.70 (s, 3 H), 2.66 (s, 3 H), 3.18 (t, 2 H), 4.23 (s, 2 H), 4.63 (m, 1 H), 4.80 (m, 1 H), 6.60–7.45 (m, 12 H).

5c: mp 222–223 °C; IR 1770 (w), 1710 (s), 1690 (s), 1600 (w), 1460 (s); NMR 0.83 (d, 3 H, J = 7 Hz), 1.10 (d, 3 H, J = 7 Hz), 1.91 (s, 3 H), 2.55 (s, 3 H), 3.09 (m, 2 H), 3.70–4.40 (m, 1 H), 4.80 (m, 2 H), 7.00–7.46 (m, 7 H).

6c: mp 219–220 °C; IR 1780 (w), 1700 (s), 1680 (s), 1620 (w), 1590 (w); NMR 0.84 (d, 6 H, J = 7 Hz), 1.76 (s, 3 H), 2.70 (s, 3 H), 3.13 (m, 2 H), 3.60–4.30 (m, 1 H), 4.63 (m, 1 H), 4.86 (m, 1 H), 6.90–7.55 (m, 7 H).

5d: mp 216–218 °C; IR 1780 (w), 1710 (s), 1620 (w), 1590 (w); NMR 0.71 (t, 3 H, J = 7 Hz), 1.93 (s, 3 H), 2.58 (s, 3 H), 3.20 (m, 4 H), 4.86 (m, 2 H), 7.00–7.60 (m, 7 H).

6d: mp 230–231 °C; IR 1770 (w), 1700 (s), 1680 (s), 1590 (w); NMR 0.40 (t, 3 H, J = 7 Hz), 1.78 (s, 3 H), 2.73 (s, 3 H), 2.95–3.33 (m, 4 H), 4.70 (m, 1 H), 4.90 (m, 1 H), 6.90–7.10 (m, 7 H).

7: mp 243–244 °C; IR 3250 (m, NH), 1780 (w), 1720 (s), 1680 (s), 1620 (w), 1600 (w), 1540 (m); NMR 0.87 (dd, 6 H, J = 7 Hz, $\Delta\nu$ = 2 Hz), 2.25 (brs, 3 H), 3.15 (t, 2 H), 3.70–4.30 (m, 1 H), 4.80 (m, 1 H), 5.10 (m, 1 H), 7.10–7.60 (m, 8 H).

Preparation of 8 and 9. 1-Diacetamidoanthracene (**8**) and 1-diacetamidoanthraquinone (**9**) were obtained by refluxing 1-acetamidoanthracene and 1-aminoanthraquinone, respectively, with acetic anhydride. The compound **8** was recrystallized from ethanol and **9** from a ethanol–acetone mixture.

8: mp 164 °C; IR 1710 (s), 1685 (s), 1620 (w), 1460 (m); NMR 2.33 (s, 6 H), 7.25–8.43 (m, 9 H).

9: mp 216–217 °C; IR 1710 (s), 1670 (m), 1590 (m), 1465 (m); NMR 2.32 (s, 6 H), 7.50–8.51 (m, 7 H).

Results and Discussion

The two isomeric Diels–Alder adducts have different (N–H) stretching vibrations in their IR spectra: one of the adducts shows an absorption at 3380 (cm^{-1}) characteristic of normal secondary amide vibrations and the other has a characteristic (N–H) absorption at 3250 (cm^{-1}). The absorption at 3250 (cm^{-1}) could result from the possible hydrogen bonding between the (N–H) and the anhydride ring. Since an intramolecular hydrogen bonding between the (N–H) and the anhydride ring is possible in the syn adduct, the absorption at the lower frequency (3250 cm^{-1}) can be attributed to the syn adduct **1** and that at the higher frequency (3380 cm^{-1}) to the anti adduct **2.**

Restricted rotation about the N–N bond in tetraacylhydrazine systems has been successfully exploited in assigning the configuration of various Diels–Alder adducts,[2,4] and when applied to the present adducts this system also discloses considerable information. In the NMR spectrum (Figure 1) of **6a,** each of the diacetyls has a pair of singlets, one at δ 0.96 (3 H) and 2.50 (3 H) for the N'-diacetyls ($\Delta\nu$ = 92.4 Hz) and another at δ 1.81 (3 H) and 2.71 (3 H) for the C(1)-N-diacetyls ($\Delta\nu$ = 54 Hz). The chemical shifts of the N'-diacetyls are almost exactly the same as were observed in the case of the unsubstituted anthracene adduct.[5] The magnetic environ-

