Stereochemistry of the Addition Product of *N*-Aminosuccinimide Moiety to an Acetylenic Ester

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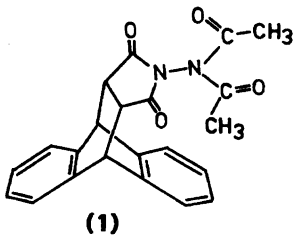
(Received September 24, 1993)

^{1}H, ^{13}C NMR and X-ray crystallography have demonstrated the azomethine structure of the addition product obtained from *N*-amino-2,3-(9,10-dihydro-9,10-anthracenediyl)succinimide and diethyl acetylenedicarboxylate. The *exo* cyclic nitrogen exists in sp^2-state and its lone pair lies in *anti* orientation while the diethyl succinate moiety has been demonstrated to be *syn* to the cage and orthogonal to the succinimide plane. On acetylation the product is transformed into *N*-acetyl derivative which exhibits restricted rotation about N–N bond and a preferred conformation with *N*-acetyl in *syn*-orientation.

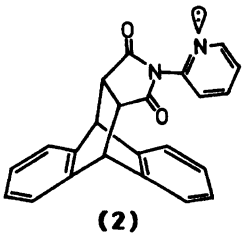
Korsch and Riggs[1] demonstrated the restricted rotation and nonplanar conformation (**1**) about N–N bond in tetraacylhydrazines through an unsymmetric cage moiety. Interaction of the lone electron pairs in the p-orbitals of the nitrogen atoms has been attributed to be an important factor for the torsional barrier about N–N bond.[2] While evaluating the effective bulk of lone pair of nitrogen in sp^2-state through conformational analysis about N–C bond it was observed that the lone pair of pyridyl nitrogen exhibits a strong repulsion from the benzene ring of the cage moiety and remains in *anti*-orientation (**2**) (Chart 1).[3,4]

In this paper we report the stereochemistry of an addition product obtained from *N*-amino-2,3-(9,10-dihydro-9,10-anthracenediyl)succinimide (**3**) and diethyl acetylenedicarboxylate in ethanol through ^{1}H NMR, ^{13}C NMR and X-ray crystallography (Chart 2).

Nucleophilic addition to activated alkynes[5,6] have been studied and the *cisoid*[7,8] and *transoid* addition[9,10] of amines with acetylenic compounds have been reported.[11] *N*-Amino compound **3** undergoes Michael addition with diethyl acetylenedicarboxylate and yields a product **4**. ^{1}H NMR spectrum of the compound exhibits a singlet (2H) at $\delta=2.44$ and two overlapping triplets and quartets along with normal resonances. On D_2O shake, the intensity of the singlet at $\delta=2.44$ is reduced to half (1H). IR of the compound (**4**) shows a stretching vibration at 1630 cm^{-1} (C=N) in KBr and 1625 cm^{-1} the $CHCl_3$ and does not exhibit any N–H stretching in the solid (KBr) and in the solution ($CHCl_3$).



(1)



(2)

Chart 1.

The spectral pattern suggests the azomethine structure (**5**) in the solid as well as in solution. It is well known the imine form is more stable than enamine form.[12] In case of acetone hydrazone (**6**) restricted rotation about N–N bond and the isopropylideneamino moiety orthogonal to the succinimide plane with the lone electron pair in *anti* orientation have been proposed on the basis of the shielding parameters of the methyl protons and VT NMR studies (Chart 3).[13] On these considerations a geometry (**5**) of the product (**4**) has been proposed with the restricted rotation about N–N bond and the azomethine moiety orthogonal to the succinimide plane and *syn* to the cage moiety. ^{13}C NMR of the compound exhibits a –$\underline{C}H_2$COOEt resonance at $\delta=35.70$ because of aromatic ring current and further supports the proposed geometry (**5**).

X-Ray crystallography of (**4**) has demonstrated the tautomeric azomethine structure (**7**). The *exo*-cyclic nitrogen is sp^2-hybridized and the lone pair is in *anti*-orientation to the cage moiety (Chart 4). The group –$CH_2COOC_2H_5$ is *syn* to the cage. The computer generated perspective drawing of the molecule is shown in Fig. 1.

