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Structural Assignment by NMR Analyses of *N*-(Diacylamino)imide Derivatives. Diels-Alder Adducts of 2,3-Dimethylnaphthalene and 6,6-Diphenylfulvene with Maleic Anhydride

Shiva Mohan VERMA and Ashok Kumar SINGH
Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

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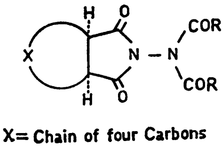
The configurations of the Diels-Alder adducts of maleic anhydride with 2,3-dimethylnaphthalene and 6,6-diphenylfulvene have been investigated by NMR spectroscopy. Restricted rotation and non-planar conformations about the N–N bond in the corresponding *N*-aminoimide derivatives of the adducts have been employed in solving the structural problem. While the *N′*,*N′*-diacetyl system has been shown to be a suitable probe for configurational assignment, *N′*-acetyl-*N′*-aroyl-*N*-aminoimide derivatives have been found to be a more diagnostic probe even to simple adducts.

Preferred conformations about N–N bond in the system of type I have been reported with the help of a cage-moiety which is asymmetric about the plane of the succinimydyl ring.[1–3] Hindered rotation and non-planar conformations about N–N bond in *N′*,*N′*-diacylaminoimides of Diels-Alder adducts have been used for their configurational (*endo*/*exo*) assignments. The utility of this NMR technique was first explored with naphthalene maleic anhydride adducts and their reduction products as model compounds. It is shown that *N′*-acetyl-*N′*-aroyl-*N*-aminoimide system can be a versatile probe for direct determination of the configurations of such adducts.[4,5] It is evident that this system enables the assignment of correct configuration to either *endo* or *exo*-adduct without a comparison with the pattern of the corresponding isomer, and therefore, this method offers a distinct advantage over the earlier methods especially when one of the isomers is not formed.



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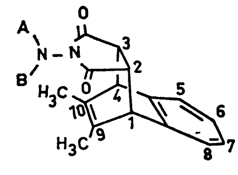
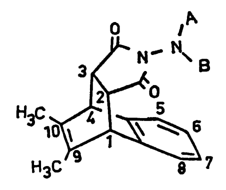
In this communication we have demonstrated the configurational assignment of 2,3-dimethylnaphthalene–maleic anhydride and 6,6-diphenylfulvene–maleic anhydride Diels-Alder adduct with the help of NMR spectral studies of their *N*-aminoimide derivatives (IIa—IId, IIIa—IIIf, IVa—IVd, and Va—Vd).



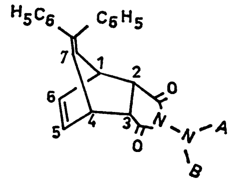
II-*exo**

(IIa) $A=B=H$
(IIb) $A=B=COCH_3$
(IIc) $A=COCH_3$
$B=COC_6H_5$
(IId) $A=COCH_3$
$B=COC_6H_4CH_3(p)$



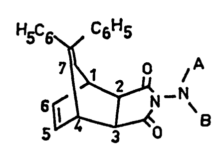
III-*endo**

(IIIa) $A=B=H$
(IIIb) $A=B=COCH_3$
(IIIc) $A=COCH_3$
$B=COC_6H_5$
(IIId) $A=COCH_3$,
$B=COC_6H_4CH_3(o)$
(IIIe) $A=COCH_3$
$B=COC_6H_4CH_3(m)$
(IIIf) $A=COCH_3$
$B=COC_6H_4CH_3(p)$



IV-*endo***

(IVa) $A=B=H$
(IVb) $A=B=COCH_3$
(IVc) $A=H$
$B=COC_6H_5$
(IVd) $A=COCH_3$
$B=COC_6H_5$



V-*exo***

(Va) $A=B=H$
(Vb) $A=B=COCH_3$
(Vc) $A=H$
$B=COC_6H_5$
(Vd) $A=COCH_3$
$B= COC_6H_5$

The Diels-Alder reaction of 2,3-dimethylnaphthalene with maleic anhydride was reported by Kloetzel and Herzog[6] to give adducts having the benzobicyclo[2.2.2]octene system. The configuration of anhydride group of the adduct was studied by these workers with the help of UV absorption and also by chemical methods but the problem remained unsettled. This Diels-Alder reaction has also been carried out in the presence of aluminium chloride and the product was assigned the *exo*-configuration[7] which was later shown to have the *endo*-configuration. The configuration of these adducts has been proposed with the help of their NMR spectra: the one which has deshielded C-2 and C-3 methine protons (δ 3.41) was assigned the *endo*-configuration while the other having shielded C-2 and C-3 methine protons (δ 3.28), the *exo*-configuration.[8,9] The *exo*- and *endo*-adducts were also confirmed by lactonization studies: the adduct which formed an iodolactone was assigned an *exo*-configuration, while the other isomer which did not undergo lactone formation but yielded

