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Restricted rotation about Nsp^2-Csp^3 bond through π-electronic interactions : A ^1H NMR study

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The electronic repulsion of a carboxyl group from a phenyl ring has been found to restrict rotation about Nsp^2-Csp^3 bond. A stable sp^3-geometry of a carbon in N-CHR-COOH derivatives of α,β-(9,10-dihydroanthracene-9,10-diyl)succinimide has been demonstrated on the basis of shielding parameters of N′-alkyls. The carboxyl group does not exhibit hydrogen bonding with the carbonyls of the succinimide and remains in *anti* orientation. Though the anisotropic effect of an olefinic bond is fairly small, the interaction of carboxyl group with the olefinic bond is evident in CPD-MA adduct derivative.

In a recent communication[1], it was demonstrated that the electrostatic repulsion of the lone electron pair of sp^3-nitrogen the π-electronic system of a phenyl ring (**1**) has been sufficient to restrict pyramidal inversion of the lone electron pair of nitrogen. On similar electrostatic behaviour we have attempted to design a stable tetrahedral carbon of the type (**2**) with a suitable repellent substituent-X from a phenyl ring. The geometry of **2** is reported in this communication on the basis of ^1H NMR study.

Asymmetric cage systems have been very helpful in conformational analysis about Nsp^2-Csp^3 bonds[2,3]. In **3a**, two non-planar conformations *syn* and *anti* about N-C bond in the ratio of 1 : 1.1 have been explained on the steric grounds[2]. Among the different 2′-substituents reported for hindering rotation about N-C bond in **3**, −COOH group has been shown to remain only in *anti* orientation[4]. Though some p-π^* transition in the carboxyl group has been proposed when the benzene and carboxyl groups are brought close together through their interaction in space to explain the increased Cotton effect in aryl succinic acids[5,6], the exclusive existence of *anti* conformation in **3b** suggests a repulsive interaction of the −COOH with the phenyl ring of the cage moiety. In **3c** where R = −OH, a seven membered hydrogen bonded cyclic structure has been proposed on the basis of magnetic non-equivalence of α-(δ 3.20) and β-(δ 3.52) protons as well as the shielding parameter of 6′-H (δ 6.1)[7].

^1H NMR of the compound **4a** shows a doublet at δ 0.8(3H) for the methyl and a quartet at δ 4.3(1H) for −C*H*COOH along with other resonances (Table I). Rotation about an sp^2-sp^3 bond is known to possess a low energy barrier[8,9], a signal for the methyl protons in **4a** suggests that either there is fast roation about Nsp^2-Csp^3 bond or the molecule exists in a preferred conformation. As compared to the phthaloyl derivative (**5a**), the method of **4a** is shielded by $\Delta\delta$ = 1.0 ppm and indicates the possibility of restricted rotation about N-C bond with the methyl in *syn* orientation. Similar shielding parameter has been reported for the methyl resonances ($\Delta\delta$ = 1.0

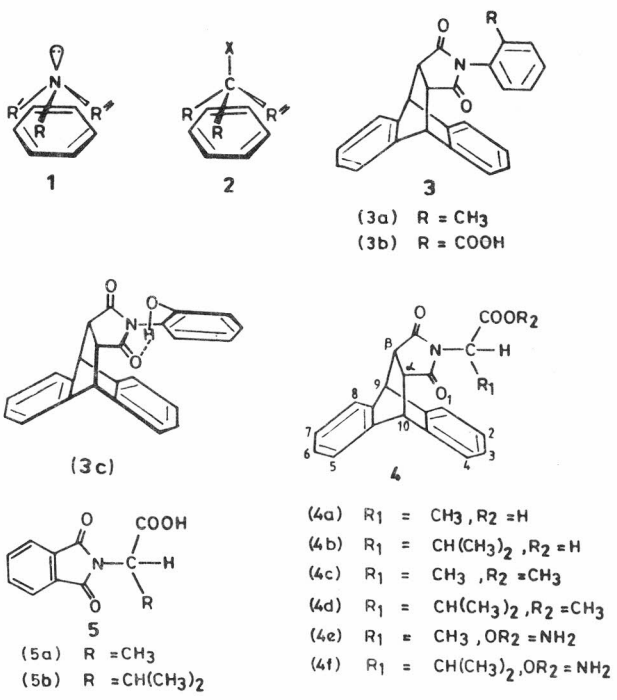


Table I—^{1}H NMR spectral data of compounds (chemical shift in δ, ppm)

