Conformational Analysis About N-N Bond by NMR Spectroscopy: *N'*-Sulphonyl Derivatives of *N*-Aminoimides of Anthracene-Citraconic Anhydride and Naphthalene-Maleic Anhydride Adducts

S. M. VERMA, O. SUBBA RAO, and K. O. P. SINHA
Department of Chemistry, Banaras Hindu University, Varanasi-221005, India
(Received February 4, 1974)

A series of *N',N'*-disulphonyl and *N'*-sulphonyl-*N'*-acetyl derivatives of *N*-amino-9,10-dihydroanthracene-9,10-*endo*-α-methyl-α,β-succinimide and *N*-amino-1,2,3,4-tetrahydro-1,4-etheno/ethano-naphthalene-2,3-*exo*/*endo*-dicarboximides with a benzo ring in the cage-moiety were prepared and their NMR spectra were studied. Shielding constants of the substituents provide evidence for the non-eclipsed conformations of the *N'*-substituents with the ring carbonyls. The preferred conformations of *N'*-sulphonyl-*N'*-acetyl derivatives are explained on steric grounds. In *N'*-tosyl-*N'*-acetyl derivatives the tosyl group takes up a fixed conformation about *N'*-SO_2 bond in which the aryl part of the tosyl group projects away from the cage-moiety.

Preferred conformations about N–N bond in systems of type I have been reported with the help of a cage-moiety which does not possess symmetry about the plane of the succinimidyl ring.[1-4] Nonplanar conformations about the N–N' bond in *N',N'*-diacetyl-*N*-amino-1,2,3,4-tetrahydro-1,4-etheno/ethano-naphthalene-2,3-*endo*/*exo*-dicarboximides have been used to assign *endo*/*exo*-configurations to the Diels-Alder adducts.[5] A study has been made of the steric and electronic effects of a sulphonyl substituent at the *exo*-cyclic nitrogen of the *N*-aminocamphorimide[6] leading to the synthesis and conformational study of a series of *N'*-sulphonyl derivatives of *N*-amino-9,10-dihydroanthracene-9,10-*endo*-α-methyl-α,β-succinimide (II) and *N*-amino-1,2,3,4-tetrahydro-1,4-ethano/etheno-naphthalene-2,3-*endo*/*exo*-dicarboximides (III and IV) with a cage benzo ring.

Torsional barriers to rotation about N–N bond ($\Delta G^{\ddagger}$ of the order of 23 kcal/mol) have been reported in *N',N'*-dimesyl and *N'*-mesyl-*N'*-acetyl-*N*-aminocamphorimides.[6] The NMR spectra of the compounds at 45 °C gave further support for the non-planar ground states in *N',N'*-disulphonyl and *N'*-sulphonyl-*N'*-acetyl-*N*-aminoimide systems. Variable temperature NMR spectra have provided evidence for some slow conformational changes in the molecule in solution. The general spectral pattern in nitrobenzene was similar to that observed in $CDCl_3$.

Results and Discussion

N',N'-Dimesyl Compounds (IIb and IIIc). The NMR spectra of compounds IIb and IIIc (Fig. 1) in $CDCl_3$ are similar and show two sharp singlets of equal

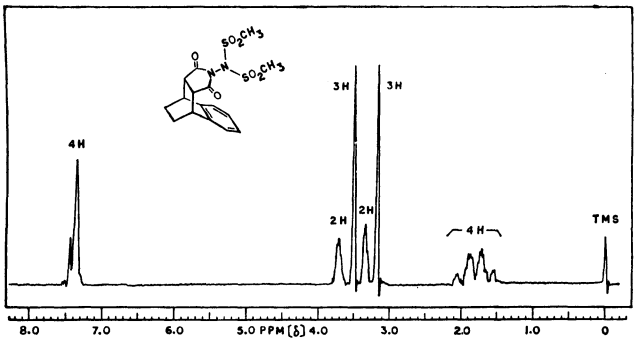


Fig. 1. 60 MHz NMR spectrum of *N',N'*-dimesyl-*N*-amino-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-*endo*-dicarboximide (IIIc) in $CDCl_3$ at 45 °C.