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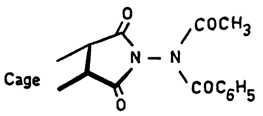
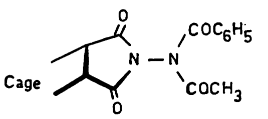
* The prefixes *endo* and *exo* are used in the sense that substituents on the same side of the bicyclo[2.2.2]octene ring as benzene ring are *endo*, those on the other side are *exo*.

** The prefixes *endo* and *exo* are used in the sense that the isomer with the succinimidyl ring towards the cage olefinic system is *endo* and that with the succinimidyl ring away from the olefinic system is *exo*.


VI


VII

its carboxylic acid was given *endo*-configuration.[9] Based on aromatic solvent induced shift studies in rigid cyclic ketones,[10] the configurations of these adducts have also been reported.[9] These adducts showed a small shift difference for the methyl protons and the configuration of either *exo*- or *endo* can be assigned only when the spectrum of the other corresponding isomer is available.

The configuration of 6,6-diphenylfulvene and maleic anhydride adduct was first studied by the ozonization method and was assigned the *exo*-configuration, no *endo*-isomer being produced.[11] The work was reinvestigated and the *endo* and *exo* configurations were established by chemical methods. The *endo*-adduct on treatment with hypobromous acid formed bromolactone acid which subsequently yielded a dilactone. The *exo*-adduct formed a lactone acid with hypobromous acid.[12]

Results and Discussion

N-(Diacylamino)imide Derivatives (IIb—IId and IIIb—IIIf) The NMR spectra of the isomeric *N*-(diacylamino) imide derivatives (IIb and IIIb) are in accordance with the restricted rotation about N–N bond showing two singlets each for the *N*′-acetyl protons with an internal chemical shift of 10 Hz and 97 Hz, respectively (Table 1). On shielding considerations on one of the *N*′-acetyl groups, IIIb could be assigned the *endo*-configuration and IIb the *exo*-configuration.[5]

The spectra of *N*′-acetyl-*N*′-benzoyl derivatives (IIc and IIIc) exhibit two conformations VI and VII resulting from the restricted rotation about N–N bond. Splitting in the cage-methyl resonances by the *N*′-benzoyl group in the compound IIc confirms the *exo*-configuration of the adduct (Table 1). In the other isomeric product IIIc, the cage-methyl resonances remain unaffected and the splitting in the *N*′-acetyls ($\Delta\nu=60$ Hz) demonstrates the *endo*-configuration of the adduct.

A careful study of the spectra shows the preference for conformation (VII) in both the *endo* and *exo*-isomers, where the *N*′-benzoyl group lies *anti* to the cage-moiety. While the conformational preference (VI) has been reported in the *exo*-derivatives of naphthalene-maleic anhydride adduct,[5] sterically the same conformer is not favoured in the case of IIc. The other *N*′-acetyl-*N*′-aroyl compounds (IId and IIId—IIIf) also support the configurational assignment.

N′,N′-Diacetyl Derivatives (IVb and Vb). The NMR spectra of *N*′,*N*′-diacetyl-*N*-amino [2.2.1] bicyclo-5-heptene-7-diphenylmethylene-2,3-*endo*/*exo*-dicarboximide (IVb) and (Vb) in $CDCl_3$ exhibit a similar pattern (Table 2). These isomeric compounds show two singlets, one each for *N*′-acetyl protons, with an internal chemical shift of 16 and 20 Hz, respectively, along with other proton resonances. These observations suggest that the C-5 and C-6 olefinic protons and 7-diphenylmethylene group exert a similar shielding effect on the *N*′-acetyl protons. In such a system where *N*′-acetyls do not appear to be a diagnostic probe for the configurational study, introduction of a group at the *exo*-cyclic nitrogen, which can strongly influence the resonance of the cage protons, would give useful information. *N*′-Acetyl-*N*′-benzoyl-*N*-amino-