Compd	R_1	R_2	$-CHCOOR_2$	α-,β-,H	9-,10-,H	ArH
4a	0.8 (d, 3H, J=7 Hz)	10.35 (bs, 1H)*	4.0 (q, 1H, J=7 Hz)	3.0 (bs, 2H)	4.8 (bs, 2H)	7.15-7.6 (m, 8H)
4b	0.2, 0.8 (dd, 6H, J=7 Hz) 2.2 (m, 1H)	10.47 (bs, 1H)*	4.1 (d, 1H, J=7 Hz)	3.3 (bs, 2H)	4.8 (bs, 2H)	7.15-7.6 (m, 8H)
4c	0.8 (d, 3H, J=7 Hz)	3.6 (s, 3H)	4.5 (q, 1H, J=7 Hz)	3.3 (bs, 2H)	4.8 (bs, 2H)	7.15-7.6 (m, 8H)
4d	0.2, 0.8 (dd, 6H, J=7 Hz) 2.2 (m, 1H)	3.6 (s, 3H)	4.5 (d, 1H, J=7 Hz)	3.3 (bs, 2H)	4.8 (bs, 2H)	7.15-7.6 (m, 8H)
4e	0.8 (d, 3H, J=7 Hz)	$-OR_2=NH_2$ 5.7 (bs, 2H)	4.3 (q, 1H, J=7 Hz)	3.3 (bs, 2H)	4.8 (bs, 2H)	7.1-7.6 (m, 8H)
4f	0.2, 0.8 (dd, 6H, J=7 Hz) (m, 1H)	$-OR_2=NH_2$ 5.6 (bs, 2H)	3.9 (d, 1H, J=7 Hz)	3.2 (bs, 2H)	4.8 (bs, 2H)	7.1-7.6 (m, 8H)

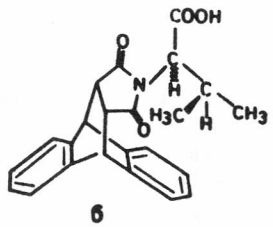
*D_2O exchangeable.

ppm) of **3a** in the two conformations. The magnetic equivalence of α and β protons in **4a** eliminates the possibility of intramolecular hydrogen bond of the $-COOH$ with one of the carbonyls of the succinimidyl ring.

^{1}H NMR of compound **4b** is quite characteristic in demonstrating the conformational preference about Nsp^2-Csp^3 bond. The spectrum shows two doublets at δ 0.2 and 0.8 for the isopropyl methyls, a multiplet at δ 2.2 for the isopropyl methine proton, a doublet at δ 4.1 (1H) for C*H*COOH proton and other resonances (Table I). Coupling constants of the methyl doublets and the methine doublet are of similar magnitude (7.0 Hz) and the isopropyl methine signal resembles an octet. The isopropyl methyls are diastereotopic due to a chiral carbon[10] and the appearance of methyl protons at a highly shielded position ($\Delta\delta$ = 0.8 ppm) as compared to **5b**, suggests restricted rotation and a preferred conformation having one of the methyl of the isopropyl group *syn* to the cage. A large difference in the magnetic environment of the two isopropyl methos ($\Delta\delta$ = 0.6 ppm) further suggests a preferred conformation about Csp^3-Csp^3 bond and a geometry lime **6** where one of the methyls is held exactly over the phenyl ring. Rotational isomers about Csp^3-Csp^3 bonds have been well documented[11] and the restricted rotation about C-C bond may be explained on the steric grounds. The preference of only one conformation having carboxylic group in *anti* orientation clearly indicates that the torsional barrier about N-C bond has resulted from the strong electrostatic repulsion of the carboxylic group with the cage phenyl ring. The spectrum of **4b** is very much similar to the N-alkyl resonances of **7** whose pyramidal geometry of the exocyclic nitrogen has been established by X-ray crystallography[1].

