Structural Assignment by NMR Spectroscopy: Restricted Rotation about Aryl C-N Bond and Configurations of Diels-Alder Adducts

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(Received February 28, 1977)

Restricted rotation and non-planar conformations about the aryl C–N bond in *ortho* substituted arylimides have been studied in order to assign the *endo* and *exo* configurations of Diels-Alder adducts, employing the adducts of maleic anhydride with naphthalene and cyclopentadiene as model compounds. The adducts are readily transformed into their *o*-tolylimide derivatives and the *N*-*o*-tolyl probes satisfactorily into the magnetic environment of the cage moiety. In 1-naphthylimide derivatives, the *naphthyl* group causes splitting in the cage-proton resonances and is found to be more diagnostic for structural assignment.

Recently we reported restricted rotation and non-planar ground state conformations about the aryl C–N bond in a system of type (I).[1] The high energy barrier (ΔG^* 22 kcal/mol) was attributed purely to the steric interaction of the *o*-substituent, the carbonyl groups of the succinimidyl ring which is of similar order as that of the N–N bond in tetracylhydrazines (II) having lone pair electronic interactions at the two nitrogens.[2] With the help of conformational studies about the N–N bond through their *N*-aminoimide derivatives the *endo*/*exo* configuration of Diels-Alder adducts of maleic anhydride with cyclic dienes such as cyclopentadiene,[3] β-naphthol,[4] naphthalene,[5,6] and substituted anthracenes[7] was demonstrated. In this communication the applicability of the N–C bond conformations in the structural assignment of the Diels-Alder adducts is discussed. *o*-Substituted phenylimide(I) is quite diagnostic and effective in the structural elucidation which can easily be obtained from the DA adducts in one step under ordinary experimental conditions. Earlier studies revealed that *o*-CH_3 or 2,3-*benzo* substituents in the *N*-phenyl(I) can be more diagnostic than *o*-OCH_3, *o*-Cl, and *o*-Br substituents in the structural assignments.[1] *o*-Substituted anilides of cyclopentadiene–maleic anhydride and naphthaline–maleic anhydride and their reduced products (III to X) have been prepared and their NMR spectra are discussed in the light of their configurational assignment.

Results and Discussion

Naphthalene–Maleic Anhydride Adducts (endo/exo) *1) o-Toluidide Derivatives (IIIa, IVa)*: The NMR spectrum of the compound IIIa shows two singlets for the *o*-tolyl methyl protons at δ 1.0 and 2.0 and a multiplet of 0.58 H intensity at δ 5.45 along with the other normal proton resonances (Table 1). In the other isomeric derivative (IVa), the *o*-tolyl protons also appear as two singlets at δ 2.10, and 2.13 along with other normal resonances (Table 1). These spectral multiplicities are due to the hindered rotation about aryl C–N bond[1] and the existence of the two conformations XI and XII is indicated.

On the basis of shielding effect on the syn-*o*-tolyl protons by the cage-moiety (XII) a reasonable assignment of the configuration of the adduct is possible. A high degree of shielding on the *o*-methyl protons ($\Delta\nu$= 60 Hz) suggests the *endo* configuration for IIIa while

TABLE 1. 60 MHz NMR SPECTRAL DATA[a] (δ ppm) OF THE COMPOUNDS IIIa, IIIb, IVa, IVb, Va, Vb, VIa, VIb