TABLE 1. NMR SPECTRAL[a] DATA OF COMPOUNDS IIa—IIf

Compound	δR₁	δR₂	δ9	δ10	δ11	δ12	δ1—8
IIa	(s, 3H) 3.50	—	(d, 1H) 5.10	(s, 1H) 4.75	(s, 3H) 1.28	(d, 1H) 3.08	—
IIb	(ds, 3H) 3.37; 1:1; 18 Hz	(ds, 3H) 3.37; 1:1; 18 Hz	(d, 1H) 4.93	(s, 1H) 4.58	(s, 3H) 1.28	(d, 1H) 2.90	(m, 8H) 7.45
IIc	(s, 3H) 3.45	(s, 3H) 0.95	(d, 1H) 4.90	(s, 1H) 4.57	(s, 3H) 1.28	(d, 1H) 2.88	(m, 8H) 7.44
IId	(s, 3H) 2.47; (m, 4H) 7.60	(s, 1H) 6.66	(d, 1H) 4.80	(s, 1H) 4.41	(s, 3H) 1.17	(d, 1H) 2.75	(m, 8H) 7.60
IIe	(bs, 3H) 2.50; (m, 4H) 7.66	(bs, 3H) 2.50; (m, 4H) 7.66	(d, 1H) 4.83	(s, 1H) 4.50	(s, 3H) 1.23	(d, 1H) 2.78	(m, 8H) 7.66
IIf	(s, 3H) 2.46; (m, 4H) 7.63	(s, 3H) 0.80	(d, 1H) 4.93	(s, 1H) 4.61	(s, 3H) 1.37	(d, 1H) 2.97	(m, 8H) 7.63

a) The NMR spectra of all the compounds (Tables 1 and 2) were recorded in $CDCl_3$ except IIa which was recorded in pyridine and IIIb, IIIe, and IVb which were recorded in nitrobenzene. The total number of protons and the multiplicity of the bands are indicated in 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. s=singlet, t=triplet, q=quartet, m=multiplet, ds=double singlet, nm=narrow multiplet, bs=broad singlet. TMS was used as internal reference.

TABLE 2. NMR SPECTRAL[a] DATA OF COMPOUNDS IIIa—IIIg AND IVa—IVd

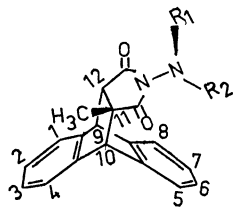
Compound	δR_1	δR_2	$\delta(1+4)$	$\delta(2+3)$	$\delta(9+10)$	$\delta(5-8)$
IIIa	(m, 1H) 3.90	(m, 1H) 3.90	(m, 2H) 3.66	(m, 2H) 3.16	(q, 4H) 1.79	(nm, 4H) 7.33
IIIb	(s, 3H) 3.56	—	(m, 2H) 3.76	(m, 2H) 3.41	(q, 4H) 1.62	—
IIIc	(ds, 3H) 3.32; 1:1; 20 Hz	(ds, 3H) 3.32; 1:1; 20 Hz	(m, 2H) 3.71	(m, 2H) 3.34	(q, 4H) 1.80	(m, 4H) 7.40
IIId	(s, 3H) 3.43	(s, 3H) 0.80	(m, 2H) 3.72	(m, 2H) 3.40	(q, 4H) 1.81	(m, 4H) 7.40
IIIe	(s, 3H) 2.48	—	(m, 2H) 3.78	(m, 2H) 3.43	(q, 4H) 1.65	—
IIIf	(bs, 3H) 2.53; (m, 4H) 7.50	(bs, 3H) 2.53; (m, 4H) 7.50	(m, 2H) 3.73	(m, 2H) 3.33	(q, 4H) 1.75	(m, 4H) 7.50
IIIg	(s, 3H) 2.47; (q, 4H) 7.81	(s, 3H) 0.70	(m, 2H) 3.78	(m, 2H) 3.51	(q, 4H) 1.81	(nm, 4H) 7.34
IVa	(m, 1H) 4.41	(m, 1H) 4.41	(m, 2H) 4.60	(t, 2H) 3.03	(m, 2H) 6.67	(m, 4H) 7.44
IVb	(s, 3H) 3.50	(m, 1H) 2.41	(m, 2H) 4.80	(m, 2H) 3.38	(m, 2H) 6.41	—
IVc	(ds, 3H) 3.58; 1:4; 4 Hz	(ds, 3H) 2.20; 1:4; 5 Hz	(m, 2H) 4.72	(t, 2H) 3.26	(m, 2H) 6.80	(m, 4H) 7.45
IVd	(bs, 3H) 2.53; (m, 4H) 7.73	(bs, 3H) 2.53; (m, 4H) 7.73	(m, 2H) 4.61	(t, 2H) 3.09	(m, 2H) 6.75	(m, 4H) 7.73

