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New cascade transformations of 3-(2-aminophenylamino)-5,5-dimethyl-2-cyclohexen-1-one

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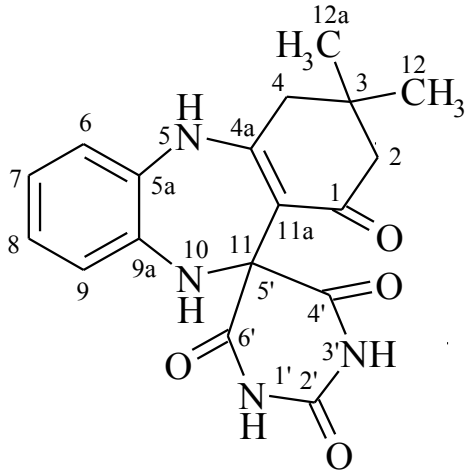
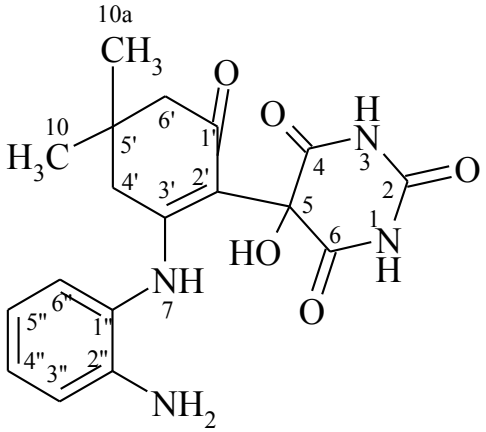


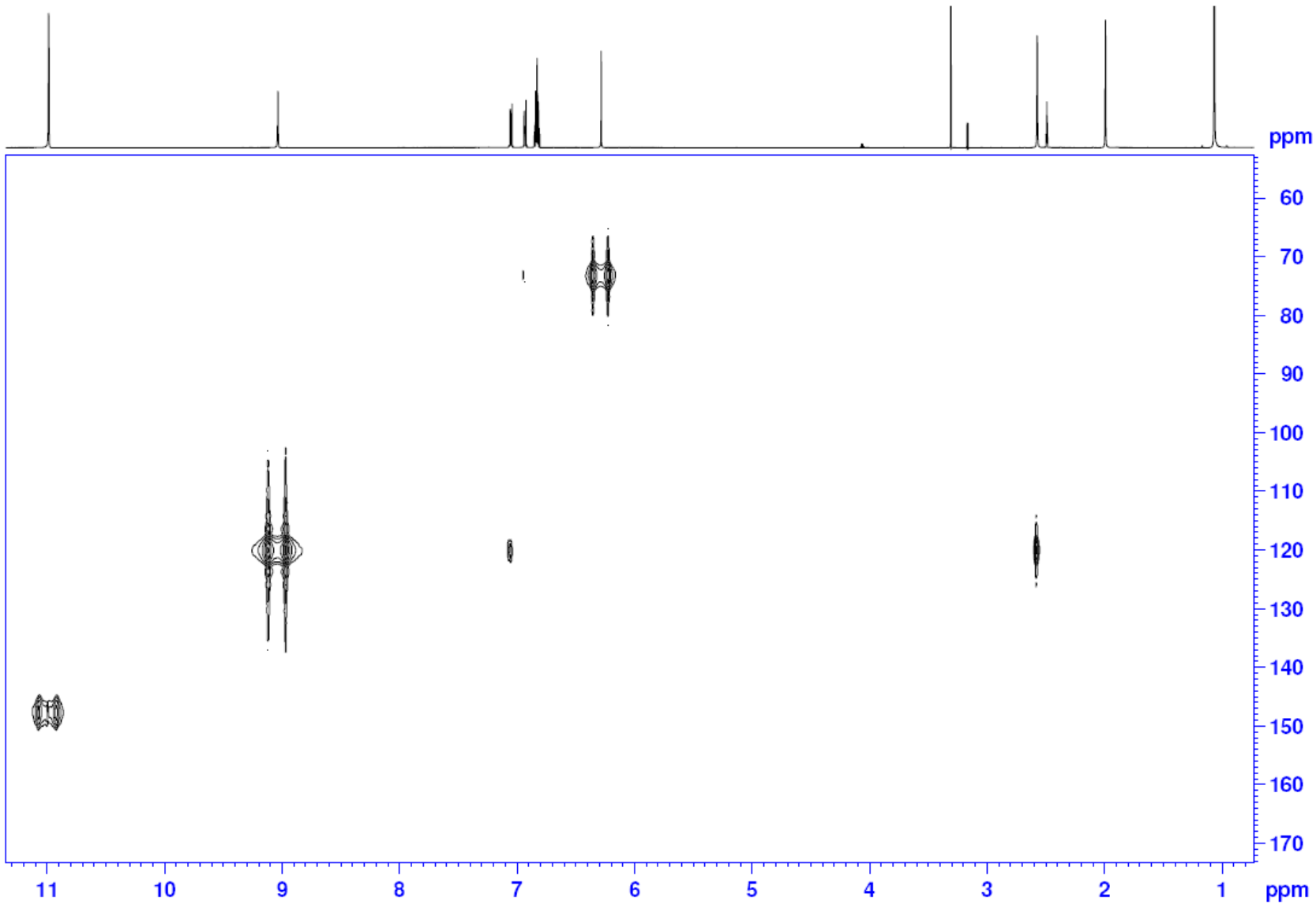
Nucleus	1	2	3	4	4a	5(^{15}N)	5a	6	7	8	9	9a	10(^{15}N)	11a	1'(^{15}N)	2'	3'(^{15}N)	4'	5'(11)	6'	12,12a
^{1}H		1.99		2.57		9.04		7.04	6.83	6.82	6.92		6.28		10.99		10.99				1.06
^{13}C/^{15}N	194.67	48.76	31.34	44.46	155.16	120.00	132.93	120.16	121.44	123.41	121.48	135.57	72.50	106.44	147.90	150.44	147.90	169.43	65.72	169.43	27.45