Compound	R	Ortho (*N*-phenyl)	2+3	1+4	9+10	5–8+*N*-phenyl (m & p)
IIIa	1.0, 2.0 (ds, 2: 3, 3H)	5.45, 7.16 (dm, 3: 2, 1H)	3.23 (t, 2H)	4.5 (m, 2H)	6.65 (q, 2H)	7.16 (m, 7H)
IIIb	7.33 (m, 4H)	5.33, 7.33 (dm, 2: 1, 1H)	3.33 (t, 2H)	4.53 (m, 2H)	6.5 (q, 2H)	7.33 (m, 6H)
IVa	2.10, 2.13 (ds, 6: 7, 3H)	7.18 (m, 1H)	3.13 (t, 2H)	4.48 (m, 2H)	6.65 (q, 2H)	7.18 (m, 7H)
IVb	7.5 (m, 4H)	7.5 (m, 1H)	3.15 (m, 2H)	4.51 (m, 2H)	6.66, 6.83 (dq, 1: 1, 2H)	7.5 (m, 6H)
Va	0.9, 2 (ds, 2: 3, 2H)	5.45, 7.25 (dm, 3: 2, 1H)	3.27 (t, 2H)	4.51 (m, 2H)	1.53 (q, 4H)	7.25 (m, 7H)
Vb	7.43 (m, 4H)	5.3, 7.43 (dm, 2: 1, 1H)	3.33 (t, 2H)	3.73 (m, 2H)	1.66 (q, 4H)	7.43 (m, 6H)
VIa	2.15, 2.31 (ds, 5: 7, 3H)	7.25 (m, 1H)	3.01 (m, 2H)	3.61 (m, 2H)	1.66 (bq, 4H)	7.25 (m, 7H)
VIb	7.43 (m, 4H)	7.43 (m, 1H)	3.12 (m, 2H)	3.81 (m, 2H)	1.68 (m, 4H)	7.43 (m, 6H)

a) The NMR spectra of all the compounds were recorded in $CDCl_3$. The total number of protons and the multiplicity of the bands are indicated in brakets. In the case of multiplicity due to slow rotation, the ratio of the intensity of the upfield to down field signales are indicated. Signals are abbreviated as: s=singlet; t=triplet; ds=double singlet; dt=double triplet; q=quartet; dq=double quartet; bq=broad quartet; dm=double multiplet.

the small shielding value ($\Delta\nu$=2 Hz) suggests the *exo*-configuration for IVa.

The *endo* configuration for IIIa is further demonstrated by the observation of a multiplet at δ 5.45 (0.58 H) which could arise from the shielding of the *ortho*-hydrogen of the *N*-phenyl by the cage benzo ring in the conformer XI.

2) 1-Naphthylimide Derivatives (IIIb, IVb): The spectra of 1-naphthylimide derivatives of the isomeric adducts (*endo*/*exo*) are diagnostic in the configurational assignment of the adducts as the 2,3-benzo group of the 1-naphthylimide strongly influences the resonances of the cage protons providing fruitful results.

The NMR spectrum of VIb shows a double quartet for the C9 and C10 olefinic protons at δ 6.66 and 6.83 ($\Delta\nu$=10 Hz) with other normal proton resonances, while the spectrum of the other isomeric adduct IIIb shows a single quartet for the C9 and C10 olefinic protons at δ 6.5 and a multiplet at δ 5.33 (0.68 H) for the *ortho* proton of the naphthylimide. The appearance of the olefinic protons as a double quartet in IVb indicates the *exo* configuration of the adduct, whereas no multiplicity in the olefinic proton resonances as well as the appearance of the *ortho* naphthyl proton at a shielded postion in IIIb suggest the *endo* configuration.

3) o-Toluidides of Reduced Products (Va, VIa): The NMR spectra of both the isomeric adducts (Va, VIa) show a double singlet each for the tolyl methyl protons with internal chemical shifts of 66 Hz and 10 Hz respectively. The spectrum of Va also shows a multiplet for the *ortho N*-phenyl proton at an upfield position and a quartet for the C9 and C10 methylene protons at δ 1.53, while the spectrum of VIa shows a broad quartet at δ 1.66 for the C9 and C10 methylene protons (Table 1). These observations further support the assignment of the *endo* (Va) and *exo* configurations (VIa).

4) 1-Naphthylimide Derivatives of the Reduced Products (Vb, VIb): The NMR spectra exhibit similar features to those of the unreduced derivatives (IIIb, IVb). The spectrum of Vb shows a quartet for the C9 and C10 protons at δ 1.66, while (VIb) shows a broad multiplet at δ 1.68 for C9 and C10 protons (Table 1). The appearance of the broad multiplet for the C9 and C10 protons is caused by the shielding of the 2,3-*benzo* group and the adduct could be assigned as *exo*, while a quartet in the spectrum of Vb for C9 and C10 indicates the *endo* configuration.