a) Refer to footnote, Table 1.

intensity for the two mesyl groups with an internal chemical shift of 20 Hz. The other cage proton resonances are given in Tables 1 and 2. The spectra are temperature dependent and the two mesyl proton signals move closer as the temperature is raised.

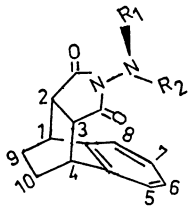
The structure of the *exo*-cyclic trivalent nitrogen atom is assumed to be nearly planar, since the sulphonyl group is as efficient as a carbonyl group for the delocalization of the nitrogen lone-pair electrons.[7] The possibility of slow rotation about N′–SO_2 bond is discarded since the free rotation about this bond is possible with effective and continuous $p\pi$-$d\pi$ delocalization.[7,8] Hence, slow rotation about N–N′ bond could be the only possible explanation for the observed multiplicity.

Non-planar conformations about the N–N′ bond similar to tetraacyl hydrazines, could explain the large $\Delta\nu$=20 Hz between the two mesyl signals as compared to the $\Delta\nu$=5.7 Hz of *N*′,*N*′-dimesyl-*N*-aminocamphorimide.[6] In the proposed conformation (V and Fig. 1) the mesyl group *syn* to the cage-moiety is shielded by the cage benzo ring, whereas the mesyl group *anti* to the cage-moiety appears at the normal position. Non-bonding repulsions between the ring carbonyls and the sulphonyl groups and also some steric factors could make the N–N′ bond torsional barrier sufficiently high.



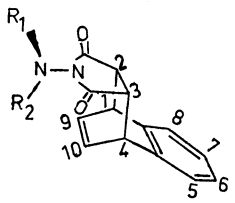
II

Compd.	R_1	R_2
IIa	SO_2CH_3	H
IIb	SO_2CH_3	SO_2CH_3
IIc	SO_2CH_3	$COCH_3$
IId	$SO_2C_6H_4\cdot CH_3$-*p*	H
IIe	$SO_2C_6H_4\cdot CH_3$-*p*	$SO_2C_6H_4\cdot CH_3$-*p*
IIf	$SO_2C_6H_4\cdot CH_3$-*p*	$COCH_3$



III *endo**

Compd.	R_1	R_2
IIIa	H	H
IIIb	SO_2CH_3	H
IIIc	SO_2CH_3	SO_2CH_3
IIId	SO_2CH_3	$COCH_3$
IIIe	$SO_2C_6H_4CH_3$-*p*	H
IIIf	$SO_2C_6H_4CH_3$-*p*	$SO_2C_6H_4CH_3$-*p*
IIIg	$SO_2C_6H_4CH_3$-*p*	$COCH_3$



IV *exo*

Compd.	R_1	R_2
IVa	H	H
IVb	SO_2CH_3	H
IVc	SO_2CH_3	$COCH_3$
IVd	$SO_2C_6H_4CH_3$-*p*	$SO_2C_6H_4CH_3$-*p*

N′,N′-*Ditosyl Compounds (IIe, IIIf, and IVd).* The *N*′,*N*′-ditosyl compounds show, in their NMR spectra, a slightly broad singlet of 6H intensity near δ 2.50 for the two tosyl-methyl protons, whereas the monotosyl compounds show a sharp singlet (width at half height 1.5 Hz) for its tosyl methyl protons (Tables 1 and 2).