Ester derivatives **4c** and **4d** exhibit a singlet at δ 3.6, (3H) for the ester methyl protons along with other resonances (Table I). Normal ester methyl resonances further support the restricted rotation about N-C bond with the ester group in *anti* conformation. In case of a fast rotation, the ester methyl would experience the anisotropic effect of the cage. The carboxylic group in **4a** and **4b** is not involved in the intramolecular hydrogen bond with one of the carbonyls of the succinimidyl ring. When the carboxyl group was transformed into the amido group, $-CONH_2$, compounds **4e** and **4f** showed similar spectral pattern (Table I) as observed for **4a** and **4b**. These supported a preferred conformation about N-C bond and the absence of intramolecular hydrogen bonding by the amido substituent with the carbonyls of the succinimidyl ring.

In order to investigate the role of an isolated olefinic bond in controlling the conformation about N-C bond, compounds **8** and **9** were pre-



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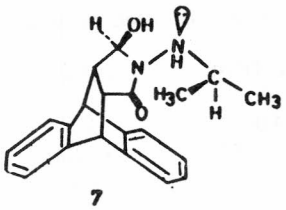

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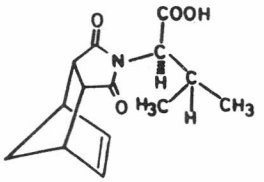

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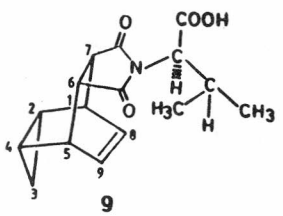

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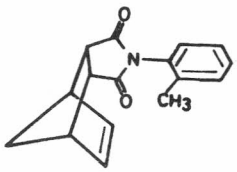

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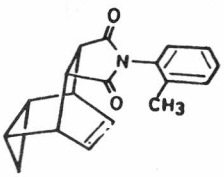

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pared. The spectrum of **8** shows a shielding of isopropyl protons ($\Delta\delta$ = 0.2 ppm) due to the anisotropic effect of the olefinic bond and suggests a preferred conformation similar to **6**. In case of **10** a small shielding of ($\Delta\delta$ = 0.03 ppm) in 2′-methyl resonances in the two conformations has been reported[12]. Compound **9** exhibits a similar ($\Delta\delta$ = 0.2 ppm) shielding parameter for the isopropyl methyls and supports the preferred conformation about N-C bond. The spectrum of **11** showed two conformations *syn* and *anti* about N-C (phenyl) bond in the ratio of 60 : 40 (δ = 0.1 ppm). The higher shielding parameter indicated the reinforcement of the cyclopropyl moiety with the olefinic bond.

Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on Jeol FX 90Q multinuclear spectrometer and IR spectra in KBr on a Jasco FT/IR 5300 spectrometer. Melting points, analytical and IR data of the compounds are given in the Table II. Diels-Alder adduct of anthracene-maleic anhydride was obtained according to the reported method[13].

***α,β*-(9, 10-Dihydroanthracene-9, 10-diyl)succinimido-N-acetic acid (4a).** It was prepared by heating anthracene-maleic anhydride adduct with dl-alanine in equimolar proportion at 180-85° for half an hour. The resulting product was refluxed with an excess of acetic acid for 3 hr. The excess of acid was distilled off and the pasty material obtained was solidified on trituration with cold methanol. It was recrystallized from ethanol. Compound **4b** was obtained in a similar way from the anthracene-maleic anhydride adduct and dl-valine.