Cyclopentadiene–Maleic Anhydride Adducts.

1) o-Toluidide Derivatives (VIIa, VIIIa): The configuration of the adducts (*endo*/*exo*) could be assigned by comparing the spectra of their *o*-toluidide derivatives. The NMR spectrum of VIIa shows two singlets for the *o*-tolyl methyl protons at δ 2.06 and 2.09 with an internal chemical shift of 2 Hz and an AB quartet for C7 methylene protons at δ 1.53 and δ 1.78, while the other isomer (VIIIa) shows a singlet of 3H intensity at δ 2.16 for the *o*-tolyl protons and a multiplet at δ 1.58 for the C7 methylene proton (Table 2).

The spectral pattern is in conformity with the restricted rotation about N–C bond and the existence of two conformations XI and XII is indicated. The multiplicity in methyl resonances of the *o*-tolyl group indicates the *endo* configuration (VIIa) whereas its appearance as a singlet suggests the *exo* configuration (VIIIa) resulting from the less magnetic interaction of methylene bridge.

2) 1-Naphthylimide Derivatives (VIIb, VIIIb): Compound VIIb shows a double triplet for the C5 and C6 olefinic protons at δ 6.4 and 6.58 ($\Delta\nu$=11 Hz) and an AB quartet for the C7 methylene protons with other normal proton resonances (Table 2). The spectrum of the other isomeric compounds (VIIIb) shows a triplet at δ 6.3 for the olefinic protons along with duplication in the resonances of C7, C2+C3, and C1+C4 protons (Table 2). The multiplicity in the olefinic protons suggests the *endo* configuration for (VIIb), while a single triplet for the olefinic protons as well as the multiplicity in methylene proton resonances indicate the *exo* configuration (VIIIb).

3) o-Toluidide of Reduced Products (IXa, Xa): The spectra of the reduced products (IXa and Xa) also exhibit similar features to those of their unreduced de-

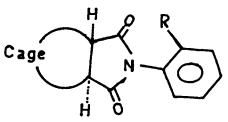
Table 2. 60 MHz NMR spectral[a] data (δ ppm) of the compounds VIIa, VIIb, VIIIa, VIIIb, IXa, IXb, Xa, Xb

Compound	R	2+3	1+4	7 AB	5+6	Aromatic
VIIa	2.06, 2.09 (ds, 7: 8, 3H)	3.4 (s, 2H)	3.4 (s, 2H)	1.53, 1.78 (q, 2H)	6.28 (t, 2H)	7.06 (m, 4H)
VIIb	7.5 (m, 4H)	3.53 (s, 2H)	3.53 (s, 2H)	1.61, 1.85 (q, 2H)	6.40, 6.58 (dt, 6: 4, 2H)	7.5 (m, 3H)
VIIIa	2.16 (s, 3H)	2.88 (s, 2H)	3.43 (m, 2H)	1.58 (bm, 2H)	6.4 (t, 2H)	7.18 (m, 4H)
VIIIb	7.11 (m, 4H)	2.88, 2.93 (ds, 1: 1, 2H)	3.35 (m, 2H)	1.63, 1.8 (dbm, 2H)	6.3 (t, 2H)	7.11 (m, 3H)
IXa	2.11, 2.23 (ds, 7: 8, 3H)	2.93 (m, 2H)	3.26 (m, 2H)	1.66 (m, 2H)	1.66 (m, 4H)	7.2 (m, 4H)
IXb	7.5 (m, 4H)	2.93 (m, 2H)	3.71 (m, 2H)	1.7 (m, 2H)	1.7 (m, 4H)	7.5 (m, 3H)
Xa	2.15 (s, 3H)	2.83 (m, 2H)	2.83 (m, 2H)	1.58 (m, 2H)	1.53 (q, 4H)	7.08 (m, 4H)
Xb	7.55 (m, 4H)	2.81 (ds, 2H)	3.4 (bm, 2H)	1.55 (bm, 2H)	1.55 (bm, 4H)	7.55 (m, 3H)

