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ROLE OF (–OCH_3) GROUP ON CONFORMATIONAL ANALYSIS ABOUT N-C (PHENYL) BOND : A ^{1}H NMR STUDY

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ABSTRACT

Role of substituent (-OCH_3) on the conformation about N-C(phenyl) bond at different positions in arylimides of anthracene-maleic anhydride and hexachloro cyclopentadiene-maleic anhydride system has been demonstrated through 1H NMR spectroscopy.

KEYWORDS : Conformation, configuration, ^{1}H NMR.

Flexibility of a chemical bond is one of the important factors that determine the properties and reactivity of a molecule. One finer aspect of molecular structure deals with the arrangements of atoms or groups around a single bond known as conformational analysis. Many physical methods have been used for conformational studies but over recent years, the Nuclear Magnetic Resonance (NMR) spectroscopy has surpassed all other techniques in its application. The position of resonance signals and their fine structures provide detailed information about the bonding situation of magnetic nuclei and their spatial relationships. In addition to the chemical shifts and coupling constants, NMR spectra are a function of certain time dependent phenomena ,called intramolecular rate processes. The energy barriers called torsional barriers can be calculated by variable temperature NMR spectroscopy.

Hindered rotation and two non planar conformations about N-C (phenyl) bond in ortho substituted arylimides have been demonstrated with the help of asymmetric cage moieties (Verma et al 1976) and this is used in configurational assignment of Diels –Alder adducts (Verma et al., 1978).Configuration of N-carboethoxy 1,2 dihydro pyridine-maleimide D.A. adduct demonstrated with the help of conformational analysis (kamal et al., 1996) .C NMR spectroscopy is used as additional tool for conformational analysis about N-C (phenyl) bond in N-arylimides of anthracene-maleic anhydride D.A. adduct(Nishi et al 1991). With increasing non-bonded compression between the ortho substituent and the cage, preference of anti-conformation has been observed . In addition to the bulk of ortho substituent, the nature and position of other substituent plays some role in configurational stability of the compound, (Kamal et al 1993), and cage also plays some rolein controlling the energy barrier(Kamal et al 1999).

MATERIALS AND METHODS

General: Melting points were determined on a 'Buchi' melting point apparatus and are uncorrected . The analytical data of carbon and hydrogen were determined on a Perkin-Elmer C,H,N analyser (Model no. 24^{0}C), IR spectra were recorded in KBr on a JASCO-FT/IR-5300 spectrophotometer . ^{1}HNMR spectra were recorded in a jeol FX90Q multinuclear spectrometer in $CDCl_3$ using tatramethyl silane (TMS) as internal standered at 25^{0}C.

Preparation of Compounds

N-arylimide derivative of anthracene-maleic anhydride adduct.

Anthracene-maleic anhydride adduct was mixed with an equimolar amount of corresponding aryl amines and the mixture was heated in a round bottom flask fitted with an air condenser at 130-40^{0}C for 3-4 hrs. The products obtained were washed with water and recrystallized from benzene.

N- arylimide derivative of hexacloro cyclopentadiene maleic anhydride adduct(endo adduct):

These compounds were obtained by heating the adduct with equimolar amount of corresponding aryl amine in a round bottom flask at 120-130^{0}C on an oil bath for about 2-4 hrs , products were recrystallized from benzene .

RESULTS AND DISCUSSION

^{1}H NMR spectrum of compound (I) shows two

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Table 1 : Melting point, I.R and 1H NMR spectral Data of Compounds (I-VI).