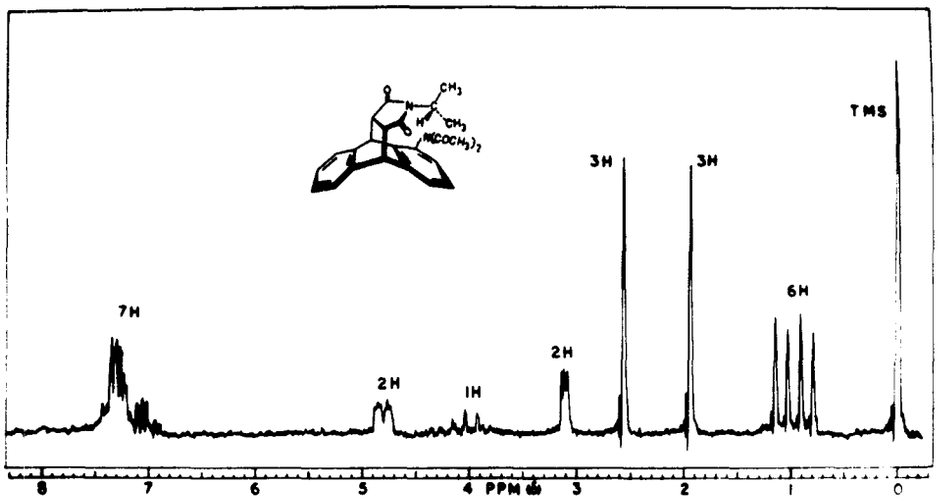


Figure 3. 60-MHz NMR spectrum of **5c** in $CDCl_3$ at 45 °C.

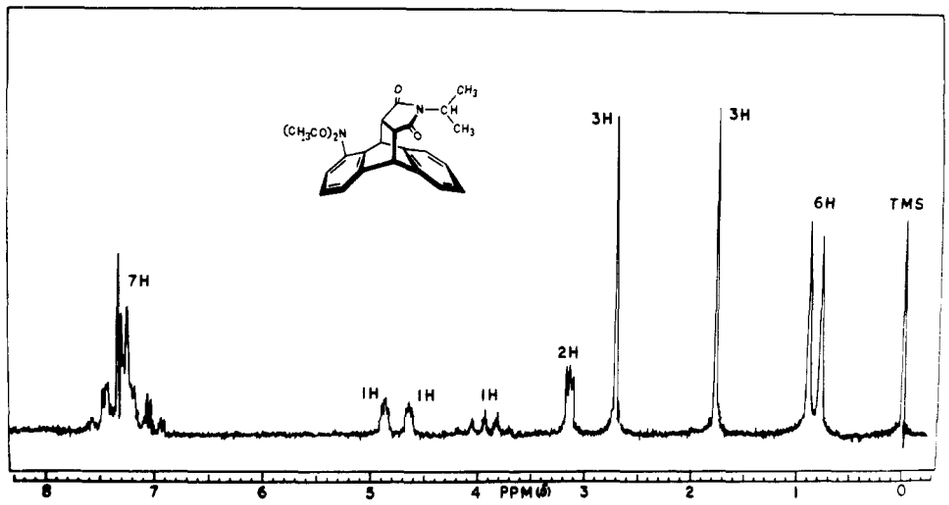


Figure 4. 60-MHz NMR spectrum of **6c** in $CDCl_3$ at 45 °C.

ments of the N′ substituents are more or less the same in the anti adduct and unsubstituted anthracene adduct. The C(1) substituent, being far away, fails to interact with the N′ substituent. In the case of **5a,** the NMR spectrum (Figure 2) exhibits a similar pattern, showing two resonance signals at δ 1.33 (s, 3 H) and 2.50 (s, 3 H) for the *N′*-diacetyls and a pair of singlets at δ 1.63 (3 H) and 2.70 (3H) for the C(1)–*N*-diacetyls. One of the *N′*-diacetyls that is syn to the cage moiety in the nonplanar conformation in **5a** has been deshielded by the C(1) substituent and appears at δ 1.33 instead of appearing at the usual position at δ 0.96. Such a deshielding effect on the *N′*-diacetyls was also observed in the case of the syn (cis) adduct of 2-diacetamidoanthracene.[2] While the C(1)–*N*-diacetyl resonances remain almost the same in the spectra of **4** and **6a**, a large difference in the resonances of the C(1)–*N*-diacetyl in **3** and **5a** indicates the possible influence of the imide group on the C(1) substituent. From the spectra of **5a** and **6a** a possible configurational assignment can be made. The two adducts **1** and **2** are virtually similar except for the orientation of the C(1) substituent with respect to the anhydride ring, and one could expect different substituent effects in the derivatives of the two isomers. The isomer **5a,** where the N′ substituent has been influenced by the C(1) substituent, can be assigned the syn configuration, while the other, where the C(1) substituent has little effect on the N′ substituent, the anti configuration. To substantiate this argument further, we have introduced a few centers at the imide plane (**5b–d, 6b–d**) that could be influenced by the C(1) substituent. The C(1)–*N*-diacetyl has caused a large dissymmetry about the imide plane in the syn adduct and its effects are readily observed in the spectra of **5b–d.**