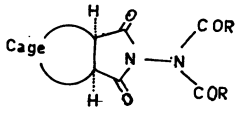
a) The NMR spectra of all the compounds were recorded in $CDCl_3$. The total number of protons and the multiplicity of the bands are indicated in brackets. In the case of multiplicity due to slow rotation the ratio of the intensity of the upfield to down field signals are indicated. Signals are abbreviated as: s=singlet; t=triplet; m=multiplet; ds=double singlet; dt=double triplet; dm=double multiplet; bm=broad multiplet; dbm=double broad multiplet.

rivatives (VIIa and VIIIa). In IXa, the tolyl methyl protons appear as two singlets at δ 2.11 and 2.23 with an internal chemical shift of 7 Hz and C5 and C6 protons appear as a quartet at δ 1.66, whereas the *o*-methyl protons in Xa appear as a singlet at δ 2.15 and C5 and C6 protons as a multiplet (Table 2). The *endo* configuration can thus be assigned to IXa and *exo* configuration to Xa.

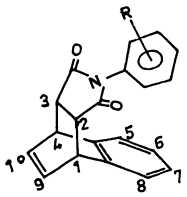
4) 1-Naphthylimide Derivatives of Reduced Products (IXb, Xb): The spectra of these derivatives also provide valuable information regarding the structural elucidation of the adducts. The naphthyl group influences the C5 and C6 cage methylene protons in IXb, indicating the *endo* configuration, while C5 and C6 methylene protons remain unaffected in Xb suggesting the *exo* configuration (Table 2).



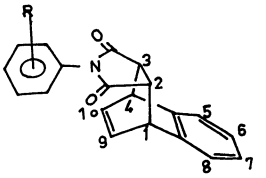
(I)



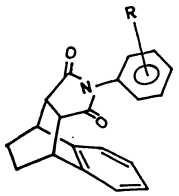
(II)



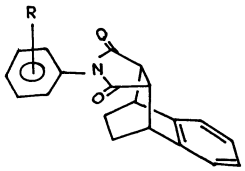
(III) *endo**
(III) a R=*o*-CH_3
b R=2,3-benzo



*exo** (IV)
(IV) a R=*o*-CH_3
b R=2,3-benzo

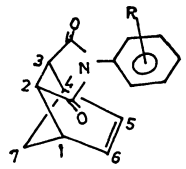


(V) *endo**
(V) a R=*o*-CH_3
b R=2,3-benzo

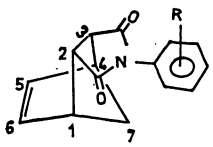


*exo** (VI)
(VI) a R=*o*-CH_3
b R=2,3-benzo

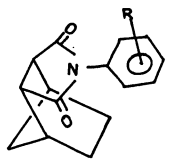
* Prefixes *endo* and *exo* are used in the sense that substituents on the same side of the bicyclo[2.2.2]octene ring as benzene ring are *endo*, those on the other side are *exo*.



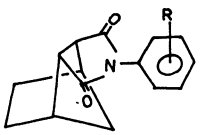
(VII) *endo***
(VII) a R=*o*-CH_3
b R=2,3-benzo



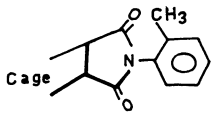
*exo*** (VIII)
(VIII) a R=*o*-CH_3
b R=2,3-benzo



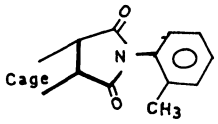
(IX) *endo***
(IX) a R=*o*-CH_3
b R=2,3-benzo



*exo*** (X)
(X) a R=*o*-CH_3
b R=2,3-benzo



(XI)



(XII)

** Prefixes *endo* and *exo* are used in the sense that substituents on the same side of [2.2.1]bycyclo-5-heptene are *endo* and those on the other side are *exo*.