Details of the X-Ray Analysis (7).

1. The lone-pair electrons are pointing away from the ring system (*anti*-orientation).
2. The substance is recrystallized from ethanol m.f. $C_{26}H_{24}N_2O_6$ in the space group $P2_1/c$ with unit cell parameters $a=11.212(5)$, $b=15.555(1)$, $c=14.120(4)$ Å, $\beta=111.63(3)°$, $V=2289.03$ Å, $Z=4$, $D_{calcd}=1.336$ g cm^{-3}, Cu $K\alpha$ ($\lambda=1.5418$ Å) $\mu=7.5$ cm^{-1}, $F(000)=968$. Final $R=0.075$, $R_w=0.079$, maximum $2\theta=130°$, crystal size ($0.25\times0.30\times0.2$ mm). Three dimensional data collection using CAD_4 diffractometer with monochromated Cu $K\alpha$ radiation with $\omega/2\theta$, scan mode, 4537 reflections measured, 4051 unique and 3102 with $F_o>3\sigma(F_o)$. The intensity was corrected for Lorentz polarization and absorption corrections. Structure solution by SHELX. Full matrix least squares refinements on F_o with non-H atoms anisotropic and H-atoms isotropic converged to a R factor of 0.075.

Dihedral Angle between Planes (7).

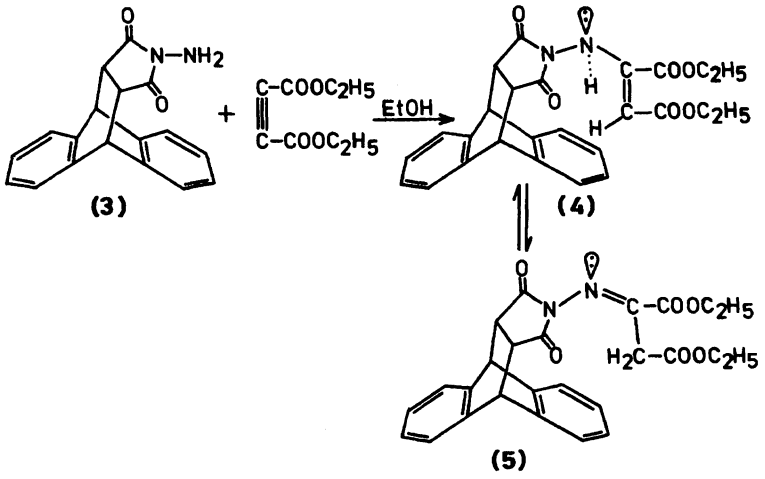


Chart 2.

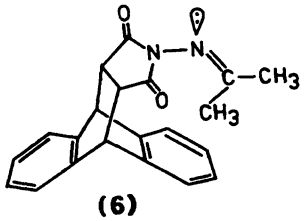


Chart 3.

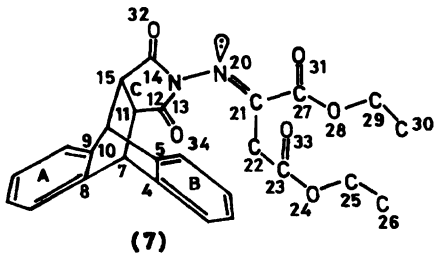


Chart 4.

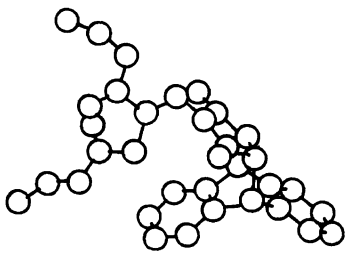


Fig. 1. X-Ray crystallographic computer-generated perspective drawing of **5**.