* 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 the benzene ring are *endo*, those on the other side are *exo*.

The broadness of the singlet (width at half height 3 Hz) observed for the two tosyl-methyl groups may be due to hindered rotation about the N–N′ bond. A preferred conformation about the N–N′ bond in these compounds could give two signals for the two tosyl-methyl groups as in *N′,N′*-dimesyl compounds IIb and IIIc, but the appearance of a broad singlet indicates that the two tosyl-methyl protons lie away from the effective magnetic zone of the cage-moiety.

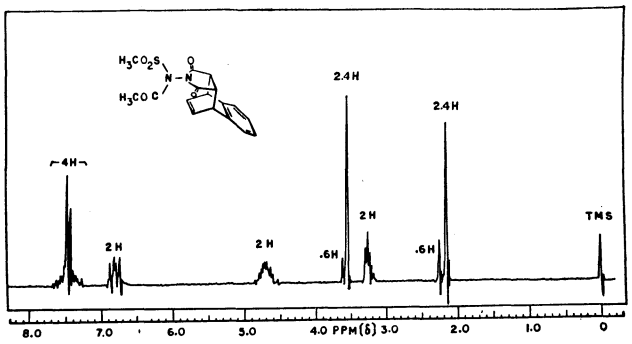


Fig. 2. 60 MHz NMR spectrum of N′-mesyl-N′-acetyl-N-amino-1,2,3,4-tetrahydro-1,4-ethylenonaphthalene-2,3-*exo*-dicarboximide (IVc) in $CDCl_3$ at 45 °C.

N′-Suphonyl-N′-acetyl Derivatives (IIc, IIf, IIId, IIIg, and IVc). The NMR spectrum of *N′*-mesyl-*N′*-acetyl compound (IVc) in $CDCl_3$ (Fig. 2) shows along with other normal resonances (Table 2), two singlets for mesyl protons and two singlets for acetyl protons.

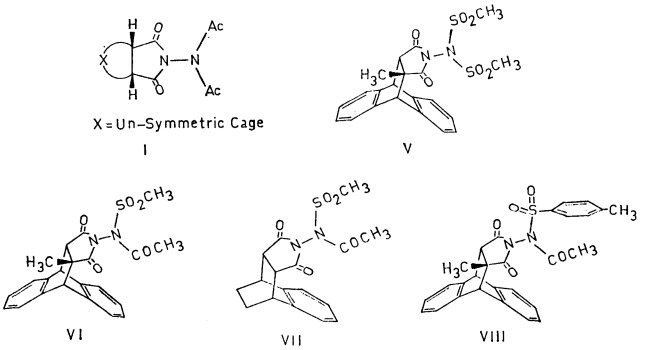
The splitting of the mesyl and acetyl proton signals in the spectrum indicates the possibility of two conformations due to the restricted rotation about the N–N′ bond. In the two different conformations the mesyl protons experience different magnetic environments and therefore, appear as a pair of singlets. The conformer in which the acetyl group lies *syn* to the cage-moiety, while the bulkier mesyl group lies *anti*, is predominant (Fig. 2).

Compounds IIc and IIId in $CDCl_3$ exhibit different patterns in their NMR spectra. Each compound shows a singlet of 3H intensity for the mesyl protons at a normal position ($\delta \approx 3.43$) and another singlet of 3H intensity for the acetyl protons at a shielded position ($\delta \approx 0.80$). As in the case of compound IVc, restricted rotation about N–N′ bond could also be expected in IIc and IIId. Appearance of the acetyl signal with 3H population at the shielded position indicates that the conformation (VI and VII) in which the acetyl group lies *syn* to the cage-moiety is preferred.