TABLE 3. MP, ELEMENTAL ANALYSES AND CHARACTERISTIC IR PEAKS

Compound	Mp, °C	Calcd		Found		IR ν_{max}, cm^{-1}
		C%	H%	C%	H%	
IIIa	188—189	79.98	5.43	79.79	5.32	1705s, 1780w, 765m
IIIb	185—186	82.03	4.88	81.98	4.65	1700s, 1780w, 765m
IVa	205—208	79.98	5.43	79.76	5.25	1700s, 1780w, 760m
IVb	210—211	82.03	4.88	82.13	4.66	1705s, 1775w, 765m
Va	214—215	79.47	6.03	79.31	5.98	1700s, 1770w, 780m
Vb	248—251	81.56	5.42	81.38	5.28	1705s, 1780w, 785m
VIa	174—177	79.47	6.03	79.29	6.23	1700s, 1775w, 780m
VIb	200—201	81.56	5.42	81.32	5.35	1700s, 1770w, 770m
VIIa	126—129	75.87	5.97	75.72	5.79	1700s, 1775w, 750m
VIIb	152—153	78.87	5.23	78.69	5.45	1705s, 1780w, 775m
VIIIa	228—229	75.87	5.97	75.69	5.72	1705s, 1775w, 760m
VIIIb	208—211	78.87	5.23	78.69	5.03	1710s, 1780w, 760m
IXa	143—146	75.27	6.71	75.37	6.98	1700s, 1775w, 775m
IXb	193—194	78.33	5.88	78.13	5.62	1705s, 1770w, 765m
Xa	198—199	75.27	6.71	75.37	6.81	1700s, 1770w, 770m
Xb	228—230	78.33	5.88	78.13	5.63	1710s, 1780w, 770m

m=medium, s=strong and w=weak

Experimental

NMR spectra were recorded on a Varian A60D spectrometer at 45 °C. Spectral data of the compounds are given in Tables 1 and 2. Infrared spectra were recorded in Nujol mull on a Perkin Elmer-720 spectrometer. Melting points, chemical analyses and IR bands of the compounds are given in Table 3.

*Naphthalene–Maleic Anhydride Adducts (*endo/exo*) and Their Derivatives (IIIa, IVa, IIIb, IVb, Va, VIa, Vb, VIb).* The *endo* and *exo* adducts of maleic anhydride with naphthalene were obtained according to the method of Takeda *et al.*[8] and separated from ethanol by fractional crystallisation. Adducts were transformed into their toluidide (IIIa and IVa) and naphthylimide derivatives (IIIb and IVb) by heating carefully with equimolar amounts of *o*-toluidine and, 1-naphthylamine respectively in a round bottomed flask fitted with an air condenser at 80 °C for *ca.* 2 h. The products obtained were crystallised from ethanol. The toluidide and naphthylimide derivatives on further refluxing with hydrazinehydrate (slightly excess than 2 mol) in ethanol in the presence of animal charcoal gave the reduced products[9] (Va, VIa, Vb, VIb). These compounds were recrystallised from ethanol.

Cyclopentadiene–Maleic Anhydride Adducts and Their Derivatives (VIIa, VIIIa, VIIb, VIIIb, IXa, Xa, IXb, Xb). [2.2.1] Bycyclo-5-heptene 2,3 *endo/exo* dicarboxalic anhydride were prepared according to the method of Craig.[10]

Toluidide (VIIa and VIIIa) and naphthylimide (VIIb and VIIIb) derivatives were obtained on heating the isomeric adducts with equimolar amounts of *o*-toluidine and 1-naphthylamine, respectively, in a round bottomed flask attached to an air condenser at 100—120 °C for 3 h. The products obtained were crystallised from ethanol. These compounds on further refluxing with hydrazinehydrate (slightly excess than 2 mol) in ethanol in the presence of animal charcoal gave the reduced products[9] (IXa, Xa, IXb, Xb) which were recrystallised from ethanol.

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