In the spectrum of **5b,** the methylene protons of the benzyl group resonate as a multiplet at δ 4.30 (approximately an overlapping AB quartet) and the C(1)–*N*-diacetyl signals are separated by 10 Hz ($\Delta\nu$). In the case of **6b** the benzyl methylene protons appear as a singlet at δ 4.23 (2 H) and the two C(1)–*N*-diacetyl signals are separated by 58 Hz ($\Delta\nu$). The appearance of a multiplet for the methylene group could be due to the nonequivalence of the hydrogens arising out of the influence of the C(1) substituent which helps in developing a prochiral center[6] at the methylene carbon. Such chemical-shift nonequivalence of the methylene group is comparable to that observed in the case of **10**,[6,7] *dl*-2,2′-bis(acetoxymethyl)diphenyl,[8] and in 9-benzyltriptycenes,[9] where the diastereotopicity of the methylene protons has been explained on steric grounds. For the same reason, the isopropylmethyl groups in **5c** are diastereotopic and appear as a pair of doublets (Figure 3) at δ 0.83 (3 H) and 1.10 (3 H) (J = 7 Hz, $\Delta\nu$ = 16 Hz). In the case of **6c,** there is only a doublet (Figure 4) for the isopropylmethyls at δ 0.84 (6 H, J = 7 Hz). The C(1)–*N*-diacetyls appear as two singlets at δ 1.91 and 2.55 ($\Delta\nu$ = 38.4 Hz) in the case of **5c,** while they appear at δ 1.76 and 2.70 ($\Delta\nu$ =

56.4 Hz) in the case of **6c**. In the case of **5d** and **6d**, each of the diacetyls appears as a pair of singlets with an internal chemical shift ($\Delta\nu$) of 39 and 57 Hz, respectively. The methyl group of ethylimide has been appreciably deshielded (δ 0.71) by the C(1) substituent in the syn adduct **5d** as compared to that in the anti adduct **6d** (δ 0.40).

We have observed the effect of the C(1) substituent R on the resonance of the imide substituent R′ in **5a–d**. Another interesting feature observed in all these derivatives is the effect of R′ on R. In all four derivatives **6a–d** the C(1)–*N*-diacetyl resonances R remain almost unaffected with different substituents R′ in the anhydride ring, whereas in the case of the syn adduct **5a–d** a continuous change in the resonance of the C(1) substituent is observed, indicating the possible influence of R′ on R. These observations demonstrate further the *syn*-**1** and *anti*-**2** configurations of the two isomeric adducts.

In the case of the Diels–Alder reaction of 2-acetamidoanthracene and maleic anhydride, a 52:48 ratio of the isomeric adducts syn/anti was reported.[1] Though the electronic factors contributed by the acetamido group at the C(1) and C(2) positions of anthracene toward reacting centers appear to be almost the same, in the present case the anti isomer has been found to be the major product (65%). Sterically, the acetamido group at the C(1) position will have a larger effect on the reacting center as compared to that at the C(2) position of anthracene and, possibly, steric factors might have caused such a variation in the isomer ratio (35:65) of the syn/anti.

Restricted Rotation about the Aryl C(1)–N Bond. The appearance of two singlets for the C(1)–*N*-diacetyls in the NMR spectra of both the configurational isomers could possibly be due to the restricted rotation about the aryl C(1)–N bond, comparable to that observed in the case of ortho substituted arylimides.[10] High-energy barriers[10,11] ($\Delta G^{\ddagger}$ = 17–24 kcal/mol) to rotation about the aryl C–N bond in various ortho-substituted arylimides have been attributed to the steric interaction between the ortho substituent and the carbonyl groups in the planar transition state. Steric hindrance about the C(1)–N bond in *N*-benzenesulfonyl-8-nitro-1-naphthylglycine enabled Mills and Elliot[12] to resolve it. Such steric interactions between the C(1)–*N*-diacetyls and the C(9) substituent are expected in the present adducts and in compounds **8** and **9**. Molecular models further support that even the C(9)–H will hinder the rotation of the acyl system about the C(1)–N bond. However, the C(1)–*N*-diacetyls appear as a sharp singlet in the spectra of both **8** (δ 2.33, 6 H) and **9** (δ 2.32, 6 H), indicating the magnetic equivalence of the acetyl groups in both cases. The introduction of the C(9)–C(10) bridge in the anthracene nucleus (as in the present adducts) could be responsible for the nonequivalence of the C(1)–*N*-diacetyls.