(1) Between A and B is 57.1°(**1**)
(2) Between A and the plane thro' 7, 11, 15, and 10 is 120.4(2)°.
(3) Between B and the plane thro' 7, 11, 15, and 10 is 63.3(2)°.
(4) Between plane C and plane thro' 7, 11, 15, and 10 is 58.5(2)°.
(5) Plane C deviates from planarity.
(6) Plane C and A is 61.9(1)°.
(7) Plane C and B is 5(1)°.
(8) Torsion angles
(a) N_{20}–C_{21}–C_{27}–O_{28}=9.88(6)°.
(b) N_{20}–C_{21}–C_{22}–C_{23}=−121.7(5)°.
(c) C_{21}–C_{27}–O_{28}–C_{29}=−173.4(4)°.
(d) C_{27}–C_{21}–C_{22}–C_{23}–=63.1(5)°.
(e) N_{13}–N_{20}–C_{21}–C_{27}=172.8°.
(f) N_{13}–N_{20}–O_{21}–C_{22}=−2.3(6)°.
(g) C_{27}–O_{28}–C_{29}–C_{30}=−84.1(5)°.
(h) C_{21}–C_{22}–C_{23}–O_{24}=−153.3(4)°.
(i) C_{22}–C_{23}–O_{24}–C_{25}=−177.8(4)°.
(j) C_{23}–O_{24}–C_{25}–C_{26}=−141.4(5)°.

Bond Distances.
(a) C_{21}–C_{22}=1.339(4) Å.
(b) N_{20}–C_{35}=1.414(4) Å.

Weighting scheme based on counting statistics $w=4(F_o)^2/[\sigma^2(F_o^2)]$ where $\sigma(F_o^2)=[\sigma^2(I)+0.05I^2]^{1/2}L\rho$.

The product (**4**) on acetylation yields a compound (**8**) which exhibits a characteristic singlet at δ=0.86 (3H) in ^{1}H NMR spectrum indicating restricted rotation about N–N bond and a preferred conformation with the acetyl group in *syn*-orientation (Chart 5).[1] The shielding parameter ($\Delta\delta$=1.75) of *N*-acetyl suggests the *endo*-orientation of the acetyl methyl in *syn*-conformation (**1**). Computer generated perspective drawing of the X-ray crystallographic studies is shown in Fig. 2 which confirmed the proposed geometry on the basis of spectral studies.

Details of the X-Ray Analysis (8). A transpar-

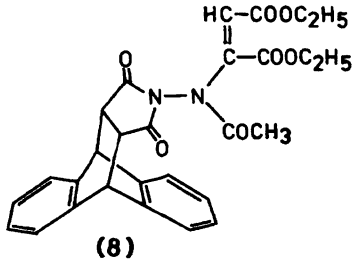


Chart 5.

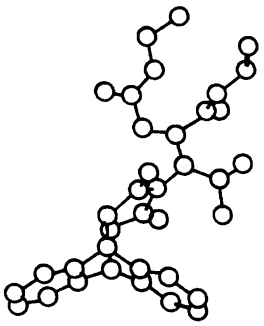


Fig. 2. X-Ray crystallographic computer-generated perspective drawing of **8**.

ent rhombhohedral crystal of $C_{28}H_{26}N_2O_7$ having approximate dimensions of 0.4×0.25×0.20 mm was crystallized from ethanol. The monoclinic cell parameters are $a=13.1889(3)$, $b=8.955(1)$, $c=21.797(4)$ Å, $\beta=103.85(2)°$, $V=2499.7$ Å^3, for $Z=4$ and F.W.=502.54, $\rho_c=1.33$ g cm^{-3}, $\mu=8.1$ cm^{-1}, space group $P2_1/c$, $Z=4$ intensity data collected using Nonius CAD-4 diffractometer, Cu $K\alpha$ ($\lambda=1.5418$ Å) radiation, $\omega/2\theta$ mode, $2\theta_{max}=130°$, 23 reflection in the range of $9<\theta<25°$ for lattice parameter measurement and refinement data correct for $L\rho_1$ absorption correction with an average correction factor 0.967, $0\leq h\leq 15$, $0\leq k\leq 10$, $-24\leq l\leq 24$, 4561 reflections measured, 3652 with $I\geq 3.0\sigma I$. Full matrix least square refinement on Fols with non-hydrogens anisotropic and hydrogen isotropic with individual weighting scheme gave a final $R=0.053$ and $R_w=0.055$-$(\Delta/\sigma)_{max}=0.08$, goodness of fit(s)=1.18. Highest peak in the final differences Fourier is 0.33 ρ/Å^3. The packing of the molecule is stabilized by Van der Waals forces only. The two phenyl rings are planar within experimental errors. Angle between the two phenyl ring planes is 51.4(1)°.