^{1}H, ^{13}C, ^{15}N NMR spectroscopic data for compound **4** (DMSO-d_6, δ)

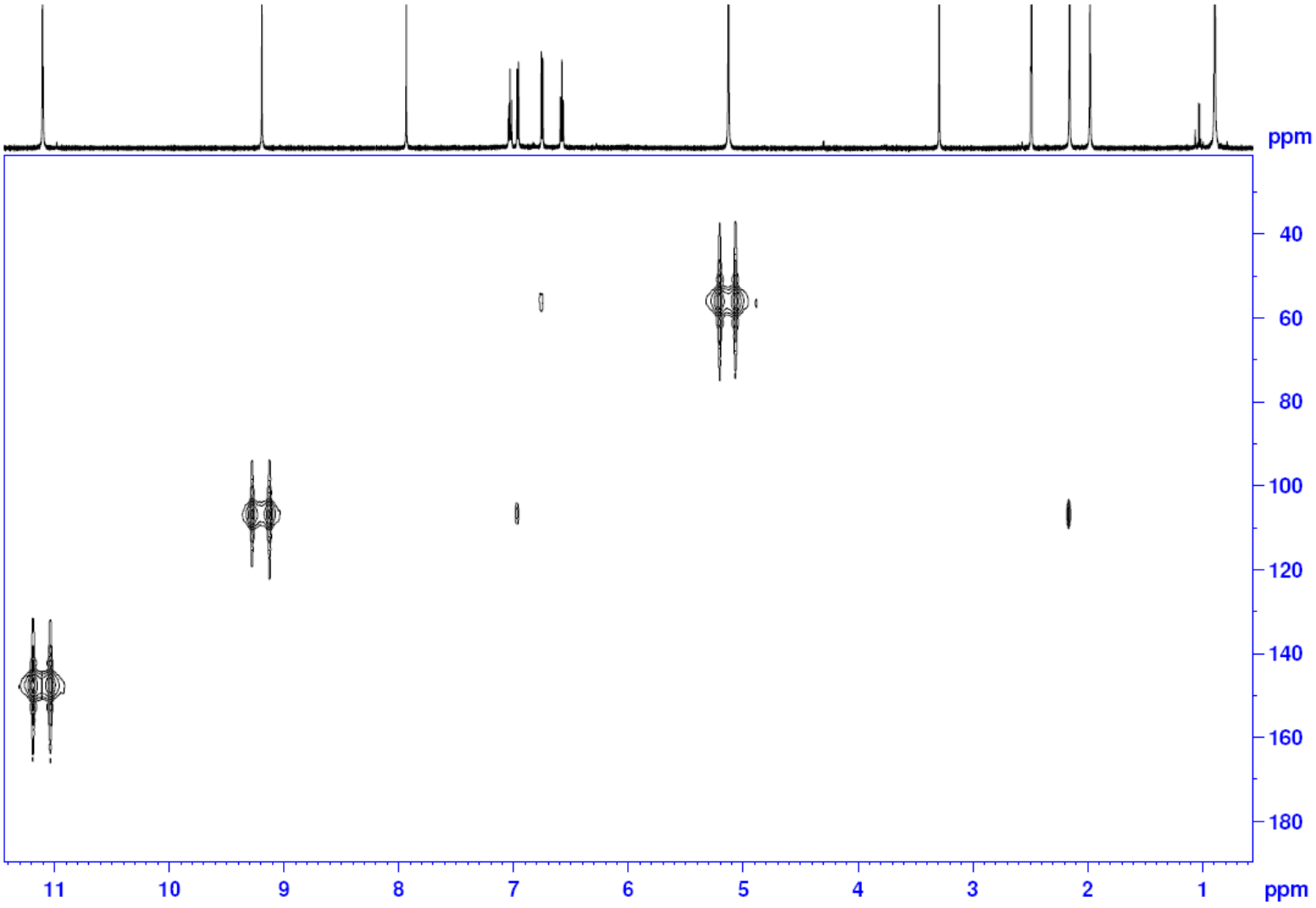


Nucleus	1(^{15}N)	2	3(^{15}N)	4	5	6	7(^{15}N)	8(^{15}N)	9(OH)	10	10a	1’	2’	3’	4’	5’	6’	1’’	2’’	3’’	4’’	5’’	6’’	9
^{1}H	11.10		11.10				9.19	5.13	7.94	0.89	0.89			2.16		1.98				6. 57	6.75	7.04	7.02	7.94
^{13}C/^{15}N	147.30	150.44	147.30	171.09	65.72	171.09	106.70	55.80		27.52	27.52	106.02	165.16	39.96	31.97	48.91	192.82	182.20	144.97	114.89	116.02	128.09	128.28	

^{1}H, ^{13}C, ^{15}N NMR spectroscopic data for compound **5** formed upon dissolution of compound **3** in DMSO (DMSO-d_6, δ)



2D ^{1}H-^{15}N (HMBC) NMR spectrum of compound **4**.



2D ^{1}H-^{15}N (HMBC) NMR spectrum of compound **5** formed upon dissolution of compound **3** in DMSO.

Crystallographic study.

Compound **3** is crystallized as a solvate with ethanol and water and contains two molecules of **3** (A and A') in the symmetrically independent part of the unit cell.[1] In both molecules, the central five-membered ring has a flattened envelope conformation (with a small deviation of the C7(C7') atom; the annelated cyclohexenone moiety has a conformation intermediate between the sofa and semi-chair configurations, whereas the 2-aminophenyl substituent is turned in a nearly perpendicular direction, apparently due to steric interactions. The *N*-aminocarbonylcarboxamide substituent at the C7 atom has a planar structure. The central nitrogen atom (N3) is more conjugated with the C17=O4 carbonyl group due to the donor properties of the amino group at C18. It manifests itself as shortening of the N3-C17 bond (1.358(3) and 1.354(3)Å for the molecules of **3** (A and A') in comparison with the N3-C18 bond (1.400(3) Å in both independent molecules).