From the spectral patterns observed for the derivatives of both isomers and for **8** and **9**, a nonplanar conformation **11** about the C(1)–N bond, where the acyl system lies in a plane perpendicular to the plane of the cage benzo ring, could be proposed. In such a nonplanar conformation, the C(9)–C(10) bridge would provide different magnetic environments for the two acetyl groups, while the latter would assume a symmetrical pattern in the case of **8** and **9**. The acetyl group oriented syn to the bridge appears upfield and the other anti to the bridge resonates at a lower field. The possibility of a partial double-bond formation about the C(1)–N bond, that may also account for the restricted rotation, is very unlikely, not only because the N atom is attached to two carbonyl groups, but any planar arrangement about the C(1)–N bond will suffer from a severe steric crowding. Free rotation about the C–N bond, and, hence, a singlet for the diacetyls, was observed in the corresponding syn and anti adducts with the diacetamido substituent at the C(2) position,[2] demonstrating further that it is the C(9) substituent (or C(9) hydrogen) and not the ortho hydrogens that influence the rotation of the C(1)–N bond in the present case.

Intrinsic Asymmetry of the Imide (N_{sp^2}–C_{sp^3}) Group. The spectral pattern shows that the methylene protons in **5b** and the isopropyl methyl groups in **5c** are diastereotopic. Accordingly, similar behavior of these groups is expected in the derivatives of the anti adducts **6b** and **6c**, but the benzylic methylene protons in **6b** appear as a singlet and the isopropyl methyl groups in **6c** as a normal doublet (Figure 4). The observed multiplicity in the resonance signals of these protons, only in the case of the syn isomer, can be explained on the basis of the chirality[9] of these compounds where the methylene protons in **5b** and the isopropyl methyl groups in **5c** are magnetically nonequivalent. In the case of the anti isomer, since the site of chirality [the C(1) substituent] lies away from the diastereotopic groups, the degree of nonequivalence diminishes and, hence, no signal multiplicity of the diastereotopic groups has been observed. The C(1) substituent R exerts a strong steric influence to induce intrinsic asymmetry[6,13] on these imide groups R′ and this is vividly seen on a comparative examination of the spectral patterns of the derivatives of the two isomeric adducts. With the monoacetyl substituent at the C(1) position, the isopropyl methyl groups in **7** resonate as an interlacing double doublet at δ 0.87 (6 H, J = 7 Hz, $\Delta\nu$ = 2 Hz), indicating thereby a small interaction with the C(1) substituent, while the two isopropyl methyl groups in **5c** resonate at δ 0.83 and 1.10 (Figure 3) with an internal chemical shift of 16 Hz. On steric considerations, preferred conformations of the type **12** and **13** could be proposed for **5b** and **5c**, where the steric interactions between the C(1) substituent R and the imide substituent R′ would be reduced to a minimum.

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Registry No.—**1**, 63512-03-8; **2**, 63568-21-8; **3**, 63512-04-9; **4**, 63568-22-9; **5a**, 63512-05-0; **5b**, 63512-06-1; **5c**, 63512-07-2; **5d**, 63512-08-3; **6a**, 63568-23-0; **6b**, 63568-24-1; **6c**, 63568-25-2; **6d**, 63597-42-2; **7**, 63512-09-4; **8**, 63512-10-7; **9**, 63512-11-8; 1-aminoanthracene, 610-49-1; 1-aminoanthraquinone, 82-45-1; 1-acetamidoanthracene, 63512-12-9; maleic anhydride, 108-31-6; hydrazine hydrate, 7803-57-8; benzylamine, 100-46-9; ethylamine, 75-04-7; isopropylamine, 75-31-0.

References and Notes

(1) (a) The prefixes syn and anti were used in the sense that the adduct with the anhydride ring toward the substituent is syn and that with the anhydride ring away from the substituent is anti.[1b] These terms are retained in the present text. Cis and trans[2] terms for such isomeric adducts have also been used. (b) F. Kaplan and H. Conroy, *J. Org. Chem.*, **28**, 1593 (1963).
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