Table 1. 60MHz NMR Spectral data[a] of the compounds IIa—IId and IIIa—IIIf

Compound	δA	δB	$\delta(1+4)$	$\delta(2+3)$	$\delta(9+10)$	$\delta(5-8)$
IIa	4.28 (m, 1H)	4.28 (m, 1H)	4.08 (t, 2H)	2.92 (t, 2H)	1.7 (s, 6H)	7.13 (m, 4H)
IIb	2.28 (ds, 3H), 1: 1; 10 Hz	2.28 (ds, 3H), 1: 1; 10 Hz	4.21 (t, 2H)	3.1 (t, 2H)	1.76 (s, 6H)	7.23 (m, 4H)
IIc	2.44 (ds, 3H), 2: 1; 11 Hz	7.39 (m, 5H)	4.12 (m, 2H)	2.89 (dt, 2H), 1: 2; 23 Hz	1.57 (ds, 6H), 2: 1; 22 Hz	7.39 (m, 4H)
IId	2.47 (ds, 3H), 2: 1; 6 Hz	2.33 (s, 3H) 7.28 (m, 4H)	4.16 (m, 2H)	2.85 (dt, 2H), 1: 2; 19.5 Hz	1.60 (ds, 6H), 2: 1; 20 Hz	7.28 (m, 4H)
IIIa	3.67 (m, 1H)	3.67 (m, 1H)	4.17 (t, 2H)	3.09 (t, 2H)	1.84 (s, 6H)	7.21 (m, 4H)
IIIb	1.67 (ds, 3H), 1: 1; 97 Hz	1.67 (ds, 3H), 1: 1; 97 Hz	4.17 (t, 2H)	3.32 (t, 2H)	1.83 (s, 6H)	7.14 (m, 4H)
IIIc	1.70 (ds, 3H), 1: 7; 60 Hz	7.31 (m, 5H)	4.15 (t, 2H)	3.23 (t, 2H)	1.82 (s, 6H)	7.31 (m, 4H)
IIId	1.71 (ds, 3H), 1: 8; 58 Hz	2.27 (ds, 3H), 8: 1; 5 Hz 7.23 (m, 4H)	4.16 (t, 2H)	3.23 (t, 2H)	1.82 (s, 6H)	7.23 (m, 4H)
IIIe	1.72 (ds, 3H), 1: 10; 60 Hz	2.34 (ds, 3H), 10: 1; 2 Hz 7.30 (m, 4H)	4.19 (t, 2H)	3.27 (t, 2H)	1.86 (s, 6H)	7.30 (m, 4H)
IIIf	1.70 (ds, 3H), 1: 7; 62 Hz	2.35 (s, 3H) 7.25 (m, 4H)	4.15 (t, 2H)	3.24 (t, 2H)	1.82 (s, 6H)	7.25 (m, 4H)

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 brackets. In case of multiplicity due to slow rotation, the ratio of the intensity of downfield to upfield and the separation in Hz are indicated. In case of multiplets the mean δ values are given: s=singlet, t=triplet, m=multiplet, ds=double singlet, dt=double triplet, dm=double multiplet. TMS was used as an internal reference.