(1) Torsion Angles.

(a) N_{20}–C_{21}–C_{27}–$O_{28}=105.96(0.33)°$.
(b) N_{13}–N_{20}–N_{21}–$C_{22}=-2.09(0.39)°$.
(c) N_{13}–N_{20}–C_{21}–$C_{27}=179.36(0.22)°$.
(d) N_{13}–N_{20}–C_{21}–$C_{22}=-2.09(0.39)°$.
(e) C_{23}–O_{24}–C_{25}–$C_{26}=-171.16(0.29)°$.
(f) N_{13}–N_{20}–C_{35}–$O_{37}=169.85(0.27)°$.
(g) N_{13}–N_{20}–C_{35}–$C_{36}=-10.63(0.39)°$.

(2) Bond Distances.

(a) C_{21}–$C_{22}=1.339(4)$ Å.
(b) N_{20}–$C_{35}=1.414(4)$ Å.

Experimental

^{1}H and ^{13}C NMR were recorded on a JEOL FX 90Q multinuclear spectrometer at 25 °C in $CDCl_3$ with TMS as the internal standard (chemical shift in δ/ppm). IR spectra were recorded on a Perkin Elmer 720 spectrometer (ν_{max} in cm^{-1}).

Preparation of Compound (4). Compound **4** was obtained by refluxing the *N*-amino-2,3-(9,10-dihydro-9,10-anthracenediyl)succinimide[1] with an equimolar amount of diethyl acetylenedicarboxylate in ethanol for 2 h. On cooling the reaction mixture, the product separated out was recrystallized from ethanol, mp 180—181 °C. Found. C, 67.70; H, 5.28 %. Calcd for $C_{26}H_{24}N_2O_6$: C, 67.82; H, 5.22%. MS $[M]^+$ 460, base peak $m/z=178$ $(C_{14}H_{10})^+$; IR (KBr) 1770 (w), 1735 (m), 1720 (m), 1630 (w); ^{1}H NMR $\delta=1.31$ (6H, dt, $-CH_3$), 2.44 (2H, s, –CH–, –NH), 3.44 (2H, bs, 2- and 3-H), 4.35 (4H, dq, $-CH_2-$), 5.0 (2H, bs, 9- and 10-H), 7.44—8.75 (8H, bm, aromatic protons); ^{13}C NMR $\delta=13.82$ ($-CH_3$), 13.97 ($-CH_3$), 35.70 ($-\underline{C}H_2COOC_2H_5$), 45.49 (2- and 3-C), 45.96 (9- and 10-C), 61.32 ($-COO\underline{C}H_2CH_3$), 62.83 ($-COO\underline{C}H_2CH_3$), 140.87 (C=N), 162.11, 164.56, 165.95, 170.38, (two imide >C=O carbons and two ester >C=O carbons) along with aromatic resonances 124.26, 125.25, 126.12, 126.88, 127.38, 128.06, 131.54, 138.68.

Compound (8). Compound **8** was obtained by refluxing the compound (**4**) with an excess of acetic anhydride for about 3 h. Excess of acetic anhydride was removed under reduced pressure and the product was recrystallized from ethanol, mp 70 °C. Found: C, 67.16; H, 5.22%. Calcd for $C_{28}H_{26}N_2O_7$: C, 66.93; H, 5.18%. IR (KBr) 1790 (m), 1735 (m), 1710 (s); ^{1}H NMR $\delta=0.80$ (3H, s, $-NCOCH_3$), 1.31 (6H, dt, $J=7.5$ Hz, $-C\underline{H}_3$), 3.53 (2H, bs, 2- and 3-H), 4.26 (4H, dq, $J=7.5$ Hz, $-CH_2$), 5.08 (2H, bs, 9- and 10-H), 5.57 (1H, s, –CH), 7.35—8.62 (8H, bm, aromatic protons).

The authors thank CSIR, New Delhi for the award of a Senior Research Fellowship to A.S.

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