Table II—Characterisation data of compounds

Compd	m.p. (°C)	Found (Calc.) % C	H	IR (ν_{max} in cm^{-1})
4a	186-88	72.57 (72.62)	4.83 (4.90)	2650b, 1780w, 1720s, 1610w
4b	221-23	73.55 (73.60)	5.58 (5.60)	2500b, 1785w, 1710s, 1620w
4c	111-12	73.10 (73.13)	5.19 (5.26)	1780w, 1745m, 1705s
4d	130-31	73.00 (73.03)	5.11 (5.17)	1778w, 1745m, 1703s
4e	218-19	72.60 (72.83)	5.13 (5.20)	3418w, 3171w, 1778w, 1703s, 1673s
4f	212-14	73.25 (73.40)	5.54 (5.68)	3398w, 3175w, 1780w, 1705s, 1680s
5a	160-61	60.19 (60.27)	4.02 (4.10)	2650b, 1770w, 1710s
5b	101-2	63.09 (63.15)	5.21 (5.26)	2590b, 1775b, 1705s
8	61-62	63-67 (63.87)	6.36 (6.46)	2640b, 1780w, 1703s
9	168-70	64.39 (64.43)	6.45 (6.50)	2630b, 1776w, 1705s

Ester derivative (4c) and (4d). Methyl esters were prepared by refluxing the compounds **4a** and **4b** with an excess of methanol in the presence of conc. sulfuric acid for 3 hr and were recrystallized from methanol.

Amide derivatives (4e) and (4f). Compound **4a** was refluxed gently with thionyl chloride for 20 min and after removal of thionyl chloride it was treated with an excess of ammonia (20%). The solid separated was recrystallized from ethanol to give **4e**. Compound **4f** was obtained in the similar way.

Phthaloyl derivatives (5a) and (5b). These compounds were prepared by heating phthalic anhydride with dl-alanine and dl-valine according to the reported method[14]. ^{1}H NMR: **5a**: δ1.8 (d, 3H, J=7 Hz, $-CH_3$), 4.7 (q, 1H, J=7 Hz, $-CH$), 7.7-8.0 (m, 4H, ArH), 10.2 (bs, 1H,

$-COOH$)*; **5b** : δ1.0, 1.3 (dd, 6H, J= 7 Hz, isopropyl $-CH_3$), 3.0 (m, 1H, isopropyl $-CH$), 4.8 (d, 1H, J= 7 Hz, $-CH$), 7.7-8.0 (m, 4H, ArH), 10.4 (bs, 1H, $-COOH$)*.

Compounds 8 and 9. Compound **8** was obtained from the *endo*—adduct of cyclopentadiene—maleic anhydride[15] and dl-valine in the similar way as **4b**. Cycloheptatriene—maleic anhydride *endo*—adduct[16] with dl-valine yielded **9**; ^1H NMR : **8** : δ 0.8,1.0 (dd, 6H, J= 7 HZ, isopropyl-CH_3), 1.7 (ABq, 2H, 7-H), 2.3 (m, 1H, isopropyl $-CH$), 3.3 (S, 4H, 1,2,3 and 4-H), 4.2 (d, 1H, J= 7 Hz, $-CH$), 6.1 (s, 2H, 5 and 6-H), 10.0 (bs, 1H, $-COOH$, D_2O exchangeable); **9** : δ0.2 (m, 2H, 3-CH_2), 0.8, 1.0 (dd, 6H, J= 7 Hz, isopropyl $-CH_3$), 1.1 (m, 2H, 2 and 4-H), 2.3 (m, 1H, isopropyl $-CH$), 3.1 (s, 2H, 6 and 7-H), 3.4 (bs, 2H, 1 and 5-H), 4.2 (d, 1H, J= 7 Hz $-CH$), 5.8 (t, 2H, J= 3 Hz, 8 and 9-H), 9.9 (bs, 1H, $-COOH$)*.