The NMR spectrum of each of the *N′*-tosyl-*N′*-acetyl compounds IIf and IIIg in $CDCl_3$ shows two sharp singlets, one for the tosyl-methyl protons and the other for the acetyl protons, along with other proton resonances (Tables 1 and 2).

The spectral features of these compounds are very much similar to *N′*-mesyl-*N′*-acetyl analogues IIc and IIId. They also take up preferred conformations of types VI and VII in which the less bulkier acetyl group is *syn* to the cage-benzo ring.

The tosyl group does not have any shielding effect on the cage-moiety protons. Shielding of the cage protons by the *N′*-benzoyl group has been reported in the case of *N′*-benzoyl-*N′*-acetyl derivatives of *N*-amino-[2.2.1]bicycloheptene-2,3-*endo*-dicarboximide[2] and *N*-aminocamphorimide.[6] This observation indicates that the aryl part of the tosyl group projects away from the cage-moiety (VIII).



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 a Perkin-Elmer-257 spectrophotometer. NMR spectral data are given in Tables 1 and 2, and IR spectral data, melting points and elemental analyses of all the compounds in Table 3.

*1,2,3,4-Tetrahydro-1,4-ethenonaphthalene-2,3-*endo/exo*-dicasboxylic anhydrides* were obtained by the method of Takeda *et al.*[9] The *endo*-isomer on refluxing with hydrazine hydrate[10] (4 mol) in ethanol medium in the presence of animal charcoal gave the reduced product, 1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-*endo*-dicarboximide (IIIa). The *exo*-isomer was reacted with equimolecular amount of hydrazine hydrate in ethanol medium at room temperature to give the *N*-aminoimide (IVa). The two *N*-aminoimides were recrystallized from ethanol and gave benzal derivatives with benzaldehyde which showed a characteristic one proton singlet near δ 9.0.

*N′-Monomesyl and N′,N′-Dimesyl Derivatives of N-Amino-9,10-dihydroanthracene-9,10-*endo*-α-methyl-α,β-succinimide*[4] *and N-Amino-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-*endo*-dicarboximide IIIa (IIa, IIb, IIIb, and IIIc).* The compounds were prepared by heating the corresponding *N*-aminoimide with mesyl chloride (2 mol) in the presence of pyridine on a water bath for about 2 hr. The reaction mixture was then washed with water, filtered, dried and recrystallized from a mixture of ethanol and ethyl acetate. The product thus obtained was a mixture of both *N′*-monomesyl and *N′,N′*-dimesyl derivatives. *N′,N′*-Dimesyl derivatives were soluble in cold chloroform and were separated from the mixture.

N′-Monomesyl Derivative (IVb). This was prepared by heating *N*-amino-1,2,3,4-tetrahydro-1,4-ethenonaphthalene-2,3-*exo*-dicarboximide (1 mol) with mesyl chloride (2 mol) in the presence of a few drops of pyridine on a water bath for about 2 hr. The product was recrystallized from ethanol and was found to be exclusively a monomesyl derivative.

N′-Mesyl-N′-acetyl Derivatives (IIc, IIId and IVc). The compounds were prepared by heating the corresponding *N′*-monomesyl derivative with acetic anhydride in the presence of pyridine on a water bath for 2—3 hr. The reaction mixture was then treated with water, filtered, dried and recrystallized from ethanol.