Compound No.	M.P. (^{0}C)	IR spectral data (cm^{-1})	^{1}H NMR spectral data of compound (in ∂) at 25^{0}C in $CDCl_3$
I	242-44	1780m, 1720s, 1600w.	1.o6 (s, 1.38 H), 2.08 (s, 1.62 H),3.36 (bs,2H, α andβ-H,), 4.82 (bs, 2H, 9 and 10 –H), 5.59 (bd, 0.54 H), 7.2 – 7.4 (m, 11 H, aromatic protons)
II	267-68	1780w,1710s,1600m	3.38 (bs,2H,α and β-H) , 3.36 and 3.65(ds,3H,1:2, O-OCH_3 protons), 4.85 (bs ,2H ,9 and 10-H), 5.67 (bd, 1H, 6'-H), 7.0 -7.2(bm,11H ,aromatic protons.
III	270-71	1780W,1720S,1600W	3.35 (bs,2H,α and β-H), 3.76(S,3H,3'-OCH_3) 5.0 (bs, 2H,9&10-H), 6.26(d,1H,6'-H), 7.3-7.6(bm,11H ,aromatic protons)
IV	220-21	1780w, 1720s,1600w	3.4 (bS,2H, α&β-H) 3.76(s,3H,2'-OCH3),3.86(5,3H,5'-OCH_3), 5.04(s,2H,9&10-H), 5.32(d,1H,6'-H) 7.4-7.7(m,10H,aromatic protons)
V	249-50	1785w,1715s,1610w	3.80 and 3.83(ds,3H,1:1,O-OCH_3) 3.90 and 3.93(ds,2H,1:1,2&3-H), 7.3-7.5(bm, 4H,aromatic protons)
VI	264-65	1800m,1720s, 1610s	3.82 and 3.85(ds,3H,2'-OCH_3, 3.86 (s,3H,5'-OCH_3), 4.06 and 4.10(ds,2H, 2&3-H), 6.87.1(bm,3H,aromaticproton

singlets for 2'-methyl protons at 1.06 (1.38 H), 2.08 (1.62 H), a broad doublet at 5.59 (0.54 H) along with other normal resonances. Duplexity in the 2' – methyl resonances and the appearance of 6'-H at a shielded position indicates two non-planar conformations syn (1a) and anti (1b). The bulk of a methyl group at 2'- position in the N-aryl system has been sufficient to restrict the rotation about N-C bond.

In place of 2'-methyl group when 2'-OCH_3 group(a bulkier group) is introduced (compound II). The 1HNMR spectra of compound (II)shows a pair of singlets at ∂ 3.36 (0.63H) and ∂ 3.65 (1.73) for the ortho- OCH_3 protons along with other normal resonance. The duplexity in methoxy resonances shows the presence of two conformations (syn/anti). A comparatively small internal separation in the methoxy resonances suggests a weak anisotropic effect on the cage in the syn conformation. In syn conformation the ortho-anisyl protons may assume a preferred anti-orientation (2a) about the aryl C-O bond ,where the methyl remains out of the shielding zone of the cage moiety. The other arrangement in syn conformation in which methyl lies toward the cage (2b) would be unfavourable on steric grounds and in such cases the methyl would be highly schielded. Sharp singlets for anisyl protons indicate magnetic equivalence of all three protons, which emerge from the free rotation about the O-CH_3 bond. Electrostatic repulsive forces between electronegative oxygen of anisyl and the aromatic cage in the syn- conformation are operative and it could be responsible for low population in the syn conformation.

The ^{1}H NMR spectrum of compound (III)) shows a singlet for meta-anisyl protons at ∂ 3.76 (3H) and indicates fast rotation about N-C bond on the NMR times scale . The 1HNMR spectrum of compound (IV) shows two singlets each of (3H) intensity at ∂ 3.86(3H) and ∂ 3.76(3H) for 2'-OCH_3 AND 5'- OCH_3 –protons, a broad singlets at ∂ 5.32 (1H) for 6'-H along with other normal resonance. Appearance of 6'-H at schielded position (∂ 5.32,1H) indicates the non-planar conformation of the phenyl ring with the 2'-OCH_3 groups are magnetically non- equivalent.

^{1}H NMR spectrum of compound(V) shows two singlets for 2'-OCH_3 protons at ∂ 3.80(1.5H) and ∂ 3.83(1.5H) and two singlets for 2 and 3-protons at ∂

3.90(1H) and ∂ 3.93(1H) and suggests two non- planar conformations. With an addition of - OCH_3 substituent at 5'-position the compound (VI), shows duplexity for 2'-OCH_3 protons at ∂ 3.82(1.48), ∂ 3.85(1.52H), a singlet at ∂ 3.86(3H) for 5'-OCH_3 protons and the presence of two non-planar conformations .All compounds (I-V) show a single spot on TLC plate. They are not able to produce atropisomers due to low torsional barrier.

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