2′-Toluidine derivative (11). Equimolar amount of the cycloheptatriene-maleic anhydride adduct and *o*-toluidine was heated at 130-40°C for 3 hr. The product obtained was recrystallized from ethanol-benzene mixture (1 : 1), m.p. 188°C; IR : 1772(w), 1705(s), 1494(w) cm^{-1}; ^1H NMR : δ 0.2 (m, 2H, 3-CH_2), 1.0 (m, 2H, 2 and 4-H), 2.0 and 2.1 (ds, 3:2, 3H, 2′-CH_3), 3.1(s, 2H, 6 and 7-H), 3.4 (bs, 2H, 1 and 5-H), 5.8 (t, 2H, 8 and 9-H), 7.1-7.4 (m, 4H, ArH).

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References

1 Srivastava A, Srivastava V, Verma S M & Subramanian E, *J Org Chem*, 59, **1994**, 3560.

2 Verma S M & Singh N B, *Aust J Chem*, 29, **1976**, 295; Chaturvedi J & Verma S M, *Indian J Chem*, 29B, **1990**, 9; Verma S M & Singh R M, *J Org Chem*, 40, **1975**, 897.

3 (a) Verma A K, Mahanti S & Verma S M, *Indian J Chem*, 28B, **1989**, 457.
(b) Srivastava V, Singh R M & Verma S M, *Indian J Chem*, 25B, **1986**, 724.
(c) Verma S M & Verma A K, *Indian J Chem*, 23B, **1984**, 639.

4 Srivastava A, Srivastava V & Verma S M, *Nat Acad Sci Letters*, 16, **1993**, 219.

5 Potapov V M, *Stereochemistry* (MIR Publishers, Moscow), **1978**, 0. 493; Fric I, Spırko V & Blaha K, *Collect Czech Chem Commun*, 33, **1968**, 4008; Potapov V M, Kiryshkina G V & Tokamov G P, *Zh Org Khim*, 7, **1971**, 1652.

6 Peeling J, Glenn H & Koh K, *Can J Chem*, 67, **1989**, 1015; Banner W A, *in Topic of Stereochemistry*, Vol. 18, edited by E L Eliel & S H Wilen (Wiley, New York), **1988**, p. 124; Potapov V M & Kiryshkina G V, *Dokl Akad Nauk SSSR*, 202, **1972**, 103.

7 Vandana & Singh R M, *Indian J Chem*, 23B, **1984**, 782.

8 Rieker A & Kessler H, *Tetrahedron Lett*, **1969**, 1227.

9 Gall R E, Landman D, Newsoroff G P, Sternsheel S, *Aust J Chem*, 25, **1972**, 109.

10 Jenning W B, *Chem Rev*, 75, **1961**, 307; Shin C G & Yoshimara J, *Tetrahedron Lett*, **1973**, 2615; Meyer W L & Meyer R B, *J Am Chem Soc*, 85, **1963**, 2170; Suzuki F & Oki M, *Tetrahedron Lett*, **1974**, 2845.

11 Oki M, *Application of Dynamic NMR Spectroscopy to Organic Chemistry* (VCH Publishers), **1985**, p. 16; Oki M, *Top Stereochem*, 1, **1983**, 41.

12 Verma S M & Singh N B, *Bull Chem Soc Japabn*, 51, **1978**, 520.

13 Vogel A I, *A Textbook of Practical Organic Chemistry* (ELBS, London), **1968**, p. 943.

14 Diels O & Alder K, *Leibig's Ann Chem*, 460, **1928**, 111.

15 Kohler E P, Tishler M, Potler H, Thompson H T, *J Am Chem Soc*, 61, **1939**, 1057.

16 Vogel A I, *A Textbook of Practical Organic Chemistry* (ELBS, London), **1968**, p. 438.