N′-Monotosyl-N-aminoimides (IId and IIIe). The compounds were prepared by heating equimolar amounts of *N*-aminoimide and tosyl chloride in the presence of pyridine on a water bath for about 2—3 hr and were recrystallized

Table 3. Mps, elemental analyses and IR[a] data

Compound	Mp °C	Elemental analyses Found C%	Found H%	Calculated C%	Calculated H%	IR ν_{max} (cm^{-1})
IIa	290	62.53	4.52	62.82	4.71	3240m, 1790w, 1725s, 1160s, 760m
IIb	225	54.56	4.22	54.78	4.35	1800w, 1730s, 1165s, 770m
IIc	237	62.07	5.01	62.27	4.71	1790w, 1740s, 1170s, 760m
IId	226	68.06	4.92	68.12	4.80	3170m, 1790w, 1740s, 1590m, 1165s, 755m
IIe	280	64.35	4.43	64.70	4.57	1810w, 1750s, 1595w, 1175s, 770w
IIf	257	66.83	4.66	67.20	4.80	1800w, 1740s, 1595w, 1165s, 760w
IIIa	227—230	69.02	5.66	69.42	5.78	3315m, 3260w, 1690s, 1610w
IIIb	245—247	55.92	4.87	56.25	5.00	3255m, 1805w, 1730s, 1158s, 760w
IIIc	214—217	48.54	4.38	48.24	4.52	1808w, 1750s, 1176s, 756m
IIId	198—200	56.12	5.01	56.35	4.97	1806w, 1745s, 1728s, 1170s, 760m
IIIe	240—242	63.24	5.32	63.63	5.05	3240m, 3210m, 1805w, 1746s, 1734s, 1608w, 1180s, 765w
IIIf	250—253	60.83	4.65	61.09	4.73	1810w, 1750s, 1600m, 1188s, 1180s
IIIg	202—205	63.46	4.97	63.01	5.02	1808w, 1748s, 1730s, 1598w, 1180s, 760w
IVa	185—187	69.60	5.33	70.00	5.00	3325m, 3260m, 3200m, 1778m, 1695s, 1620m, 760m
IVb	206—208	56.28	4.32	56.60	4.40	3270m, 1800w, 1733s, 1335s, 1154s, 760m
IVc	196—197	56.59	4.56	56.66	4.44	1800w, 1730s, 1180s, 760m
IVd	176—177	61.12	4.20	61.31	4.38	1814w, 1755s, 1600m, 1175s, 1158s, 748w

a) All IR spectra were recorded in Nujol. m=medium, s=strong and w=weak.

from ethanol.

N'-*Tosyl*-N'-*acetyl Derivatives (IIf and IIIg).* The compounds were acetylated with acetic anhydride as in the case of IIc, IIIc, and IVb.

N',N'-*Ditosyl Derivatives (IIe, IIIf, and IVd).* The compounds were prepared by heating *N*-aminoimide (1 mol) with tosyl chloride (2 mol) in the presence of a few drops of pyridine on a water bath for about 3 hr. The product was then washed with water, dried and recrystallized from ethanol.

The authors thank Prof. G. B. Singh for his keen interest in the study. One of the authors (O.S.R.) is grateful to U.G.C. for the award of a Research Fellowship.

References

1) a) B. H. Korsch and N. V. Riggs, *Tetrahedron Lett.*, **1966**, 5897; b) N. V. Riggs and S. M. Verma, *Aust. J. Chem.*, **23**, 1913 (1970).

2) S. M. Verma and C. Koteswara Rao, *Tetrahedron*, **28**, 5029 (1972).

3) a) S. M. Verma and R. Prasad, *J. Org. Chem.*, **38**, 1004 (1973); b) S. M. Verma and O. Subba Rao, *Aust. J. Chem.*, **26**, 1963 (1973).

4) S. M. Verma and K. O. P. Sinha, *Ind. J. Chem.*, **11**, 1138 (1973).

5) S. M. Verma, O. Subba Rao, and C. Koteswara Rao, *Tetrahedron Lett.*, **1973**, 1639.

6) S. M. Verma and R. Prasad, *J. Org. Chem.*, **38**, 3745 (1973).

7) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **74**, 1058 (1952).

8) R. M. Moriarty, *Tetrahedron Lett.*, **1964**, 509.

9) K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takano, *Chem. Ber.*, **95**, 2344 (1962).

10) A. Furst, R. C. Berlo, and S. Hooton, *Chem. Rev.*, **65**, 51 (1965).