Compound **4** crystallizes as a solvate with two methanol molecules. The structure of molecule **4** resembles that of indoline derivatives of dibenzodiazepine that we studied previously.[2] The central seven-membered heterocycle has a distorted and flattened boat conformation while cyclohexenone has a distorted sofa conformation. The dibenzodiazepine moiety is bound to the trioxopyrimidine ring through the C4 spiro atom and has a flattened sofa conformation. (The X-ray diffraction experiment is described elsewhere.[3]).

References

1. Crystallographic data for compound **3**: $C_{18}H_{20}N_4O_5 \cdot 0.375(C_2H_6O) \cdot 0.25(H_2O)$, are triclinic, space grope *P*-1: a=9.4539(8)Å, b=10.1566(9)Å, c=23.038(2)Å, α=79.712(2)°, β=85.517(2)°, γ=65.596(2)°, V=1982.0(3)Å^3, Z=4, M=394.16, d_{calc}=1.321 g·cm^{-3}, wR_2=0.1530 calculated on F^2_{hkl} for 8611 independent reflections with 2θ<54°, (GOF=1.045, R=0.0618 calculated on F_{hkl} for 4676 reflections with I>2σ(I)). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 978821.

2. Zh. I. Orlova, L. Yu. Ukhin, K. Yu. Suponitskii, E. N. Shepelenko, L. V. Belousova, G. S. Borodkin and O. S. Popova, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 1409.

3. Crystallographic data for compound **4**: $C_{18}H_{18}N_4O_4 \cdot 2(CH_4O)$ at 120K, are monoclinic, space group $P2_1/c$: a=10.047(6)Å, b=20.773(12)Å, c=10.292(6)Å, β=99.116(7)°, V=2121(2)Å^3, Z=4, M=418.45, d_{calc}=1.311 g·cm^{-3}, wR_2=0.2196 calculated on F^2_{hkl} for 8163 independent reflections with 2θ<52°, (GOF=0.971, R=0.0753 calculated on F_{hkl} for 1361 reflections with I>2σ(I)). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 992437.