Table 2. 60 MHz NMR Spectral data of the compounds IVa—IVd and Va—Vd

Compound	δA	δB	$\delta(5+6)$	$\delta(1+4)$	$\delta(2+3)$	Aromatic Protons
IVa	3.25 (m, 1H)	3.25 (m, 1H)	6.37 (t, 2H)	3.92 (m, 2H)	3.4 (m, 2H)	7.23 (m, 10H)
IVb	2.3 (ds, 3H), 1: 1; 16 Hz	2.3 (ds, 3H), 1: 1; 16 Hz	6.35 (t, 2H)	4.05 (m, 2H)	3.68 (m, 2H)	7.24 (m, 10H)
IVc	2.15 (m, 1H)	7.28 (m, 5H)	6.52 (t, 1H)	3.97 (m, 2H)	3.52 (m, 2H)	7.28 (m, 10H)
IVd	2.53 (ds, 3H), 2: 1; 4 Hz	7.26 (m, 5H)	6.04 (dt, 2H), 1: 2; 57 Hz	3.86 (m, 2H)	3.41 (dm, 2H), 2: 1; 17 Hz	7.26 (m, 10H)
Va	3.81 (m, 1H)	3.81 (m, 1H)	6.51 (t, 2H)	3.73 (m, 2H)	2.92 (s, 2H)	7.16 (m, 10H)
Vb	2.32 (ds, 3H), 1: 1; 20 Hz	2.32 (ds, 3H), 1: 1; 20 Hz	6.62 (t, 2H)	4.03 (m, 2H)	3.03 (s, 2H)	7.2 (m, 10H)
Vc	7.82 (m, 1H)	7.18 (m, 5H)	6.54 (t, 2H)	3.86 (m, 2H)	2.86 (m, 2H)	7.23 (m, 10H)
Vd	2.2 (ds, 3H), 2: 3; 29 Hz	7.21 (m, 5H)	6.50 (t, 2H)	3.82 (m, 2H)	2.81 (m, 2H)	7.21 (m, 10H)

imide system has been found to be suitable for the purpose.

N′-Acetyl-N′-benzoyl Derivatives (IVd and Vd) The NMR spectrum of IVd shows multiplicity for C-5 and C-6 olefinic proton resonances ($\Delta\nu=57$ Hz) as well as for the *N′*-acetyl protons (intensity ratio 2: 1, $\Delta\nu=4$ Hz) with other proton resonance (Table 2) caused by restricted rotation about the N–N bond. The spectral features of the compound IVd are very similar to those of *N′*-acetyl-*N′*-benzoyl derivative of *N*-amino[2.2.1]-bicyclo-5-heptene-2,3-*endo*-dicarboximide. The compound also shows preference for the conformation (VI) where the benzoyl group lies *syn* to the cage-olefinic protons. The multiplicity in the cage-olefinic protons indicates the *endo*-configuration of the adduct. The spectrum of the isomeric compound Vd shows two singlets for *N′*-acetyl protons (intensity ratio 2: 3, $\Delta\nu=$ 29 Hz) and a triplet for C-5 and C-6 olefinic protons along with other proton resonance (Table 2). The spectral pattern is in conformity with the restricted rotation about N–N bond, showing the presence of two conformations. The appearance of *N′*-acetyl resonance at the shielded position (δ 1.96) indicates that the conformation (VII), in which the acetyl group lies *syn* to 7-diphenylmethylene, is preferred. Since no multiplicity in the cage-olefinic resonance has been observed, the spectrum indicates it to be an *exo*-adduct. Shielding of the *N′*-acetyl protons by the 7-diphenylmethylene further supports the *exo*-configuration.

Experimental

NMR spectra were recorded on a Varian A-60D spectrometer equipped with a variable temperature controller (Model No. V-6040). IR spectra were recorded for Nujol mulls on Perkin-Elmer-720 spectrophotometer. NMR spectral data are given in Tables 1 and 2, and IR spectral data, melting points and elemental analyses of all the compounds (IIa—IId, IIIa—IIIf, IVa—IVd, and Va—Vd) in Table 3.

Table 3. Mps, elemental analysis and characteristic IR peaks

Compound	Mp, °C	Found		Calcd		IR ν_{max}, cm^{-1}
		C%	H%	C%	H%	
IIa	185—187	71.48	5.89	71.62	6.01	3340m, 3260m, 3185m, 1780m, 1715s, 1620w
IIb	215—217	68.02	5.54	68.17	5.72	1800w, 1750s, 1739s, 1710m
IIc	159—160	72.40	5.29	72.45	5.35	1795w, 1750s, 1735s, 1720m, 1610w
IId	214—215	72.66	5.50	72.88	5.65	1790w, 1740s, 1730s, 1605w
IIIa	193—195	71.52	5.84	71.62	6.01	3350m, 3275w, 1780m, 1715s, 1695s, 1595w
IIIb	180—182	68.32	5.78	68.17	5.72	1795w, 1730s, 1710m
IIIc	204—206	72.15	5.15	72.45	5.35	1790w, 1735s, 1720m, 1605w
IIId	212—214	72.56	5.48	72.88	5.65	1800w, 1735s, 1710m, 1610w
IIIe	175—177	73.03	5.70	72.88	5.65	1795w, 1740s, 1715m, 1605w
IIIf	232—234	72.69	5.52	72.88	5.65	1795w, 1735s, 1710s, 1610m
IVa	150—152	76.92	5.16	77.17	5.30	3325m, 3205w, 1795m, 1705s, 1600w
IVb	204—205	73.01	5.17	73.23	5.20	1800w, 1735s, 1610w
IVc	158—160	79.21	5.04	78.01	4.97	3450m, 3175m, 1800w, 1710s, 1670s, 1635m, 1600w
IVd	199—200	76.11	4.82	76.23	4.92	1795w, 1740s, 1600w
Va	114—116	76.86	5.20	77.17	4.30	3350m, 3280m, 3195w, 1780m, 1710s, 1610m
Vb	128—130	73.44	5.29	73.23	5.20	1795w, 1735s, 1705m, 1605w
Vc	162—164	77.76	4.86	78.01	4.97	3475m, 3250m, 1790w, 1730s, 1710s, 1605w
Vd	145—147	77.19	4.86	76.23	4.92	1790w, 1730s, 1605w

m=medium, s=strong and w=weak

*1,2,3,4-Tetrahydro-9,10-dimethyl-1,4-ethenonaphthalene-2,3-*exo/endo-*dicarboxylic Anhydride.* The *exo* and *endo*-adducts of 2,3-dimethylnaphthalene and maleic anhydride were obtained by the method of Kloetzel and Herzog.[6] A mixture of 2,3-dimethylnaphthalene (1 g) and maleic anhydride (19 g) was heated on an oil bath at 99—100 °C for about 24 h. The hot reaction mixture was poured into water; unreacted maleic anhydride went into the solution leaving behind adduct (*exo/endo*) diacids and 2,3-dimethylnaphthalene. The product was subsequently washed with water and the unreacted 2,3-dimethylnaphthalene was eliminated by converting the *exo/endo*-diacids into water soluble potassium salts by treating the mixture with KOH solution (5%). These acids were liberated by acidification with hydrochloric acid, filtered and then converted into their anhydrides by heating with acetic anhydride on a water bath for about 2 h. A fractional crystallization procedure from carbontetrachloride was developed for the isolation of *exo* (mp 193—195 °C) and *endo* (mp 175—176 °C) adducts. The *exo*-isomer crystallized out first.

*[2.2.1]Bicyclo-5-heptane-7-diphenylmethylene-2,3-*endo/exo*dicarboxylic Anhydride.* These isomeric adducts were obtained according to the method of Alder *et al.*[12] The *endo*-isomer was obtained from 6,6-diphenylfulvene and maleic anhydride in benzene solution at room temperature which on recrystallisation from ethylacetate melted at 174 °C. However, the more predominant *exo*-adduct was obtained on boiling the reactants in xylene. The *exo*-adduct was more soluble in ethylacetate (mp 147 °C).

N-*Aminoimide Derivatives (IIa, IIIa, IVa, and Va).* *N*-Aminoimide derivatives of these isomeric adducts were prepared by adding hydrazine hydrate dropwise while stirring, to the equimolar quantities of adducts in ethanol at room temperature. These *N*-amino-imides were characterised by IR, NMR and chemical analyses.

N′,N′-*Diacetyl Derivatives (IIb, IIIb, IVb, and Vb).* *N′,N′*-Diacetyl derivatives were prepared by heating the corresponding *N*-aminoimides with an excess of acetic anhydride. The product was washed with water, dried and recrystallized from ethanol.

N′-*Acetyl*-N′-*aroyl Derivatives (IIc, IId, IIIc—IIIf, IVd, and Vd).* The *N′*-acetyl-*N′*-benzoyl derivatives were prepared in two steps: *N′*-mono benzoyl derivatives were obtained by refluxing equimolar amounts of *N*-aminoimides and benzoyl chloride with a few drops of pyridine in dry benzene for 4 h. After removal of the solvent, the product was washed with water and recrystallized. The mono-benzoyl derivatives thus obtained were acetylated with an excess of acetic anhydride and a few drops of pyridine on a water bath for 3—4 h. The product was washed with water, dried and recrystallized from ethanol. The other aroyl derivatives were obtained in the same way.

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